

# Monday Morning, December 8, 2014

## Biomaterial Interfaces

Room: Milo - Session BI-MoM

## Nanobio Imaging

**Moderator:** Sally L. McArthur, Swinburne University, Australia

8:40am **BI-MoM1 Multimodal Nano-Bio Imaging of Neuronal Cells and Tissues**, *DaeWon Moon*, DGIST, Korea, Republic of Korea **INVITED**

Secondary ion mass spectrometry (SIMS) provides molecular specific information but for 2D imaging, SIMS needs specimens in general, to be frozen and dried for analysis in vacuum. For 3D imaging, specimens can be sputter profiled by recently developed gas cluster ions. To compensate the distortion due to cryosection and sputter profiling, we have been trying to develop a multimodal mass and non-linear optical imaging methodology of various cells and tissues for neuronal studies. In this presentation, multimodal SIMS and CARS imaging studies on neuron cells, olfactory bulb, and nematode *C. elegans* are reported.

For time-of-flight (TOF) secondary ion mass spectrometry (SIMS) imaging, 30 keV  $\text{Bi}_3^+$  ions for 2D mass imaging and 30 keV  $\text{Ar}_{1000}$  cluster ions for depth profiling were used to analyze various tissues such as *C. elegans*, and mouse olfactory bulb. As a complementary non-linear optical imaging, coherent Anti-Stokes Raman Scattering (CARS) were used to get 3D lipid imaging down to  $\sim 50 \mu\text{m}$  with 300 nm spatial resolution in-vitro or ex-vivo.

For *C. elegans*, lipid CARS imaging was obtained for live *C. elegans* but for SIMS imaging, *C. elegans* were dried with water and sputtered with 30 keV  $\text{Ar}_{1000}$  cluster ions to get sectioned 2D SIMS images. Molecular specific SIMS imaging for lipids, neurotransmitters, and pheromones with complementary CARS lipid imaging were used to investigate the difference of molecular distributions in wild-type and various mutant *C. elegans*.

For a cryosectioned mouse olfactory bulb, SIMS imaging showed different distributions of lipid molecules and neurotransmitters which is consistent with the olfactory bulb structure of glomerulus, mitral cell layer, and granule cell layer. SIMS imaging to study the changes of neurotransmitters in an olfactory bulb upon odorant stimulus will be reported.

In conclusions, multimodal mass and non-linear optical imaging provides a practically useful platform to investigate cells and tissues for new biomedical understanding of neuronal systems. New challenges for non-cryo tissue section, plasma/fs laser based ambient mass spectrometry for live cell membrane mass imaging, and super-resolution CARS will be discussed.

9:20am **BI-MoM3 SPR Imaging Sensor for Visualization of Individual Cell Reactions and Clinical Diagnosis of Allergy**, *Yuhki Yanase*, Hiroshima University, Japan **INVITED**

A technique to visualize individual living cell activation in a real time manner without any labeling is required in the fields of life sciences and medicine. Surface plasmon resonance (SPR) sensors detect the refractive index (RI) changes on the surface of sensor chips in label-free and on a real-time basis. We previously reported that SPR sensors could detect real-time large changes of RI in response to activation of living cells, such as mast cells, keratinocytes, basophils and B lymphocytes on a sensor chip without labeling, suggesting the potential of SPR as a new method for clinical diagnosis and drug screening. Thus, SPR sensor possesses great potential to reveal nano-scale living cell actions in evanescent field. However, conventional SPR sensors detect only an average RI changes in the presence of thousands of cells in an area of the sensor chip, and could offer only small number of sensing channels. Therefore, we developed SPR imaging (SPRI) sensor with a CMOS camera and an objective lens in order to visualize RI distribution of individual living cells and their changes upon stimuli

The sensor we developed is composed of a light source, P-polarizer, prism (RI=1.72), objective lens and CMOS camera. The SPRI sensor chips (RI=1.72, 20 mm  $\times$  20 mm  $\times$  1 mm) coated with gold thin film (1 nm Cr layer and 49 nm gold layer) by means of vapor deposition. The SPRI sensor we developed could detect reactions of individual rat basophilic leukemia (RBL-2H3) cells and mouse keratinocyte cells in response to specific or nonspecific stimuli. Moreover, the sensor could detect the reactions of individual human basophils isolated from patients in response to antigens. Furthermore, we also succeeded in distinguishing reactions of basophils activated by antigens from those of non-activated basophils spotted on an area.

The technique can visualize the effect of various stimuli, inhibitors and/or conditions on cell reactions as change of intracellular RI distribution at single cell levels. Establishment of the technique to rapidly isolate cells from patient blood should enable us to utilize SPRI system as a high throughput screening system in clinical diagnosis, such as type I allergy and drug hypersensitivity, and as a tool to reveal novel phenomena in evanescent fields around plasma membrane.

10:40am **BI-MoM7 SIMS of Cells and Tissues: Blasting Our Way to New Knowledge about Biology**, *Lara Gamble, B. Bluestein, D.J. Graham*, University of Washington, USA **INVITED**

Imaging mass spectrometry can provide images of cells and tissues with chemical and molecular specificity. These chemically specific images could revolutionize our understanding of biological processes such as increasing our understanding of chemical changes in cells and tissues as a function of an applied stress or as a result of disease, and enable tracking the spatial distribution of metabolites and lipids. The mass spectral imaging capability of ToF-SIMS holds potential to achieve this goal with sub-cellular resolution. Chemistry of tumor microenvironments, lipid metabolomics relationship to cancer, delivery of nanoparticles to cells, and tissue repair could be visualized on a cellular and sub-cellular level. In this presentation, ToF-SIMS analysis of biological samples from 2D images of tissues to 3D images of nanoparticles in cells will be presented. Challenges with sample preparation for the ToF-SIMS environment and processing of the large amount of data will be discussed (including multivariate analysis of the ToF-SIMS image data). The advantage of combining ToF-SIMS images with optical images of the same samples (same slices and serial biopsy slices) will also be presented. This combination of images allows researchers to visualize a molecular map that correlates with specific biological features or functions.

11:20am **BI-MoM9 Probing the Determinants of Sphingolipid Distribution in the Plasma Membrane with SIMS**, *Mary Kraft, J. Frisz*, University of Illinois at Urbana-Champaign, *P. Weber*, Lawrence Livermore National Laboratory, *R. Wilson*, University of Illinois at Urbana-Champaign, *J. Zimmerberg*, National Institutes of Health, *H. Klitzing*, University of Illinois at Urbana-Champaign

The plasma membrane is a selectively permeable lipid bilayer that separates cells from their surroundings. Numerous different lipid species, cholesterol, and a variety of different proteins form the plasma membranes of mammalian cells. One class of lipids, the sphingolipids, and their metabolites serve both as structural components in the plasma membranes of mammalian cells, and as bioactive signaling molecules that modulate fundamental cellular processes. Though segregation of the sphingolipids into distinct membrane domains is likely essential for cellular function, the sphingolipid distribution within the plasma membrane and the mechanisms that regulate it are poorly understood. To address this issue, we have combined metabolic labeling with stable isotopes and SIMS performed on a Cameca NanoSIMS 50 to image the distributions of stable isotope-labeled sphingolipids in the plasma membranes of fixed cells with  $\sim 100$  nm lateral resolution. Using this approach, we previously discovered that the  $^{15}\text{N}$ -sphingolipids were enriched within distinct domains in the plasma membranes of fibroblast cells [1]. Here we report how we have used this approach to probe the mechanisms responsible for this sphingolipid organization. To determine whether the sphingolipid domains are dependent on molecular interactions with cholesterol or protein-based barriers that are established by the cytoskeleton and its associated membrane proteins, we used SIMS to image the  $^{15}\text{N}$ -sphingolipid distribution in the plasma membrane following cholesterol depletion and actin depolymerization. We also assessed whether these  $^{15}\text{N}$ -sphingolipid domains were co-localized with hemagglutinin, a specific membrane protein that is thought to have an affinity for sphingolipid-enriched membrane domains. Our results indicate that the sphingolipid organizations in the plasma membrane are dependent on the cytoskeleton, but not on favorable interactions with cholesterol or hemagglutinin.

[1] J. F. Frisz, K. Lou, H. A. Klitzing, W. P. Hanafin, V. Lizunov, R. L. Wilson, K. J. Carpenter, R. Kim, I. D. Hutcheon, J. Zimmerberg, P. K. Weber, M. L. Kraft, Proc. Natl. Acad. Sci. U.S.A., 2013, 110 (8), E613-E622.

11:40am **BI-MoM10 In-Situ TOF-SIMS and SFM Measurements Providing 3D Chemical Characterization of Inorganic and Organic Nanostructures**, R. Moellers, ION-TOF GmbH, Germany, E. Niehuis, ION-TOF GmbH, F. Kollmer, ION-TOF GmbH, Germany, H. Arlinghaus, ION-TOF GmbH, R. Dianoux, Nanoscan AG, Switzerland, A. Scheidemann, Nanoscan AG, **Nathan Havercroft**, ION-TOF USA, Inc.

Information on the chemical composition, physical properties and the three dimensional structure of materials and devices at the nanometer scale is of major importance in nanoscience and nanotechnology. Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) is an extremely sensitive surface imaging technique which provides elemental as well as comprehensive molecular information on all types of solid surfaces. Depth profiling of multilayers with high depth resolution as well as three-dimensional analysis is performed using additional low energy sputter beams. However, the topography of the initial sample surface as well as the subsequent evolution of the topography by sputtering cannot be identified by the technique and lead to distortions of the detected depth distribution. Scanning Force Microscopy (SFM) provides the required complementary information on the surface topography with a resolution on the nanometer level.

We have combined the techniques ToF-SIMS and SFM in one UHV instrument. The TOF-SIMS analysis is performed using a new bismuth liquid metal cluster ion gun that can achieve a lateral resolution of 20 nm [1]. For the sputtering of inorganic materials the instrument is equipped with low energy oxygen and cesium beams. Sputtering of organic materials without radiation damage is performed by using large gas clusters with low energy/atom allowing molecular depth profiles of organic multilayers with a depth resolution of 5 nm as well as 3D analysis of organic nanostructures [2]. The SFM unit is mounted on a 3-axis high precision flexure stage scanner with a small out-of-plane motion for very accurate information on the surface topography. The SFM can be operated in contact mode as well as in a variety of dynamic modes to provide additional valuable information about the physical properties of the sample. In this paper we will present first results illustrating the strength of combined in-situ TOF-SIMS / SFM measurements and the potential for a wide range of applications.

#### References

- [1] F. Kollmer, W. Paul, M. Krehl and E. Niehuis, Surf. Interface Anal. 45, 312 (2013)
- [2] E. Niehuis, R. Moellers, D. Rading, H.-G. Cramer, R. Kersting, Surf. Interface Anal. 45, (2013) 158

## Energy Harvesting & Storage

### Room: Lehua - Session EH-MoM

#### Nano-based Approaches for Photovoltaics

Moderator: Jason Baxter, Drexel University, USA

8:40am **EH-MoM1 Thin Film Solar Cells from Colloidal Nanoparticle Dispersions**, Eray Aydil, B. Chernomordik, N. Trejo, University of Minnesota

INVITED

The global installed capacity to generate electricity using solar cells has doubled every 2.5 years since 1975, an exponential growth similar to the Moore's law which states that the number of transistors on a computer chip doubles every 2 years.<sup>1</sup> Maintaining this aggressive Moore-like growth requires sustainable, high-throughput low-cost production of thin film solar cells. Copper zinc tin sulfide ( $\text{Cu}_2\text{ZnSnS}_4$  or CZTS), copper zinc tin selenide ( $\text{Cu}_2\text{ZnSnSe}_4$  or CZTSe) and their alloys ( $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})_4$  or CZTSSe) are emerging as promising solar absorber materials for thin-film solar cells because they are comprised of earth abundant elements and can potentially help increase the solar electricity production to terawatt levels without the concerns associated with the toxicity and low abundance of the elements in the current commercial thin-film solar cells. A potentially high-throughput and low-cost approach to making thin polycrystalline CZTSSe films is through annealing of coatings cast from colloidal dispersions (inks) of CZTS nanocrystals in sulfur and/or selenium vapor. In this way, the nanocrystal coatings are transformed into polycrystalline films with micrometer size grains, a suitable morphology for making solar cells. The transformation of the nanocrystal coating to a polycrystalline coating is driven by the high surface area of the nanocrystals and, consequently, the high total surface energy of the nanocrystal coating. This approach is well suited for high throughput low-cost roll-to-roll manufacturing. However, many scientific and technical challenges remain. In this talk we will review the advances made towards this end and the remaining challenges. Specifically, we will describe our most recent findings on the effects of sulfidation/selenization time, temperature, sulfur and selenium vapor

pressures, presence of alkali and carbon impurities on the microstructure of CZTSSe films.

<sup>1</sup> D. J. Norris and E. S. Aydil, "Getting Moore from Solar Cells," *Science* **338**, 625-626 (2012).

9:20am **EH-MoM3 XPS Analysis of Solution-Based Thin Films of Nano Structured Chalcogenides for Solar Cells Applications**, F.Servando Aguirre-Tostado, R. Garza-Hernández, CIMAV, Mexico

INVITED

The employment of solution based methods for the deposition of semiconductor materials for solar cells applications comes with promise of enabling large area applications at the same time of driving down costs. The optimization of thin film semiconductors such as  $\text{CuZnSnS}$  requires the understanding of the structure and chemical reactions taking place during deposition of thin films and post-deposition thermal treatments. In this respect, X-ray photoelectron spectroscopy (XPS) is uniquely suited for tracking down chemical reactions occurring at the surface and interface of nanometric layers. The chemical analysis and thermal stability for surface and interface reactions of binary chalcogenide semiconductors is presented.  $\text{CuS}$ ,  $\text{ZnS}$ , and  $\text{SnS}_2$  thin films were deposited on top of  $\text{CdS}$  by the successive ionic layer absorption and reaction method (SILAR) in a glove-box attached to the XPS load-lock chamber for in-situ analyses. Step by step XPS analysis of the SILAR process reveals an incubation period that depends on temperature and ion concentrations. Multilayer structure stability is discussed in terms of chemical reactivity and diffusion of cations. Finally, a demonstration of how the obtained results can help to engineer a more stable structures is presented.

10:20am **EH-MoM6 Nanoscale Characterization of Defects and Interfaces in Thin Film Solar Cells**, Mowafak Al-Jassim, NREL

Thin-film solar cells based on polycrystalline  $\text{CdTe}$ ,  $\text{Cu}(\text{In,Ga})\text{Se}_2$  (CIGS), and  $\text{Cu}_2\text{ZnSnSe}_4$  (CZTSe) have demonstrated high solar-to-electricity conversion efficiencies. Typically, polycrystalline thin-film solar cells are expected to exhibit poor performance compared to their single-crystalline counterparts, due to the existence of unavoidable structural defects such as dislocations and grain boundaries (GBs). It is surprising, therefore, that  $\text{CdTe}$ -, CIGS-, and CZTSe-based polycrystalline thin-film solar cells have achieved higher efficiencies than their single-crystalline counterparts.

Here, we present our results on the study of the atomic structure and electronic properties of structural defects including stacking faults, twins, dislocations, and GBs in  $\text{CdTe}$ , CIGS, and CZTSe using a combination of aberration-corrected scanning transmission electron microscopy (STEM) and first-principles density-functional theory calculation. Polycrystalline  $\text{CdTe}$  thin films were grown by closed-space sublimation, whereas CIGS and CZTSe thin films were deposited by co-evaporation. Atomic resolution scanning transmission electron microscopy (STEM) images were acquired with Nion UltraSTEM 100 and 200 microscopes. We found that intrinsic GBs in  $\text{CdTe}$ , CIGS, and CZTSe create deep levels mainly due to the anion-anion "wrong" bonding. However, these deep levels can be removed through extrinsic and/or intrinsic passivation. In addition to high resolution structural and chemical characterization, we will present data on the electrical and optoelectronic properties of defects obtained by a correlative approach that involves STEM, cryogenic cathodoluminescence defect spectroscopy and electron beam induced current imaging.

10:40am **EH-MoM7 Two-Step Thermal Annealing Improves the Morphology of Spin-Coated Films for Highly Efficient Perovskite Hybrid Photovoltaics**, ChihPing Chen, Ming Chi University of Technology, Taiwan, Republic of China

We describe the relationships between the morphologies and the power conversion efficiencies (PCE) of perovskite photovoltaics having a conventional p-i-n heterojunction structure, indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS)/ $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x/\text{PC}_{61}\text{BM}/\text{Al}$ . The PCE of such a device is highly dependent on the morphology of the perovskite film, which is governed by the concentrations of its precursors and the annealing conditions. A two-step annealing process allowed sufficient crystallization of the perovskite material, with a high coverage at a high precursor concentration. Relative to the device prepared using a one-step process (90 °C for 30 min), we observed a 60% increase in PCE for this optimized device. We observed a PCE of 10% of our optimized cells. Corresponding devices exhibited extremely high stability after long-term storage (>1368 h) in the dark in a  $\text{N}_2$ -filled glove box, with consistently high PCEs ( $\text{AM 1.5G}$ ,  $100 \text{ mW cm}^{-2}$ ).

11:00am **EH-MoM8 Charge Transport in PbS Quantum Dot Arrays for Photovoltaic Applications**, *Miquel B. Salmeron*, Lawrence Berkeley Lab, USA **INVITED**

New forms of matter can be designed by combining nanoscale building blocks to create artificial solids with novel functionalities for device applications, such as field effect transistors, solar cells, photodetectors, and light emitting diodes. Artificial atoms or quantum dots (QDs) are ideal elements for this purpose since their electronic properties can be tuned through control of their size, shape and composition, while charge transport through QD assemblies can be engineered by controlling the hopping barrier between neighboring dots. However, fabrication of the QDs comprised of hundreds to thousands of atoms is inevitably imperfect and defects and impurities are always present. The nature of the defect states is unknown and the microscopic mechanisms of charge transport are far from being understood. In this presentation we show, by means of nanoscale imaging, spectroscopy, and density functional theory (DFT), that charge transport takes place in PbS QD arrays following percolation pathways that are spatially different for electrons and holes, electrons via in-gap states (IGS) instead of conduction band states, and holes via valence band states. This novel and exotic transport phenomenon is explained by the measured electronic structure and energy level alignment of the individual QDs. In contrast with previous hypothesis that surface stoichiometry and ligands are responsible for IGS, we found that the IGS are induced by adsorbed oxygen molecules whose  $p^*$  states hybridize with QD valence band states, thus enabling inter-particle coupling and electron transport. We demonstrate that chemical treatments can be used for surface impurity engineering to achieve tunable electronic structure and transport properties.

11:40am **EH-MoM10 The Effect of n and p Delta Doping on InAs/GaAs Quantum Dot Solar Cell**, *W.J. Choi, HoSung Kim, S.H. Kim, J.D. Song*, Korea Institute of Science and Technology, Republic of Korea, *J.H. Park*, Korea University, Republic of Korea

The efficiency of single junction solar cells (SJSCs) is limited by Shockley-Queisser limit and intermediate band solar cell (IBSC) concept has been introduced in order to overcome the efficiency limit of conventional SJSC. For IBSC model, low dimensional semiconductor structures such as quantum wells and quantum dots (QDs) have been applied to the SJSC. Especially, self-assembled InAs QDs have been frequently applied to GaAs/AlGaAs SJSCs because QDs provide quantum confined states that lower the average band gap of the SJSCs to absorb longer wavelength light beyond GaAs band edge of 870 nm. Theoretical studies of QDSCs have suggested a maximum efficiency of 45 % under 1 sun and 63 % under 1000X concentration. Contrary to their expectations, actual QDSC devices suffer from photocurrent loss due to inhomogeneous distribution in QD sizes and high carrier confinement of QDs. In order to solve these problems, n delta doping techniques on QDs have been investigated. Here, we introduce the result of QDSCs with n and p delta doping on QDs.

For this study, two types of SC samples were grown on N-GaAs substrate and P-GaAs substrate respectively by molecular beam epitaxy. The undoped and delta-doped QDSCs with doping density of  $1 \times 10^{12} \text{ cm}^{-2}$  were prepared and every SC samples has spacer layer with thickness of 20 nm between InAs QD layer and delta doping layer. SC samples grown on N-GaAs and P-GaAs substrate were delta doped with Si and Be respectively. The InAs QDs were grown by modified Stranki-Krastanov growth method. With this growth technique, the QD size and density can be controlled by using the repetition period of a cycle.

The efficiency of QDSCs with and without Si delta doping are 13.6 % and 11.4 % respectively. The enhancement of the efficiency of QDSCs with Si delta doping is due to the increase of  $J_{sc}$ . This increase of  $J_{sc}$  is due to the n-delta doping and this enhances electron transitions in QDs and increase the carrier lifetime in QDs. The efficiency of QDSCs with and without Be delta doping are 8.45 % and 10.9 % respectively. Compare to the result of QDSCs grown on N-GaAs substrate, the efficiency of QDSCs with Be delta doping has been decreased. This could be attributed to the P delta doping. The Be delta doping induces suppression of the photocarrier generation in the radiative QDs because intentionally doped holes are strongly localized in the radiative QDs. We will present the result of the time-resolved photoluminescence of the QDSCs with Si and Be delta doping.

## Nanomaterials

**Room: Hau - Session NM-MoM**

### Nano Fabrication

**Moderator:** Adam Hitchcock, McMaster University, Canada

8:40am **NM-MoM1 Polymers, Peptides and Proteins as Pattern Generators and Switches for Functional Nanostructures**, *David Williams, Malstrom, Wason, Papst, Roache, Strover, Hackett, Pei, Leung, Brimble, Evans, Travas-Sejdic, Gerrard*, The University of Auckland, New Zealand **INVITED**

We have explored self-assembling proteins and block co-polymers, rationally designed peptides, and switchable polymer brushes as design elements for functional nanostructures.

Block co-polymers can self-assemble to form interesting regular nanostructures. Indeed, micro-phase separation in block copolymers has been fairly extensively explored as a means of patterning high-density memory elements. Similarly, proteins self-assemble: individual subunits can assemble into doughnuts, stacks, fibres and scaffolds. We have explored the idea of combining the two, using micro-phase separation of a block copolymer as a means to organise a protein stack which may then be used to organise something else. In the RNA-binding protein Lsm- $\alpha$ , monomeric subunits assemble into doughnuts. The doughnuts can then be induced to form stacks by a combination of protein engineering and changes in solution conditions such as pH and metal ion concentration. These nanoscale tunnels can then potentially acts as a template to organise metal ion or nanoparticle columns. In order to organise the protein stacks, we have explored the segregation of the protein into the hydrophilic domains of a hydrophobic-hydrophilic block copolymer. We illustrate the idea using thin films of poly(styrene)-b-poly(ethyleneoxide) – PS-b-PEO, with the Lsm- $\alpha$  doughnut incorporated into self-assembled hexagonally packed cylinders of PEO. The issues are choice of a solvent system that promotes structuring of the polymer, and functionalization of the protein to convey compatibility with the solvent system necessary for formation of the micro-phase separated structure, whilst still retaining the structure, function and organisation of the protein.

In a different approach to building up the elements needed to construct functional nanostructures, we have been exploring the use of rationally designed peptides as templates for nanoparticle growth, and surface-grafted polymer brushes as switchable sub-units. Peptides offer great flexibility in molecular design. We have been able successfully to incorporate, in defined spatial organisation, sites that specifically adsorb to metal surfaces, sites that control inter-particle interaction, and sites that complex the particle precursor species and thus control particle nucleation. Separately, we have been able to synthesise co-polymer brush systems that are electrochemically switchable. We present initial approaches towards integrating all these structural and functional elements and studying their interaction with living cells.

9:20am **NM-MoM3 Si, C and SiC<sub>x</sub> Nanostructures and Nano Devices Fabricated Using In Situ Liquid Cell TEM Technology**, *Xin Chen*, East China University of Science and Technology, China, *L.H. Zhou, P. Wang, H.L. Cao, X.L. Miao, F.F. Wei*, East China University of Science and Technology

Silicon, carbon and SiC<sub>x</sub> nano structures were fabricated using liquid phase electron beam induced deposition (LP-EBID) technology. SiCl<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub>, and SiCl<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> solutions of different concentrations were used as the liquid precursors, which were sealed between two Si<sub>3</sub>N<sub>4</sub> window grids in home made in situ TEM liquid cells. JEOL TEM systems operating under a 200 keV electron acceleration voltage were used for the deposition. Focused electron beams of 0.28 to ~40 nA were used to decompose the precursors and deposit the nano structures on the Si<sub>3</sub>N<sub>4</sub> window substrates.

With the beam focused on a fixed location for a certain time, nano dots have been deposited, with sizes ranging from <60 nm to ~500 nm depending on the deposition parameters, with well size controllability. Generally, the nano dot diameter increases with beam exposure time and beam intensity, but was insensitive to the composition ratio of these precursors. Under the higher beam current, the nano particle growth was observed to be retarded. The general growth trend is attributed to a secondary electron effect, while the retarded growth is attributed to the influence of the primary electrons.

By using scanning electron beams, nano wires of different sizes have been deposited. Besides a uniform straight line growth, we have also observed a branched growth behavior under certain deposition conditions. The secondary electron mechanism can be used to explain these growth behaviors.

The in situ cells were later disassembled, with platinum nano electrodes deposited on the two ends of the SiC<sub>x</sub> nano wires using a FEI Dual Beam 235 focused ion beam system, forming nano electronic devices. SEM and AFM imaging analysis showed good structural morphology of the devices, and I-V property test have been made on the devices. Issues of liquid bubbling under electron beam irradiation, image resolution and structural stability of the deposited nano structures made by in situ liquid cell TEM technology have been further discussed.

9:40am **NM-MoM4 Quantum Chemical Molecular Dynamics Approach to Chemical Mechanical Polishing Processes of Gallium Nitride by SiO<sub>2</sub> Abrasive Grain**, *Kentaro Kawaguchi, T. Aizawa, Y. Higuchi, N. Ozawa, M. Kubo*, Tohoku University, Japan

Gallium nitride (GaN) is a next-generation semiconductor material with a wide band gap and high electron conductivity. Although the atomic-level planar polished surface is essential for practical GaN devices, it is difficult to polish efficiently the GaN substrate because of its high hardness and chemical stability. The chemical mechanical polishing (CMP) is promising for efficient polishing of the GaN substrate. However, the detailed CMP mechanisms are unclear, and then the design of the processes is difficult. In this study, in order to design the efficient and precise GaN CMP processes, we investigate the GaN CMP via our tight-binding quantum chemical molecular dynamics (TB-QCMD) method.

We perform CMP simulations of a GaN(0001) surface by a SiO<sub>2</sub> abrasive grain in aqueous H<sub>2</sub>O<sub>2</sub> solution and aqueous NaOH solution to clarify the chemical reactions of each solution. We reveal that OH radicals and OH<sup>-</sup> ions are adsorbed on the GaN surface in aqueous H<sub>2</sub>O<sub>2</sub> solution and aqueous NaOH solution, respectively. According to the analysis of the atomic bond population between the Ga atoms in the first layer and the N atoms in the second layer, we elucidate that Ga-N bonds of the GaN substrate in aqueous H<sub>2</sub>O<sub>2</sub> solution are weaker than those in aqueous NaOH solution. Therefore, we suggest that the OH radicals are effective for GaN CMP. To confirm the effectivity of OH radicals, we add one OH radical into the solution every 4.0 ps until 64.0 ps during polishing simulation under pure water environment. After 8 OH radicals are added, the 8 added OH radicals are adsorbed on the GaN surface. After 10 OH radicals are added, a surface-adsorbed O atom is generated by the chemical reaction between the surface-adsorbed OH species and a OH radical in the solution. At the friction interface between the GaN substrate and the abrasive grain, the surface-adsorbed O atom is mechanically pushed into the GaN substrate by the abrasive grain. This O atom intrusion induces the dissociation of Ga-N bonds of the GaN substrate. The N-N bond in the GaN substrate is generated due to the Ga-N bonds dissociation. After 16 OH radicals are added, the Ga atom in the first layer binds with 3 OH radicals. Subsequently, Ga(OH)<sub>3</sub> is generated and desorbed from the surface. N<sub>2</sub> molecules are also generated and desorbed from the surface due to the dissociation of Ga-N bonds. We suggested that the GaN CMP process efficiently proceeds by the mechanically induced chemical reactions: a surface-adsorbed O atom is generated and pushed into the GaN bulk by the abrasive grain.

10:20am **NM-MoM6 Expanding Scalability of Scanning Probe-Based Nanofabrication**, *Wooyoung Shim*, Yonsei University, Republic of Korea  
Massively parallel scanning-probe based methods have been used to address the challenges of nanometer to millimeter scale printing, and thus revolutionize the conventional scanning probe-based nanofabrication. Such tools enable simple, high-throughput, and low-cost nano-patterning, which allow researchers to rapidly synthesize and study systems ranging from nanoparticle synthesis to biological processes. In this regard, we have developed a novel scanning probe-based cantilever-free printing method termed hard-tip, soft-spring lithography (HSL), which uses an massive array of Si tips to transfer materials and energy in a direct-write manner onto a variety of surfaces. Various related techniques such as graphene-coated and actuation of HSL are also discussed.

#### References

- 1) Shim, W.; Braunschweig, A. B.; Liao, X.; Chai, J.; Lim, J. K.; Zheng, G.; Mirkin, C. A. *Nature* **469**, 516 (2011).
- 2) Shim, W.; Brown, K. A.; Rasin, B.; Liao, X.; Zhou, X.; Mirkin, C. A. *Proc. Natl. Acad. Sci. USA* **109**, 18312 (2012).
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- 5) Brown, K. A.; Eichelsdoerfer, D. J.; Shim, W.; Rasin, B.; Boya, R.; Liao, X.; Schmucker, A. L.; Liu, G.; Mirkin, C. A. *Proc. Natl. Acad. Sci. USA* **110**, 12921 (2013).

10:40am **NM-MoM7 Mueller Matrix Ellipsometry for Detection of Foot-like Asymmetry in Nanoimprinted Grating Structures**, *Xiuguo Chen*, Huazhong University of Science and Technology, China, *C.W. Zhang, H. Jiang*, Huazhong University of Science and Technology, *S.Y. Liu*, Huazhong University of Science and Technology, China

Nanoimprint lithography (NIL), in which features on a prepatterned mold are transferred directly into a polymer material, represents a promising technique with the potential for high resolution and throughput as well as low cost. Although symmetric imprint resist profiles are expected in most cases, errors could occur in actual NIL processes and will result in undesired asymmetry and pattern transfer fidelity loss in downstream processes. Detection of imprint resist asymmetric defects leads to improvement of the template, imprint process, and imprint tooling design, and therefore guarantees pattern transfer fidelity in template replication. Both cross-sectional scanning electron microscopy (X-SEM) and atomic force microscopy (AFM) are capable of identifying imprint resist profile asymmetry, but they are in general time-consuming, expensive, complex to operate, and problematic in realizing in-line integrated measurements. Being nondestructive, inexpensive and time-effective, optical scatterometry, which is traditionally based on reflectometry and ellipsometry, has been successfully introduced to characterize nanoimprinted grating structures. However, conventional optical scatterometry techniques have difficulties in measuring asymmetric grating structures due to the lack of capability of distinguishing the direction of profile asymmetry.

In this work, we apply Mueller matrix ellipsometry (MME, sometimes also referred to as Mueller matrix polarimetry) to characterize nanoimprinted grating structures with foot-like asymmetric profiles that were encountered in our NIL processes when the processes were not operated at optimum conditions. Compared with conventional optical scatterometry, which at most obtains two ellipsometric angles Y and D, MME-based scatterometry can provide up to 16 quantities of a 4×4 Mueller matrix in each measurement and can thereby acquire much more useful information about the sample. In our recent work, MME was applied to characterize nanoimprinted grating structures with symmetric profiles. We experimentally demonstrated that improved accuracy can be achieved for the line width, line height, sidewall angle, and residual layer thickness measurement by using the additional depolarization information contained in the measured Mueller matrices. The present work will further show that MME not only has good sensitivity to both the magnitude and direction of profile asymmetry, but also can be applied to accurately characterize asymmetric nanoimprinted gratings by fully exploiting the rich information hidden in the measured Mueller matrices.

11:00am **NM-MoM8 Positioning of Catalyst-Free Vapor-Solid Growth of Highly Crystalline ZnO Nanowires by Inkjet-Printing**, *Paulina R. Martinez-Alanis, F. Güell*, Universitat de Barcelona, *S. Khachadorian, A. Franke*, Technische Universität Berlin, *M.R. Wagner*, Institut Catala de Nanotecnologia, *A. Hoffmann*, Technische Universität Berlin, *G. Santana*, Universidad Nacional Autónoma de México, *J.R. Morante*, Institut de Recerca en Energia de Catalunya

High-density arrays of uniform ZnO nanowires, with a high crystal quality have been synthesized by a catalyst-free vapor-transport method. First, a ZnO thin film on a Si substrate was used as the nucleation site. In a second approach we demonstrate spatially selective, mask-less ZnO nanowires growth using ZnO inkjet-printed patterned islands as the nucleation sites on a SiO<sub>2</sub>/Si substrate. Raman spectroscopy measurements were performed to characterize the ZnO nanowires, which reveals the high crystal quality of the grown nanowires and a tensile stress was observed in the inkjet-printed nanowires. Photoluminescence measurements demonstrate that only the ZnO nanowires were emitting and there is no contribution from the ZnO thin film or the ZnO inkjet-printed patterned islands. Two emission bands were observed at room-temperature, one strong and narrow peak in the ultraviolet region associated with the near band-edge transition, and a reduced broad band in the green-yellow visible region.

11:20am **NM-MoM9 Rheological and Electrical Properties of Sn-Ag-Cu Solder Paste for Reverse Offset Printing by the Particle Size Distribution**, *Min-Jung Son*, Sungkyunkwan University, Korea, Republic of Korea, *I. Kim, T.M. Lee*, Korea Institute of Machinery & Materials (KIMM), Republic of Korea, *S.S. Yang*, Korea Institute of Materials, Republic of Korea, *H. Lee*, Sungkyunkwan University, Korea, Republic of Korea

For flip-chip packaging technologies, which gain popularity in semiconductor packaging, forming fine solder bumps with a high aspect ratio at a low cost is an integral part. A promising alternative to the conventional methods (screen printing and electroplating) is reverse offset printing owing to its high throughput.

In the present study, we developed Sn-Ag-Cu paste customized for the reverse offset printing process to use as solder bump with a high aspect ratio.

In fabrication of the pastes, we controlled the particle size distribution using Sn-Ag-Cu particles with two different sizes (2  $\mu\text{m}$  and 100 nm in diameter) and the particles were mixed with various ratio (100 : 0, 75 : 25, 50 : 50, 25 : 75, and 0 : 100) to control the rheological properties without using viscosity-increasing agents, which usually degrade the electrical properties. Various tools were used for measurement of rheological properties such as viscosity, thixotropy index (TI), storage modulus ( $G'$ ), loss modulus ( $G''$ ), crossover point of  $G'$  and  $G''$ . The TI and crossover point of  $G'$ ,  $G''$  gradually increased with the ratio of the nano particles increasing. In other words, if the initial viscosity increases with the increase of the amount of the nano particles, the shear thinning behavior and elasticity of the paste are dominant and the paste becomes suitable for the formation of the fine solder bumps with high aspect ratio. TI, which is related to the shear thinning behavior, increased from 0.08 to 0.53, and crossover point of  $G'$ ,  $G''$ , which is related to the shear thinning behavior, increased from 0.15 to 148 Pa. In addition, we measured the electrical resistance of the paste to check the influence of the particle size on it. The resistance increased with the increase of the ratio of the nano particles. As a result, we obtained the lowest resistance in the paste made from only micro solder particles. Considering these results in terms of printability and electrical resistance, we used the paste with the particle ratio of 75 : 25 to fabricate solder bumps. We obtained 6 ~ 30  $\mu\text{m}$  height, 100  $\mu\text{m}$  pitch Sn-Ag-Cu solder bumps.

## Thin Films

**Room: Makai - Session TF-MoM**

### Self-Organized and Nanostructured Thin Films

**Moderator:** Shixuan Du, Institute of Physics, Chinese Academy of Sciences

8:40am **TF-MoM1 Growth Kinetics, Structure, and Properties of 2D Layered Materials**, *Suneel Kodambaka*, University of California, Los Angeles **INVITED**

Two-dimensional (2D) layered materials owing to a wide range of properties (e.g., graphene is metallic, h-BN is insulating, and  $\text{MoS}_2$  is semiconducting) have attracted immense attention over the past decade for a variety of optoelectronic and nanoelectronic applications. Recent efforts have focused on vertical integration of 2D layers of dissimilar materials (e.g., graphene/h-BN and graphene/ $\text{MoS}_2$ ). In these heterostructures, due to relatively weak van der Waals interactions, orientational registry between the layers is not expected and is often difficult to control. This talk will focus on the effect of interlayer orientation on the electronic structure of the resulting heterostructures. Using a combination of *in situ* low-energy electron microscopy (LEEM) and density functional theory (DFT) calculations, we investigated the electronic properties of graphene/Pd(111). From the LEEM images we determined the graphene growth kinetics and measured graphene work function as a function of orientation and layer thickness. Recently, we extended our DFT calculations to study the electronic structures of h-BN/Ni(111) and graphene/ $\text{MoS}_2$  heterostructured layers. We found that hBN can chemisorb or physisorb on Ni(111), with metallic or insulating properties, respectively and these properties are not altered when graphene is placed atop hBN. For graphene on  $\text{MoS}_2$ , we found that rotating graphene layer by 30° with respect to  $\text{MoS}_2$  changes the  $\text{MoS}_2$  band gap from 1.68 eV direct to 1.56 eV indirect. We attribute the observed orientation-dependent bandgap to the variation in the S-S interplanar distance with the  $\text{MoS}_2$ -graphene interlayer orientation.

9:20am **TF-MoM3 Deposition and Tribomechanical Properties of Hf-B-C Thin Films**, *Elham Mohimi, T. Ozkan, S. Babar, P.J. Semprout*, University of Illinois at Urbana-Champaign, USA, *A.A. Polycarpou*, Texas A&M University, *G.S. Girolami, J.R. Abelson*, University of Illinois at Urbana-Champaign, USA

The tribomechanical properties of thin film coatings can be enhanced by alloying to afford a multicomponent nanostructure. Our group previously reported the conformal growth and favorable mechanical properties of HfB<sub>2</sub> and Hf-B-N hard coatings by chemical vapor deposition (CVD) at low substrate temperature. Here, we alloy C into HfB<sub>2</sub> in order to reduce the friction coefficient and enhance the hardness. A useful analogue is C-alloyed TiB<sub>2</sub>, which exhibits super hardness and good thermal stability. However, there have been no previous studies of Hf-B-C alloys.

Hf-B-C nanocomposite coatings are deposited by CVD onto Si or stainless steel discs using the precursor hafnium borohydride,  $\text{Hf}(\text{BH}_4)_4$ , with a co-

flow of dimethylbutene (DMB),  $(\text{CH}_3)_3\text{CCH}=\text{CH}_2$ , as the carbon source. Depositions are performed in a high vacuum chamber with base pressure of 10<sup>-8</sup> Torr, hafnium borohydride pressure 0.1-0.5 mTorr and DMB pressure 0.05-0.4 mTorr at substrate temperatures of 250-600°C. DMB also acts as growth inhibitor – it reduces the film growth rate by a factor of 2-6 compared to growth using the precursor alone, an effect which enhances conformality. For higher temperature growth, DMB increases the film density and decreases the surface roughness. XPS analysis indicates a mixture of HfB<sub>2</sub>, HfCx and B4C phases, however, this is uncertain due to the small shifts between different bonding states.

As-deposited films are XRD amorphous with hardness values of 9-26 Gpa and reduced modulus of 99-208 Gpa. Upon annealing at 700°C for 3 hours under inert gas atmosphere, the films transform to a partially nanocrystalline structure, which increases the hardness to 17-34 Gpa and the elastic modulus to 158-248 Gpa. The tribological properties of Hf-B-C films are superior to those of HfB<sub>2</sub> films. This is attributed to graphitic attachment of carbon atoms on contacting surfaces as evidenced by EDS analysis of the wear scar surface. Summarizing, this system affords conformal growth at low growth temperatures, suitable for the fabrication of complex structures such as MEMS.

9:40am **TF-MoM4 Effect of Chemical Reaction on Low Friction of Diamond-Like Carbon in Water Lubrication : A Theoretical Study**, *Shandan Bai, Y. Niiyama, Y. Kobayashi, Y. Higuchi, N. Ozawa, K. Adachi, S. Mori, K. Kurihara, M. Kubo*, Tohoku University, Japan

[Introduction] Diamond-Like Carbon (DLC) coatings have low friction and anti-wear tribological performances. Furthermore, water lubrication improves the friction properties of DLC films and reduces the emission of CO<sub>2</sub>. The friction coefficient of the DLC films drastically changes under water lubrication, since some tribo-chemical reactions occur during the sliding. However, tribo-chemical reactions are difficult to be revealed only by experimental analyses in details. The computational technique is efficient method to investigate the low friction mechanism [1]. In this study, we reveal the tribo-chemical reaction between DLC film and water using the computational method on an atomic scale.

[Method] To clarify the tribo-chemical reactions of DLC films under water lubrication, we use our tight-binding quantum chemical molecular dynamics (TB-QCMD) method [2]. We construct the sliding simulation model consisting of 80 water molecules and two DLC substrates. The thickness of water is approximately 1.0 nm. The friction simulation is performed for 100,000 steps with the time step of 0.1 fs. We apply contact pressures of 0.5 and 5 GPa on the top layer of upper substrate of DLC films, while it is forcibly slid with a horizontal velocity of 10 m/s. The simulation temperature is set at 300 K, achieved by velocity scaling method.

[Results and Discussion] We perform our TB-QCMD calculations to investigate the low friction properties of DLC in water lubrication. Under a contact pressure of 0.5 GPa, one C-OH bond is generated on the DLC surface at 0.045 ps during the sliding, because of the dissociation of a water molecule. Furthermore, at 3.655 ps, we observe another C-OH bond generation on the surface. The result indicates that OH terminates the DLC surface under a contact pressure of 0.5 GPa. Under a contact pressure of 5 GPa, generation of a C-OH bond is observed on the surface at 1.380 ps. Furthermore, at 3.880 ps, it is very interesting to see the generation of C-O-C on the DLC surface, which is a different chemical reaction with that under pressure of 0.5 GPa. The friction coefficients are 0.81 and 0.05 under contact pressures of 0.5 and 5 GPa, respectively. Those results indicate that the friction coefficient decreases with increasing a contact pressure. We think that the chemical reaction leads to the structure change on the DLC surface and the low friction properties of DLC in water lubrication under high contact pressures.

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[2] S. Bai, M. Kubo et al., RSC Adv., DIO: 10.1039/c4ra04065a.

10:20am **TF-MoM6 Growth of Large-Area 2D Transition Metal Dichalcogenides**, *Lain-Jong Li*, King Abdullah University of Science and Technology, Saudi Arabia **INVITED**

The direct-gap property of the semiconducting transition metal dichalcogenide (TMD) monolayers is attractive for optoelectronics and energy harvesting. Here I would like to discuss the synthetic approaches to obtain crystalline and sub-mm sized  $\text{MoS}_2$ ,  $\text{WSe}_2$  and  $\text{WS}_2$  monolayers directly on arbitrary substrates using vapor phase reaction between metal oxides and S or Se powders.<sup>1,2</sup> These layer materials can be transferred to desired substrates, making them suitable building blocks for constructing multilayer stacking structures. By using micro-beam X-ray photoelectron spectroscopy, we report the determination of band offsets in TMD heterostructures.<sup>3</sup> These physical quantities are fundamentally important for novel devices based on heterostructures formed between dissimilar TMDs. Some possible applications based on TMD heterostructures will be discussed.

## References

- <sup>1</sup> Huang, J. K. et al. Large-Area Synthesis of Highly Crystalline WSe<sub>2</sub> Monolayers and Device Applications. *ACS Nano* 8, 923 (2014).
- <sup>2</sup> Lee, Y. H. et al. Synthesis of Large-Area MoS<sub>2</sub> Atomic Layers with Chemical Vapor Deposition. *Advanced Materials* 24, 2320 (2012).
- <sup>3</sup> M.-H. Chiu et al. Determination of band alignment in transition metal dichalcogenides heterojunctions. arXiv:1406.5137

11:00am **TF-MoM8 Influence of Testing Conditions on the Tribological Behaviour of C(N)-WS<sub>2</sub> Self Lubricating Thin Films.**  
*Albano Cavaleiro, M. Evaristo*, University of Coimbra, Portugal, *T. Polcar*, University of Southampton, UK

Transition metal dichalcogenides (TMD) have a layered structure and weak inter-layer bonding allowing to display very low friction coefficient when a tangential force is applied. Being sliding contact a surface phenomenon, these materials have been largely studied in the form of thin coatings. Whenever conditions exist for establishing stronger bonds between the layers, the friction coefficient can significantly increase. This is the reason why the industrial applicability of these coatings is still very limited due to the deficient tribological behavior in humid atmospheres, for which strong bonds can be formed through oxygen. In order to overcome this problem different approaches were followed based on alloying TMD with different elements. Among these elements, our group has developed a deep study on the addition of carbon and nitrogen. We have proved, as it was already known, that the friction coefficient could increase from the range [0.005 – 0.05] up to [0.05 – 0.3] when the coatings were tested in dry or in humid conditions, respectively.

The aim of this talk is to present a systematic study concerning the influence of humidity in the tribological behavior of TMD+C coatings. We deposited W-S-C coatings with increasing C content up to 60 at.% with two S/W ratios, close to 1.4 and 1.0. These coatings were tested by pin-on-disk in different humidity range from RH=20% up to RH=95%. Contrarily to what we have observed in previous studies, we could not find any case where the friction coefficient went down lower than 0.1. Furthermore, there was no clear trend on the effect of either the humidity or the S/W ratio on the friction coefficient. The detailed analysis of the sliding surfaces allowed to conclude that, in all tests, orientation of WS<sub>2</sub> crystals in the top sliding contact could not be achieved. The comparison with previous deposited W-S-C coatings allowed to conclude that the different tribological behavior could be attributed to a different nanostructure arrangement in the as-deposited conditions.

# Monday Afternoon, December 8, 2014

## Biomaterial Interfaces

Room: Milo - Session BI-MoE

## Biofouling

Moderator: Lara Gamble, University of Washington, USA

5:40pm **BI-MoE1 In Situ Molecular Imaging of Hydrated Biofilm Using Time-of-Flight Secondary Ion Mass Spectrometry**, Xiaoying Yu, M. Marshall, X. Hua, B. Liu, Z. Wang, Z. Zhu, A. Tucker, W. Christer, T. Thevuthasam, Pacific Northwest National Laboratory

One of the most important processes in nature involves bacteria forming surface attached microbial communities or biofilms. Biofilms possess a complex structure made of a highly-hydrated milieu containing bacterial cells and self-generated extracellular polymeric substances (EPS). We report a unique approach of molecular imaging of biofilms in their native environments using time-of-flight secondary ion mass spectrometry (ToF-SIMS) to address potentially the grand challenge of complex interfacial dynamics in biogeochemistry. Biofilm is grown on a silicon nitride (SiN) membrane window in a recently developed microfluidic single channel flow reactor. Continuous imaging of complex liquid samples can be performed with high precision and sensitivity using this technique. Direct probing of the biofilm occurs *in situ* within a windowless detection area of 2  $\mu\text{m}$  in diameter as soon as the hole is drilled through by the SIMS primary ion beam.

The microfluidic reactor consists of a SiN window for biofilm attachment and ToF-SIMS detection. Biofilm formation is conducted by scaling down a known protocol to the microfluidic regime. *Shewanella* with a green fluorescent protein was used so that biofilm formation can be followed in real time using confocal fluorescence microscopy. Biofilm is generally grown for 6 to 7 days before harvesting. ToF-SIMS analysis is performed immediately upon harvest. A ToF-SIMS V spectrometer (IONToF GmbH, Germany) is used.

Depth profiling is used to drill through the SiN membrane and the biofilm grown on the SiN substrate. Characteristic fatty acids fragments are clearly identified in the  $m/z$  spectra. When compared among dried biofilm sample, uninoculated medium solution, and the hydrated biofilm, principal component analysis (PCA) shows distinctions among them. 2D and 3D image reconstructions are conducted. Image PCA is done to further investigate biofilm spatial inhomogeneity. Detailed analysis of dried EPS in bound, loose, and total forms shows distinctions in their chemical makeup. PCA of hydrated biofilm, soluble total EPS, and medium solution provides new insight of the role of EPS in biofilm formation.

We show that molecular imaging of biofilm in the hydrated environment using ToF-SIMS is possible using the unique microfluidic device for the first time. Moreover, probing the natural biofilm microenvironment without drastic sample treatment such as freezing or drying makes it possible to investigate how biofilm develop metabolic and chemical heterogeneities in its hydrated state. The multimodal nature of our microfluidic reactor permits multiplexed *in situ* chemical imaging and advances mesoscale bioimaging.

6:00pm **BI-MoE2 Slime Versatility: Diverse Roles of Slimes in Bacterial Biofilms**, Cynthia Whitchurch, The iThree institute, University of Technology, Sydney, Australia

INVITED

Many species of bacteria produce extracellular "slimes" comprised of polysaccharides or DNA that provide several advantageous functions to the bacterium including protection from environmental stresses that include physical (e.g. dehydration, osmotic pressure), chemical (e.g. disinfectants, antibiotics, pH) and biological (e.g. mammalian immune system) challenges. A hall-mark feature of bacterial biofilms is the self-produced extracellular slime that provides intercellular connectivity and mediates attachment of cells and biofilms to abiotic and biotic surfaces. Slimes also participate in bacterial surface motilities that mediate the active expansion of bacterial biofilm communities.

Over the past decade, slime comprised of extracellular DNA (eDNA) has been found to be essential for biofilm formation by many species of bacteria where it is thought to function as an intercellular "glue" that binds cells together in mature biofilms. Interestingly, eDNA is also essential during the early stages of biofilm development by *Pseudomonas aeruginosa*, however, the precise roles of eDNA in this process have yet to be elucidated. Many species of bacteria, including *P. aeruginosa*, utilize twitching motility to actively translocate across solid and semi-solid surfaces. Twitching motility can manifest as a complex, multicellular behaviour that enables the active expansion of bacterial biofilms. We have used advanced techniques in microscopy, computer vision and image

informatics to explore the roles of eDNA during early biofilm development and active biofilm expansion by *P. aeruginosa*.

6:40pm **BI-MoE4 Towards a Scalable Biomimetic Antifouling Coating**, MaryNora Dickson, E. Liang, N. Vollereaux, CA. Choe, AF. Yee, University of California, Irvine

It has been found that the nanopillars on cicada wings are inherently antibacterial, irrespective of surface chemistry (Ivanova *et al.*, [Small](#), 2012). Thus, fabrication of devices presenting such nanostructures would obviate the requirement for any special surface chemical modification. Nano- and microstructured antibacterial surfaces have been previously proposed, including the Sharklet microstructured film (Chung *et al.*, 2007), black silicon (Ivanova *et al.*, 2013) and multi-scale wrinkled polymer films (Freschauf *et al.*, 2012); none of these approaches can be used on ordinary polymer surfaces or easily scaled up. Thus, we endeavored to apply industrial nanostructuring techniques to generate biomimetic antibacterial nanostructures at the surfaces of ordinary polymers: poly(methylmethacrylate) (PMMA) polycarbonate (PC). To begin, we replicated the nanopillars of a cicada wing utilizing a double imprinting process. First we molded the pillars in hard polydimethylsiloxane (hPDMS) and applied a backing of PDMS to produce pliable elastomeric stamps presenting a large area (diameter 15 mm) of nanoholes. Next, we utilized either dropcasting of polymer solution or thermal imprinting into a polymer thin film to generate fields of polymer pillars. Dropcasting was used for experiments that required a large area of pillars, since the natural curvature of the cicada's wing precludes large-area thermal imprinting into flat polymer thin-films. In contrast, thermal imprinting generated very flat, thin, pillared polymer films, which were more suitable for our light transmission microscopy experiments. To make the nanopatterning technique more industrially viable and generate a larger patterned area, we next employed nanoimprint lithography. A commercially available antireflective stamp (Holotools, Germany) with a nanopillared pattern very similar to that of the cicada's wing, and was used to imprint large, flat, nanostructured polymer thin films. In contaminated aqueous environments, our nanopillared surfaces 1) exhibited reduced surface adhesion of live *E. coli* determined by a standard fluorescence based viability assay, and 2) killed these bacteria, as evidenced by a decrease in colony forming units in suspension over time (up to 24 hours). Surface chemistry played a minor role. Our surfaces could be used for a wide variety of environmental and medical applications, including surgical trays / instruments and door handles (which function in air), and for implantable medical devices or catheter tubes (which function in aqueous environments).

7:00pm **BI-MoE5 Self-Organization of Bacterial Biofilm Expansion through Surface Modification**, E.S. Gloag, Lynne Turnbull, CB. Whitchurch, The iThree institute, University of Technology, Sydney, Australia

**Introduction:** Many bacterial pathogens have the capacity to actively expand their biofilm communities via complex multi-cellular behaviours. We have observed that when the biofilms of *Pseudomonas aeruginosa* are cultured at the interstitial surface between a coverslip and solidified nutrient media, the resulting biofilms are characterised by an extensive pattern of interconnected trails that emerges as a consequence of the active expansion of these communities.

**Aim:** To identify the factors governing emergent pattern formation during *P. aeruginosa* biofilm expansion.

**Experimental methods:** Bacterial biofilms were cultured at the interstitial space between solidified growth media and a glass coverslip. Biofilm expansion was observed using phase contrast time-lapse microscopy and the topography of the underlying media was imaged using atomic force microscopy (AFM) and 3D optical profilometry after the cells were removed by washing the samples with water.

**Results:** Our observations have revealed that during the migration of *P. aeruginosa* biofilms, aggregates of cells at the advancing edge forge furrows as they migrate across the semi-solid media. The formation of a series of interconnecting furrows and the re-inforcing effect of cells traversing these furrows leads to extensive remodelling of the substratum. Our analyses indicate that whilst the furrows are shallow relative to the height of the bacterial cells, this appears to be sufficient to confine cells within the furrows. We have confirmed that furrows guide the migration of biofilm bacteria using PDMS microfabricated channels. The generation and maintenance of the interconnected furrow network therefore accounts for the extensive large scale-patterning that is characteristic of these bacterial biofilms.

**Conclusion:** Our observations indicate that emergent pattern formation during biofilm expansion across semi-solid media occurs due to self-generated surface modification by the biofilm community.

7:40pm **BI-MoE7 Development of Micro/Nanofibrous Meshes as Smart Dressings for Chronic Wound Care, Martina Abrigo, P. Kingshott, S.L. McArthur,** Swinburne University, Australia

Diabetic, pressure, venous and arterial ulcers are a large social, economic and healthcare burden. These chronic non-healing wounds show delayed and incomplete healing processes exposing patients to high risk of infection. The design of wound dressings that combine the necessary morphological and physical requirements for wound healing with the value-added capability to address optimal cell responses and impair bacterial proliferation represents a major challenge in chronic wound care. Polymeric nanofibrous meshes fabricated through the electrospinning process are promising candidates as wound dressings due to their high surface area, micro-porosity and non-woven structure. In this study, the parameters of the electrospinning process (such as spinning rate and electric field intensity) were optimized to fabricate nanofibrous membrane in Polystyrene (M.W. 250,000). Electrospun materials have been used as scaffolds for tissue engineering for a number of years, but there is surprisingly little literature on the interactions of fibers with bacteria. In order to understand microbial infiltration and control in wound dressings, a number of microbiological assays (MTT, MTS and live/dead) were completed using *E. Coli*, *P. Aeruginosa*, *S. Aureus* in an effort to understand how the morphological and structural properties of the electrospun meshes influence bacterial attachment, proliferation and growth. Fiber diameter was found to affect the capacity of wound bacteria to adhere onto the fibers and spread within the fibrous network. Bacterial size and shape also resulted to play a key role in regulating the interaction of bacteria with the fibers.

8:00pm **BI-MoE8 The Geno-Toxicant Reactivity of Metal-Modification on the Surface of Nanomaterials, Yu-Tzu Huang, W.-J. Chen,** Chung Yuan Christian University, Taiwan

The metal-modification on the surface of nanomaterials are extensively used in biomedical and environmental applications recently. Numerous novel nanocomposite materials have been developed; however, reactivity of the biological effects of these nanomaterials towards living organisms is insufficient. Here, we studied the antibacterial reactivity of two kinds of metal containing nanomaterials: (1) metal organic frameworks (MOFs): iron, chromium, aluminum and (2) hydroxyapatite with metal inclusion (gold or silver). Results of the minimum inhibitory concentration (MIC), half maximal inhibitory concentration (IC<sub>50</sub>), gene expression profile, quantitative gene expression levels, and scanning electron microscopy imaging were used to investigate the possible antibacterial mechanisms. The expressions of six genes (16S ribosomal RNA, DNA polymerase I, DNA polymerase II, cytochrome d complex, glucan biosynthesis protein G, and D-glyceraldehyde-3-phosphate dehydrogenase) indicated the genotoxicity is highly related to membrane or cell wall proteins. In addition, the toxic effects were dominant in iron/silver containing nanomaterials than chromium/aluminum/gold ones. Our findings have opened doors for understanding the insight reactivities of metal-modified nanomaterials, which will help their applications with controlled safety.

## Nanomaterials

**Room: Hau - Session NM-MoE**

## Nanomaterials Characterization & Reactivity I

**Moderator:** Takhee Lee, Seoul National University

5:40pm **NM-MoE1 Interfacial Chemistry between gas-phase molecules and GaAs surfaces: morphology dependence, Sylwia Ptasińska, XQ. Zhang,** University of Notre Dame

A detailed understanding of molecular interactions at the interface of two-dimensional GaAs systems under ultra-high vacuum (UHV) conditions has been achieved over the decades. While research on the understanding of such interactions with lower-dimensional GaAs-based structures, such as one-dimensional nanowires (NWs), has not been performed despite the potential importance of these structures in developing nano-electronic devices. Moreover, surface characterization of GaAs under more realistic conditions rather than the UHV studies, are critical in any attempt to correlate surface chemistry with device properties.

Due to recent advances in the surface characterization techniques, and especially the development of Near Ambient Pressure X-ray Photoelectron Spectroscopy (NAP XPS) [1], we are able to monitor in-situ surface chemistry under elevated pressures and temperatures.

In our present work, we performed NAP XPS studies for different GaAs morphologies:

the simple planar GaAs(100) crystal and a radically non-planar GaAs surface comprised of an ensemble of GaAs NWs under elevated pressures of O<sub>2</sub> or H<sub>2</sub>O molecules. The evolution of O<sub>2</sub> and H<sub>2</sub>O molecule dissociation on GaAs NWs was tracked under in-situ conditions as a function of temperature and gas pressure to establish whether the processes of dissociation leading to oxidation and hydroxylation depend on surface morphology. In contrast to ideally flat GaAs single crystal surfaces [2], gas molecules experienced the enhanced dissociation on GaAs NW ensembles due to an increase in the surface area ratio and the presence of stepped edges, atom vacancies, and other defects on non-flat semiconductor surfaces [3].

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6:00pm **NM-MoE2 Reactivity of Hydrogen-Absorbed Pd and PdAu Alloy Surfaces, S. Ohno, S. Ogura, M. Wilde, Katsuyuki Fukutani,** University of Tokyo, Japan

Pd is a typical material that absorbs hydrogen in its bulk, and hydrogen absorbed in Pd clusters was shown to play an essential role in olefin hydrogenation reactions [1,2]. We have recently studied absorption of hydrogen in Pd(110) [3] and Pd<sub>70</sub>Au<sub>30</sub>(110) [4], and shown that hydrogen can be efficiently absorbed in Pd<sub>70</sub>Au<sub>30</sub>(110) [4]. In the present work, we have studied reactivity of Pd(110) and Pd<sub>70</sub>Au<sub>30</sub>(110) alloy surfaces towards olefin hydrogenation reactions with thermal desorption spectroscopy (TDS) and nuclear reaction analysis (NRA) that allows for high-resolution depth profiling of hydrogen [5].

When a Pd(110) surface was exposed to H<sub>2</sub> at a low temperature, TDS revealed desorption features at ~150 K and ~300 K, which are attributed to hydrogen adsorbed in the bulk and adsorbed on the surface, respectively [3]. Whereas coadsorption of C<sub>4</sub>H<sub>8</sub> with surface H on Pd(110) revealed no hydrogenation reaction, hydrogenated products of C<sub>4</sub>H<sub>10</sub> were clearly observed in presence of H in the adsorbed state. When the Pd<sub>70</sub>Au<sub>30</sub>(110) surface was exposed to H<sub>2</sub>, on the other hand, a single desorption feature was recognized at ~250 K, which is different from both the pure Pd(110) and Au(110) surfaces [4]. Examination of the Pd<sub>70</sub>Au<sub>30</sub>(110) surface with low-energy electron diffraction and Auger electron spectroscopy revealed that Au segregates at the surface of the alloy. Hydrogen is dissociated at minor Pd sites on the surface and adsorbed into bulk through the Pd site without spillover onto the Au site [4]. When C<sub>4</sub>H<sub>8</sub> was adsorbed on the D-adsorbed Pd<sub>70</sub>Au<sub>30</sub>(110) surface, TDS showed no hydrogenated products of C<sub>4</sub>H<sub>10</sub>, which is in remarkable contrast with the Pd(110) surface. Instead of the hydrogenation reaction, H-D exchange reactions were clearly observed. We discuss the reaction mechanisms on these two surfaces.

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6:20pm **NM-MoE3 Alumina Incorporated Tin Oxide (SnO<sub>2</sub>) Pellets as Co Sensors, O. Amador, Cinvestav-Ipn, Mexico City, Mexico, Krishnakarthik Venkata, A. Maldonado, Cinvestav- Ipn, Mexico City, Mexico**

In this work we have utilized a novel Chemical-physical method for synthesis of SnO<sub>2</sub> nanoparticles. In two previous works [1,2], we have reported about the homogeneous precipitation synthesis of SnO<sub>2</sub> powders by two different precipitation agents, Urea and Ammonia; those powders were further ball milled to manufacture SnO<sub>2</sub> pellets and then tested for CO gas sensing. Compared to other methods [3-4] our synthesis route offers SnO<sub>2</sub> particles with very less agglomeration, particle size in the order of 15-20 nm, and homogeneous size distribution of the particles. An research



group reported a maximum sensitivity for SnO<sub>2</sub> pellets around 8, for 1000 ppm of CO at operating temperatures of 300°C [5], whereas in our pellets, sensitivities were around 300 and 550 for CO when were measured at 300 ppm for 200 and 300°C, respectively. Later the ball milled powders were mixed with Al<sub>2</sub>O<sub>3</sub> powders (particle size around 1µm) with different ratios like 1:1, 2:1 and 4:1 in order to save tin oxide powder and also for increasing the oxygen trapping by increasing the porosity of the pellets. The effect of alumina mixing ratio on the pellets sensitivity was also studied. Maximum sensitivity obtained in pellets manufactured from ball milled SnO<sub>2</sub> powders, at 300 °C for 300 ppm, by two different powder preparation routes were **548** and **262**, whereas for mixing pellets with alumina at a 2:1 ratio (SnO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub>), were **483** and **340**, for the same two preparation methods. The tendency of increasing the sensitivity with the operation temperature and the gas concentration was achieved successfully. The sensitivities obtained for pure ball milled SnO<sub>2</sub> and alumina 2:1 mixed pellets were almost in the same range. Therefore, high sensitivities can be achieved with less sensing material.

**Keywords:** Gas Sensors; Homogenous Precipitation; Sensitivity; CO, Pellets; Tin Oxide Powders.

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#### 6:40pm NM-MoE4 Nanocatalysts at Work, *Beatriz Roldan Cuenya*, Ruhr University Bochum, Germany **INVITED**

In order to comprehend the properties affecting the catalytic performance of metal nanoparticles, their dynamic nature and response to the environment must be taken into consideration. The working state of a nanoparticle catalyst might not be the state in which the catalyst was prepared, but a structural and/or chemical isomer that adapted to the particular reaction conditions. This work provides examples of recent advances in the preparation and characterization of nanoparticle catalysts with well-defined sizes and shapes. It discusses how to resolve the shape of nm-sized Pt, Au, Pd, Cu, and PtNi catalysts via a combination of *in situ* microscopy (AFM, STM, TEM), *operando* spectroscopy (XAFS, GISAXS) and modeling, and how to follow its evolution under different gaseous or liquid chemical environments and in the course of a reaction. It will be highlighted that for structure-sensitive reactions, catalytic properties such as the reaction rates, onset reaction temperature, activity, selectivity and stability against sintering can be tuned through controlled synthesis. Examples of catalytic processes which will be discussed include the gas-phase oxidation of alcohols (methanol and butanol), the oxidation of NO, and the electrochemical reduction of CO<sub>2</sub>. Emphasis will be given to elucidating the role of the nanoparticle size, shape, and chemical state in the activity and selectivity of the former reactions.

#### 7:40pm NM-MoE7 Surface Chemistry of Environmentally and Biologically Relevant Molecules on Nanoparticle Surfaces, *Vicki Grassian*, University of Iowa, USA **INVITED**

The adsorption of environmentally and biologically relevant molecules on the surface of metal oxide nanoparticles can impact the properties of these small particles and thus their behavior. In particular, the impact of surface adsorption of environmentally and biologically relevant molecules from the gas and liquid phase on the properties of nanoparticles in aqueous suspensions (dissolution, aggregation and reaction chemistry) will be presented. Additionally, the role of size, particularly for nanoparticles below 10 nm in diameter, will be discussed. The approach in these studies is to combine nanomaterial characterization using a wide range of techniques including microscopy, spectroscopy, light scattering measurements, along with molecular probes of surface adsorption and surface chemistry to better understand the behavior of oxide nanomaterials in the presence of environmentally and biologically relevant ligands.

#### 8:20pm NM-MoE9 Novel Fabrication of Titanium Dioxide Nanotubes for Cancer Photothermal Therapy, *W. Srituravanich*, Department of Mechanical Engineering, Chulalongkorn University, Thailand, *Bunlaporn Thumrongthanyaluk*, International School of Engineering, Chulalongkorn University, Thailand

Titanium dioxide nanotubes (TiO<sub>2</sub> NTs) have attracted significant attention in biomedical applications due to their biocompatibility and photocatalytic properties. Such a nanomaterial can be coupled with near-infrared irradiation to heat bio-molecules such as cancer cells causing them to death so-called cancer photothermal therapy. In this work, we proposed a novel method to fabricate isolated TiO<sub>2</sub> NTs and utilized them as a therapeutic agent in cancer photothermal therapy. TiO<sub>2</sub> NTs were synthesized by anodization of titanium electrode using diethylene glycol (DEG) +2 vol% HF as electrolyte. TiO<sub>2</sub> NTs were then isolated from Ti substrate by sonication in isopropanol (IPA) for 20 mins. The hepatic cancerous cells (HepG2) were treated with different concentrations of isolated TiO<sub>2</sub> NTs; 0, 6.25, 12.5 and 25 mg/ml under three exposure conditions; dark (no irradiation), UV and Near-Infrared (NIR) irradiation. After the treatment, *in vitro* cell experiment was performed to measure the viability of the cells. According to the results, the viability of cells under NIR irradiation dropped with the increment of the concentration of TiO<sub>2</sub> NTs. At the concentration of 25 mg/ml the viability was reduced by 31%. Thus, isolated TiO<sub>2</sub> NTs shows promising results for cancer photothermal therapy.

#### 8:40pm NM-MoE10 Surface Chemistry of Ore-Binder Mixture System in Relation to Iron Ore Pelletisation, *Akira Otsuki*, University of Lorraine, France

The surface property of single and multi-minerals (hematite and gangue) with bentonite

binder was investigated to produce quality pellets by properly controlling the surface properties of

minerals and to beneficiate low grade/fine iron ores. The results showed that zeta potential of

hematite-bentonite mixture did not change with the bentonite dosage. On the other hand, the type and

amount of gangue minerals greatly affected the zeta potential of the mineral mixture with bentonite.

Specifically, the amount of silica presented in the system governed the changes in zeta potential due to

the bentonite adsorption on silica surface and its charge while alumina had no effect. This is due to

their nature of the charges and interaction with bentonite. This study indicated that the mineral

composition of iron ores significantly affected the surface charge of the ore, and can noticeably

influence the quality of pellets formed by iron ores with the binder.

#### Thin Films

##### Room: Lehua - Session TF+NM-MoE

#### Nanostructures, Graphene, and Magnetism

**Moderator:** Stephen Muhl, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México

#### 5:40pm TF+NM-MoE1 Low-Dimensional Electronic System on Metal-Adsorbed Germanium Surfaces, *Kan Nakatsuji*, Tokyo Institute of Technology, Japan **INVITED**

The electronic properties of metallic nano-materials attract much interests not only because of their potential application to novel electronic devices but fundamental low-dimensional physics point of view. One of the ways to fabricate nano-materials is to deposit small amount of metal atoms on crystalline semiconductor surfaces. In the present study, we have investigated atomic and electronic structures of gold adsorbed Ge(001) and Ge(111) surfaces which exhibit one- and two-dimensional atomic structure, respectively, by scanning tunneling microscopy (STM), angle-resolved photoelectron spectroscopy (ARPES) and density functional calculations.

The Au-adsorbed Ge(001) surface has periodic arrangement of one-dimensional (1D) chain structure and a metallic surface state. This metallic state has been reported to be strictly 1D showing Tomonaga-Luttinger liquid (TLL) behavior[1]. In the present study, its band shape was precisely investigated using a single-domain surface prepared on a vicinal substrate. Our ARPES results clearly revealed that the band has anisotropic two-dimensional (2D) shape in contrast to the previous report. The band dispersion is steeper in the direction perpendicular to the chain contrary to

the intuitive expectation from 1D structure[2]. Our STM study revealed that the top of the 1D chain shows 8 times periodicity on average along the chain with a lot of defects[3]. This rather high density of defects may cause the reduction of density of states at the Fermi level which was previously interpreted as a TLL behavior.

The Au-adsorbed Ge(111) surface exhibits  $\sqrt{3}\times\sqrt{3}$  periodicity. Two metallic surface states,  $S_1$  and  $S_2$ , were observed around  $\Gamma$ , which is consistent with the calculated band structure of the CHCT model. 2D electronic system is confirmed by a rounded hexagonal Fermi surface of  $S_1$  band[4] which has contributions from surface Au and Ge atoms.  $S_2$  is originated only from the Ge atoms. These surface bands split into spin-polarized bands owing to the strong spin-orbit interaction[5]. The modification of the electron filling of the  $S_1$  band by additional Au atoms will be also discussed[6].

The author thanks Y. Motomura, R. Niikura and Prof. F. Komori in Institute for Solid State Physics, University of Tokyo for their close collaboration, and Y. Oda and Prof. A. Ishii in Tottori University for their collaboration in theoretical part of this work.

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**6:20pm TF+NM-MoE3 Effective Mass of a Two-Dimensional  $\sqrt{3}\times\sqrt{3}$  Ga Single Atomic Layer on Si(111), Michael Schnedler,** Forschungszentrum Jülich GmbH, Germany, *Y. Jiang*, Peking University, China, *K.H. Wu*, Institute of Physics, Chinese Academy of Sciences, China, *E.G. Wang*, Peking University, China, *R.E. Dunin-Borkowski*, *P. Ebert*, Forschungszentrum Jülich GmbH, Germany

The transport of charge carriers in semiconductor nanostructures is particularly important for nanoscale devices. In a semi classical approach, the transport of charge carriers is to a large degree governed by the effective masses of electrons and holes, which are reasonably well known for most bulk materials. However, with ongoing miniaturization of semiconductor devices and the trend towards the use of nanostructures, the increasing surface to volume ratio reduces the relative fraction of bulk material. Hence, transport in semiconductor nanostructures is to a large degree determined by surface and/or interface effects, where little is known about the effective masses.

The effective masses of surface states can be derived from angle-resolved photoemission spectroscopy (ARPES), but it is hardly applicable on individual nanostructures. In contrast scanning tunneling spectroscopy (STS) is ideally suited for probing the local density of states of an individual nanostructure, but it is a very difficult task to quantitatively measure the involved  $k$  vectors and hence the dispersion relation and the effective mass.

Therefore, we illustrate here a methodology applicable to individual semiconducting nanostructures for extracting effective masses of a two dimensional  $\sqrt{3}\times\sqrt{3}$  Ga single atomic layer on Si(111) directly from scanning tunneling spectra. The methodology is based on calculating the tunnel current using its dependence on the effective density of states mass and a parabolic band approximation followed by fitting to the measured tunneling spectra. An effective mass of  $m_{\text{eff,C}}=0.59\pm 0.06$  is obtained for the empty surface state, in good agreement with a band structure calculation and inverse photo electron spectroscopy data.

**6:40pm TF+NM-MoE4  $\alpha'$ , $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> Interstitial Compound as a New Candidate for Rare Earth Free Permanent Magnet - From Thin Film to Bulk -, M. Takahashi, Masahiro Tobise,** Tohoku University, Japan  
**INVITED**

After surprising first report ( $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> phase exhibited a giant saturation magnetization in 1972 as a thin film form [1]), many researches challenged to realize single phase  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub>. At 1993, present author et al. established the method in thin film to attain a relatively high volume fraction of  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> using a reactive sputtering [2]. Precisely determined value of  $M_s$  of  $\approx 240$  emu/g ( $\approx 2.2$  T) even though relatively small value compared to initially reported one and value of  $K_u$  ( $\approx 10^7$  erg/cm<sup>3</sup>) are very attractive as rare earth free permanent magnet material [3]. But as it was very difficult to form metastable  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> single phase even in the thin film, it had been believed that the synthesis of a single phase  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> in bulk form was almost impossible. In 2013, our group established the synthesis procedure of single-phase  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> nanoparticle for the first time, and reported  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> exhibit  $M_s$  of  $\approx 234$  emu/g and  $K_u$  of  $\approx 10^7$  erg/cm<sup>3</sup> [4]. This nanoparticle powder could be synthesized starting from the reduction of Fe-oxides and following nitriding with ammonia gas at temperatures around 145 °C under the very low moisture and oxygen contents less than 1 ppm

through the all process. Mössbauer spectra also revealed that the perfect formation of the single phase  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub>. In order to improve coercivity through the evaluation of magnetic interaction and the quality of  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> crystalline, the anisotropy field  $H_k^{\text{pic}}$  and switching field  $H_p$  are determined by rotational hysteresis loss analysis using randomly oriented nanoparticles assembly. Coercivity of nanoparticle assembly consisting of single-phase  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> formed around 145 °C exceeds 2000 Oe. Normalized coercive force  $H_p/H_k^{\text{pic}}$  and normalized switching field  $H_p/H_k^{\text{pic}}$  are about 0.16 and 0.3, respectively. Coercivity has been improved by surface treatment and reached 3200 Oe at present. Detail on the relationship between these magnetic properties and reversal mechanism is discussed.

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**7:40pm TF+NM-MoE7 Interfaces between Transferred, CVD-Grown Graphene and MoS<sub>2</sub> Probed with STM and ARPES,** *H. Coy-Diaz*, Department of Physics, University of South Florida, Tampa, FL 33620, USA, *J. Avila*, *M.C. Asensio*, 2. Synchrotron Soleil, Orme des Merisiers - Saint Aubin, BP 48 - 91192 - GIF SUR YVETTE Cedex, France, *Matthias Batzill*, Department of Physics, University of South Florida, Tampa, FL 33620, USA

Heterostructures made of different van der Waals materials are of increasing interest because of potential applications in energy harvesting and combination of spin- and valley-ronics. However, the interface properties of these materials are not yet well characterized. One challenge for their characterization is the preparation of large-area high quality materials that enable employment of surface characterization techniques such as scanning probe microscopy and photoemission spectroscopy. Here we demonstrate the transfer of CVD-grown graphene to bulk MoS<sub>2</sub> substrates and report the first STM and ARPES studies of such a system. As expected for weakly interacting materials STM studies only exhibit a very weak moire-superstructure and (nano) ARPES measurements show that the Dirac cone of graphene is maintained. However, (nano) ARPES also shows the formation of band-gaps in the pi-band of graphene where the out-of-plane molecular orbitals of MoS<sub>2</sub> intersect with the electronic-states of graphene. This modification of the electronic structure of graphene in the graphene/MoS<sub>2</sub> heterostructure is contrary to expectations of simple van-der Waals stacked materials. The high quality of the samples will enable further studies of the spin state of the graphene and MoS<sub>2</sub> substrate as well as enable preparation of other heterostructure materials and thus will give a detailed description of the interaction in these heterostructure systems.

**8:00pm TF+NM-MoE8 Universality of Seebeck Coefficients in Graphene/h-BN Nano-Composites,** *Yosuke Ayako*, *A. Akaishi*, *J. Nakamura*, The University of Electro-Communications (UEC-Tokyo) and JST-CREST, Japan

Thermoelectric materials have attracted much attention because of their promising applications in power generation. Recently, we have shown that the superlattices consisting of zigzag graphene nanoribbons (GNRs) and BN nanoribbons (BNNRs) have giant Seebeck coefficients [1]. Such giant Seebeck coefficients of the superlattice models stem from the so-called pudding-mold band with a finite energy gap [2]. Although such types of superlattices have great fascination with thermoelectricity, the experimental synthesis of these two-dimensional structures may be an extremely-challenging task.

In the present study, we suggest more easy-to-make, practical one-dimensional structures possessing the pudding-mold band. We propose the graphene/h-BN hybrid nanoribbons with zigzag edges (hereafter referred to as "nano-composites"), in which both edges of GNRs are terminated with BNNRs. In this study, we specify the models using integer  $n$  and  $m$ , which are the numbers of dimer lines of GNRs and BNNRs, respectively. The Seebeck coefficients of nano-composites have been evaluated on the basis of the Boltzmann transport theory. Electronic band structures have been calculated using the first-principles calculations within the framework of the density functional theory. We have also employed the armchair nano-composites for comparison.

We have shown that the pudding-mold bands have been confirmed for the zigzag nano-composites, but not for the armchair ones. The Seebeck coefficients for the zigzag nano-composites decrease monotonically with increasing  $n$ . Their maximum values become higher than those for graphene and GNRs, though not to the extent of the superlattices [1]. On the other

hand, the Seebeck coefficients for the armchair nano-composites do not become higher compared with those for the pristine armchair GNRs, since the mechanism of the enhancement based on the pudding-mold band does not work for these composites. Here, we should not overlook that the Seebeck coefficients for the armchair nano-composites show the oscillatory-decreasing behavior with increasing  $n$ , and their dependence on  $n$  can be classified into three categories of  $3n$ ,  $3n+1$ , and  $3n+2$ , being analogous to the electronic structure of the zigzag carbon nanotubes [3]. Nevertheless, the Seebeck coefficients shows the universal dependence on the band gaps: the maximal, absolute Seebeck coefficient depends only on the bandgap irrespective of the structural category of nano-composites.

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8:20pm **TF+NM-MoE9 Reduction of Oxygen on Nitrogen-Doped Graphene**, *Akihide Ichikawa, A. Akaishi, J. Nakamura*, The University of Electro-Communications (UEC-Tokyo) and JST-CREST, Japan

Recently, several groups have reported high oxygen reduction reaction (ORR) activities in nitrogen-doped carbon nanomaterials which are candidates of metal-free catalysts for ORR [1]. Lee *et al.* have successfully fabricated nitrogen-doped graphene with the high ORR activity in acid media [2]. It has been confirmed that local atomic configurations of dopants in nitrogen-doped graphene are classified into three functional groups (pyrrole-like, pyridine-like, and graphite-like configurations) [3]. However, the mechanism of the ORR on the nitrogen-doped graphene has not fully understood.

In this work, we examine the ORR on the nitrogen-doped graphene containing the graphite-like N in a basal plane using first-principles calculations. In general, the ORR occurs mainly two pathways: The two-electron pathway ( $2e^-$ ) that is reduced to hydrogen peroxide ( $H_2O_2$ ), and the direct four-electron pathway ( $4e^-$ ) that reduces to water ( $H_2O$ ). Thermodynamic electrode potentials of each process at standard conditions are about 0.68V ( $2e^-$ ) and 1.23V ( $4e^-$ ), respectively. In case of the associative mechanism for the two- and four- electron reduction pathways, the electrocatalytic activity is governed by the stability of reaction intermediates like  $OOH^*$ ,  $OH^*$ , and  $O^*$  (where “\*” refers to a surface site). Free energies of the reaction intermediates have been calculated based on the computational hydrogen electrode model suggested by Norskov *et al.* [4]. We have taken account of effects of electrode potential,  $\Phi$  of a solution, a local electric field in double layer, and water environment.

We have constructed energy diagrams at several electrode potentials on the basis of the first-principles calculations. It has been shown that the  $2e^-$  and  $4e^-$  reduction processes proceed at potentials up to about 0.5V and 0.8V, respectively. This means that we can control the reduction pathway for the nitrogen-doped graphene with the graphite-like N. Proton-electron transfer to  $OOH^*$  (the  $2e^-$  pathway), and the formation of  $OOH^*$  (the  $4e^-$  pathway) are confirmed to be the rate-limiting steps, respectively. The effects of electric field and water environment will also be discussed in the presentation.

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## Thin Films

**Room: Makai - Session TF-MoE**

## Electronics and Displays on Flexible and Hard Substrates

**Moderator:** Lain-Jong Li, King Abdullah University of Science and Technology

5:40pm **TF-MoE1 Organic Thin Film Transistors: Materials, Device Interfaces and Performances**, *Yunqi Liu*, Institute of Chemistry, CAS, China **INVITED**

Organic/polymer thin-film transistors (O/PTFTs) are of great interest for practical applications in active-matrix displays, radiofrequency identification tags, biosensors, and integrated circuits owing to their

advantages of low cost, light weight, and mechanical flexibility. In this presentation, I will report a few results on O/PTFTs from my research group,<sup>[1-10]</sup> including materials, device interfaces and performances.

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6:20pm **TF-MoE3 Investigation of Strain Sensors Based on Thin Graphite Wires**, *Takanari Saito, M. Matayoshi, J. Shirakashi*, Tokyo University of Agriculture & Technology, Japan

Among the flexible electronic devices, the strain sensors have attracted a great deal of interest due to its wide range of utility in real life, for example, the detection of human motion, monitoring personal health and therapeutics. Previously, we have reported that thin graphite wires are simply and easily fabricated from pyrolytic graphite sheet (PGS) [1] which is commercially available from Panasonic Corporation and have potential applications in microheaters [2]. In this report, we focus on the thin graphite wires fabricated on sticky tapes as flexible devices and investigate the electrical properties of the thin graphite wires for strain sensors.

The experimental procedures are as follows. First, graphite wires with the length of 45 mm and the width of 1 mm were cut off from PGS. Then, we prepared thin graphite wires with thickness down to about 3  $\mu$ m using mechanical exfoliation. The electrical properties of the thin graphite wires were studied by applying a tensile bending stress with the radius of curvature from 5 to 25 mm. When applying tensile strains by bending the graphite wires, resistance of the graphite wires could show increasing response. The relative change in resistance ( $\Delta R/R_0$ ) under a bending radius of 5 mm was 48 %, where  $R_0$  is the resistance under zero strain;  $R$  is the resistance under strain; and  $\Delta R=R-R_0$ . It has been proposed that resistance of graphite-based strain sensors under the bending stress changes due to variations in length and cross-sectional area as well as the distance between conductive particles [3]. Hence, the resistance changes of our thin graphite wires are caused by similar mechanism. Therefore, it is suggested that thin graphite wires simply and easily fabricated from PGS can be used as strain sensors.

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[2] M. Matayoshi *et al.*, ICN+T (2014 International Conference on Nanoscience + Technology), July 20-25, 2014, Vail, Colorado, USA.

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6:40pm **TF-MoE4 Photovoltaic Devices, Sensor and Electrostatic Self-Assembly Based on Conjugated Polymers**, *Chang-Lyoul Lee*, Advanced Photonics Research Institute (APRI), Gwangju Institute of Science and Technology (GIST), Republic of Korea, *N.C. Greenham*, Cavendish Laboratory, University of Cambridge, UK, *S.-H. Han*, Mokpo National Maritime University, Republic of Korea, *W.-E. Lee*, Advanced Photonics Research Institute (APRI), Gwangju Institute of Science and Technology (GIST), Republic of Korea, *G. Kwak*, Kyungpook National University, Republic of Korea

INVITED

**In this talk, I will introduce two topics. One is polymer photovoltaic devices and the other is sensor for detecting biomolecules (or heavy metal ions) and patterning application of conjugated polyelectrolyte through *in-situ* electrostatic self-assembly.**

The roll of triplet states in photovoltaic devices (PV) is less studied than in PLEDs. Recent studies show that utilization of triplet excitons in conjugated polymer improves PV device performance. The triplet exciton dynamics of conjugated polymer in phosphorescent dye blended polymer PV device was investigated by photo-induced absorption (PIA) spectroscopy. From the low temperature PIA experiments of phosphorescent dye blended conjugated polymer films, the origin of the enhancement of triplet exciton population of conjugated polymer was revealed. And also, the PIA and PV response studies of phosphorescent dye blended conjugated polymer : fullerene bulk heterojunction PV device as well as phosphorescent dye blended conjugated polymer : fullerene bilayer PV device reveal the photo-physical interaction among the conjugated polymer, phosphorescent dye and fullerene and effects of triplet excitons to the PV device performance. (*Adv. Funct. Mater.*, **20**, 2945, 2010).

The second section of this talk is sensor and patterning application of conjugated polyelectrolyte (CPE). Conjugated polyelectrolyte (CPE) with new signal transduction mechanism, based on sulfonated poly(diphenylacetylene), was developed. The CPE showed relatively weak FL emission in water due to a highly dense stack degree of side phenyl rings, while the stack structure was consistently relaxed by being combined with proteins, showing a great PL amplification. Consequently, the CPE was highly responsive to even a little amount of proteins because each of numerous side phenyl rings act as FL probes. (*Chem. Commun.*, **49**, 9857, 2013).

A new method for patterning conjugated polymer (CP) by *in-situ* electrostatic self-assembly (ESA) of conjugated polyelectrolyte (CPE) with surfactants in a film was reported. The *in-situ* ESA was simply realized by contacting the film to appropriate surfactant solutions. The contacting parts on the CPE film have completely different solubility from the non-contacting parts; the polymer chains in the contacted part also undergo supramolecular rearrangement, consequently resulting in dramatic PL emission enhancement. The optical and structural properties of the contacted part were regulated by varying the alkyl tail length of the surfactants employed. Highly resolved CP patterns can be readily obtained through this *in-situ* ESA approach. (*unpublished results*)

7:40pm **TF-MoE7 Substrate Dependant Film Growth Mechanism for the Production of Highly Durable Multi-Layer Plastic Mirrors**, *Colin Hall, K. Zuber, E. Downey, E. Charraut, D. Evans, P. Murphy*, University of South Australia

The use of polymers to replace traditional materials in the automotive, aerospace and other industries is continuing at a high pace. Polymers offer distinct advantages over glass and metals, such as weight, impact strength, and the ability to be formed into complex shapes. To ensure long service life, however, in some applications the polymers must be coated to provide protection from damage due to mechanical abrasion or chemical attack. This coating can also enhance the plastic's functionality, such as changing its optical, electrical or surface properties.

One such example of this is the development of a highly durable plastic mirror through the deposition of a physical vapour deposition (PVD) multi-layer stack.<sup>1,2</sup> The growth of sputtered layers on plastic substrates requires the use of a relatively thick "hardcoating" (some 3 to 8  $\mu\text{m}$  thick). This hardcoating is used in the ophthalmic and automotive industries and is typically a thermal cured organosilicone nanocomposite resin. Subsequently, a silica and chromium PVD multilayer was deposited to form the durable mirror coating. In developing this coating system to meet automotive glass mirror performance, it was found that there were substrate dependant effects on the sputtered layers characteristics. That is, the type of hardcoating had a direct influence on the growth of the sputtered layers. Interestingly, it was found that the mechanical properties of this hardcoating correlated with changes in optical, electrical and mechanical properties of the grown multi-layer stack.

The understanding developed has aided in the successful commercialisation of the plastic mirror, as the spotter mirror in the Ford F250 truck. However, as the plastic/hardcoat/PVD architecture is used extensively elsewhere (ophthalmic and decorative coatings) the phenomenon is of wide interest.

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8:00pm **TF-MoE8 Investigation of Peculiar Spin Electronic States Induced by Spin-Orbit Interaction Using High-Resolution Spin-Resolved Photoemission**, *Taichi Okuda*, Hiroshima University, Japan

INVITED

Spin-orbit-interaction induced spin polarized surface states such as Rashba spin split states or topological surface states(TSS) are the new class of quantum matter and getting much attention as the key materials for the realization of spintronic devices. Spin polarization reversal in the surface state bands with respect to time reversal symmetry point in these materials expects to suppress backscattering by nonmagnetic impurities and to realize dissipationless spin transport.

In case of Rashba systems, however, the possible back scattering to the spin split pair band having opposite spin polarization hampers the complete suppression of backscattering. In addition, some quasi particle interference pattern of STM measurements show the existence of the scattering path even in the topological insulators. Furthermore, for the real application one should also consider to protect the surface states from the contamination. It has been reported that small amount of gas adsorption can produce the band bending in the topological insulators and changes the property of the TSS dramatically. Thus, in order to use the spin-polarized surface states and realize the spintronic devices one should eliminate these problems.

Here I present some recent results of spin- and angle-resolved photoelectron spectroscopy (SARPES) that show the hints to solve these problems. The first example is a Rashba system on one-dimensional surface states. High-resolution SARPES of Au induced chain structure on vicinal Si(111) surface shows clearly one-dimensional Rashba spin-split states. Interestingly the spin polarization vector is not in-plane but points perpendicular to the surface deviating from the normal Rashba spin-split states. This out-of-plane spin polarization and the one-dimensional band structure will help to reduce the scattering probability of the electron in the system.

Bi film on vicinal Si(111) surface also shows interesting spin structure having out-of-plane spin polarization. Unlike the Bi film on normal Si(111) surface that has (111) orientation, the film on the Si(557) surface shows LEED pattern and surface band structures similar to those of Bi(110) surface. Because of the lower symmetry ( $C_{1h}$ ) of the sample structure not only in-plane but also significant out-of-plane spin polarization has been observed.

As the other examples, the investigation of lead based topological insulator  $\text{PbBi}_4\text{Te}_7$  will be presented. Surface and bulk sensitive SARPES measurement proved the existence of spin-polarized topological surface states protected physically under the quintuple layer. This protected TSS will open the pathway to utilize the spin-split electrons in the future.

8:40pm **TF-MoE10 Spin Current at Surfaces of Strong Spin-Orbit Coupling Materials**, *Shuji Hasegawa, N. Fukui, R. Hobara*, University of Tokyo, Japan, *T. Hirahara*, Tokyo Institute of Technology, Japan, *A. Takayama*, University of Tokyo, Japan

Recent studies have shown that the surface states exhibit spin-split and spin helical structures when spin-orbit coupling is strong enough. This is due to break down of space-inversion symmetry at crystal surfaces. Surface Rashba systems and topological insulators (TI) are the typical examples. This causes interesting phenomena relating to flow of spins, such as spin-polarized current [1] and spin current (without charge current) at crystal surfaces and edges of thin atomic layers of such materials. Such spin current may be useful for future spintronic devices because spin current causes no energy dissipation.

"Spin Hall Effect" (SHE) is one of such phenomena, which produces spin current perpendicular to the charge current. Due to bending of electron flow in opposite directions depending on the spin orientation, caused by strong spin-orbit coupling, a flow of spin is produced in the direction perpendicular to the charge current. Its time-reversal process also occurs (inverse SHE) in which the spin current produces charge current, by which we can detect he effects.

By using a H-shaped pattern of thin  $\text{Bi}_2\text{Se}_3$  film, one of the topological insulators, we have tried to detect the SHE. The pattern was fabricated in a UHV-FIB (Focused Ion Beam) combined with a four-tip STM and MBE chambers [2]. In order to verify the SHE, we measured the nonlocal voltage drop caused by SHE and inverse SHE. All the processes including the film growth, patterning and measurements were done *in situ* in UHV to protect the surface states with a four-tip STM equipped with FIB [2]. The nonlocal voltage drop obtained was mainly explained by the classical Ohm's law,

with small deviation. The deviation is explained by the SHE. From the data fitting we could deduced the spin-Hall angle and spin relaxation length.

[1] T. Tono, et al., New J. Phys. **15**, 105018 (2013).

[2] N. Fukui et al., e-J. Surf. Sci. Nanotech., submitted.

# Tuesday Morning, December 9, 2014

## Biomaterial Interfaces

Room: Milo - Session BI-TuM

### Biomaterial & Wet Interface Characterization

**Moderator:** Xiaoying Yu, Pacific Northwest National Laboratory

8:00am **BI-TuM1 Engineering of Bio-Nano Interfaces with Self-Assembled Peptides**, *Yuhei Hayamizu*, Tokyo Institute of Technology, Japan **INVITED**

Developing elegant hybrid systems of biological molecules on two-dimensional nanomaterials is a key in creating novel bio-nanoelectronic devices. Biomolecules self-assembling into ordered structures on these nanomaterials offer a novel bottom-up approach, where organized supramolecular architectures spatially govern the electronics of nanomaterials. Despite the enormous potential in bridging nano- and bio-worlds at the molecular scale, no work has yet realized a way to control electronic properties of nanomaterials by these biomolecular structures. Our research target is the control of the interface between biotechnology and nanotechnology. In this work, we employ solid binding peptides or artificially-designed peptides which have specific binding affinities to solid surfaces and an ability to form peptide nanostructures on atomically flat surfaces [1,2]. These peptides self-assemble monolayer-thick long-range ordered nanostructures on surfaces of single-layer graphene, and on other two-dimensional materials. We observed that self-assembled peptides on a single layer graphene modify its conductivity depending on their assembled structures.

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[2] T. R. Page, Y. Hayamizu, C. R. So, and M. Sarikaya, "Electrical Detection of Biomolecular Adsorption on Sprayed Graphene Sheets," *Biosens. Bioelectron.*, **33** (1) 304-308 (2012)

8:40am **BI-TuM3 Peptide Control of Biological Membranes — A Molecular View on Lipid Structure, Peptide Folding and Hydration**, *Johannes Franz, D. Schach*, Max Planck Institute for Polymer Research, *J.E. Baio*, Oregon State University, *D.J. Graham, D.G. Castner*, University of Washington, USA, *M. Bonn*, Max Planck Institute for Polymer Research, *T. Weidner*, Max Planck Institute for Polymer Research, Germany

The cell membrane is the most important biological surface as its interaction with peptides is an integral part of transport, communication, energy transduction and survivability. However, an intrinsic difficulty in monitoring peptide interaction with membranes is the required surface sensitivity. Sum frequency generation (SFG) vibrational spectroscopy is well suited to study protein monolayers at lipid surfaces<sup>[1]</sup> because of its inherent surface specificity and is used to investigate molecular interactions of peptides with model membranes. In this study, three different peptides are shown to interact with model membranes in very different ways.

The internalization mechanism of the negatively charged cell-penetrating peptide SAP(E) is proposed as an aggregation on the cell surface followed by an endocytic uptake. Our data suggest peptide affinity is strongly dependent on the lipid headgroup charge with phosphocholine having the strongest interaction with SAP(E). Moreover, the interaction is limited to the headgroup region with no further insertion observable proving the first step of the proposed uptake mechanism. These findings were supported with complementary surface-sensitive UHV-techniques, i.e. X-ray photoelectron spectroscopy (XPS), near edge X-ray absorption fine structure (NEXAFS) spectroscopy and time-of-flight secondary ion mass spectrometry (ToF-SIMS).

In contrast, viral fusion proteins can disrupt membranes and escape from endosomes when triggered at low pH. We are interested in the interaction of GALA, a peptide mimicking viral fusion proteins. While the peptide is unfolded and inactive around neutral pH, the sequence folds into its active  $\alpha$ -helical state at lower pH and causes membrane leakage. We follow GALA activity at the molecular level and probe peptide folding as well as the disturbance and hydration of individual leaflets within model bilayers.

Besides binding to and shredding bilayers, peptides can also help stabilize lipid membranes. For example, bovine serum albumin and specific antifreeze proteins can maintain cell membrane integrity at low temperatures. We briefly discuss preliminary results about the effects of protein-lipid interactions on the temperature stability of lipid mono- and bilayers.

[1] Chen, X., Chen, Z., *BBA* 1758 (2006), 1257-1273.

9:20am **BI-TuM5 Development and Characterization of Tunable Porous 3D Materials for Biomedical and Environmental Applications**, *M.J. Hawker, A. Pegalajar-Jurado, M.N. Mann, Ellen Fisher*, Colorado State University

Porous 3D materials are used in a range of applications from tissue engineering to water filtration to drug delivery systems. In many instances, the surface properties of these materials are not, however, ideal for the intended applications. Low temperature plasmas offer a versatile method for delivering tailored functionality to a range of materials. Despite the vast array of choices offered by plasma processing techniques, there remain a significant number of hurdles that must be overcome to allow this methodology to realize its full potential, especially with porous 3D structures such as membranes and scaffolds. Challenges include ensuring uniform composition following treatment, controlling morphology and damage, characterization of both the external and internal features as well as accurate assessment of bioactivity. Here, we present results demonstrating the relative biocompatibility of various plasma treatment strategies for polymeric membranes and scaffolds. Results from mammalian cell (human dermal fibroblasts) cytotoxicity experiments (MTS, Live/Dead, plating efficiency and morphological studies) will be demonstrated for a range of plasma treated surfaces including bio-nonreactive (e.g. fluorocarbon coated) and bio-reactive (e.g. H<sub>2</sub>O plasma treated) 3D poly( $\epsilon$ -caprolactone) scaffolds. All materials were characterized using X-ray photoelectron spectroscopy, scanning electron microscopy and contact angle measurements. Additional results demonstrating the efficacy of our plasma treatments in creating low fouling antimicrobial membranes and scaffolds will also be presented. Here, tunable hydrophilic surface modification strategies for different polymeric architectures are evaluated, including plasma modification of NO-releasing materials, ultrafiltration membranes, and polylactic acid constructs. Notably, many of the strategies result in 3D constructs that enhance cell growth and proliferation, retain antibacterial properties and offer promising results for applications including tissue engineering, noble water filtration systems, and advanced biomedical devices.

9:40am **BI-TuM6 The Formation of a Self-Hydrated Artificial Phospholipid Membrane on Ultra-Thin Chitosan Layer Deposited from the Gas-Phase**, *M.J. Retamal, M.A. Cisternas*, Pontificia Universidad Católica de Chile, Instituto de Física, Chile, *S.E. Gutierrez-Maldonado, T. Perez-Acle*, Fundación Ciencia & Vida, Chile, *B. Seifert*, Pontificia Universidad Católica de Chile, Instituto de Física, Chile, *M. Busch, P. Huber*, Hamburg University of Technology (TUHH), Germany, *U.G. Volkmann*, Pontificia Universidad Católica de Chile, Instituto de Física, Chile, *Valeria del Campo*, Universidad Técnica Federico Santa María, Chile

The design of interfaces between solid surfaces and biological molecules such as membranes and/or proteins using Si(100)/SiO<sub>2</sub>, a.k.a. *bio-silicon interfaces*, is an important and rapid developing area of both scientific and applied research. Preparation and characterization of artificial biological membranes is a necessary step for the formation of nano-devices or sensors. A soft hydrophilic polymer cushion could help to provide a "bio-mimetic" environment for the membrane and for membrane-spanning proteins. Several candidates to be used as soft-cushion polymers are currently under research, such as dextran, hyaluronic acid and other polysaccharides. Chitosan is a linear polysaccharide obtained by the deacetylation of chitin, which can be found in the shells of crustaceans, exoskeletons of insects, fungi and plants, thus being very easy to obtain from nature at low cost. In the last years, device manufacturing for medical applications adapted the so-called bottom-up approach, from nanostructures to larger devices. We describe the formation and characterization of a phospholipid bilayer (DPPC) on a mattress of a polysaccharide (Chitosan) that keeps the membrane hydrated. The deposition of Chitosan (~25Å) and DPPC (~60Å) was performed from the gas phase in high vacuum onto a substrate of Si(100) covered with its native oxide layer. The layer thickness was controlled *in situ* using Very High Resolution Ellipsometry (VHRE). Raman spectroscopy studies show that neither Chitosan nor DPPC molecules decompose during evaporation. With VHRE and Atomic Force Microscopy (AFM) we have been able to detect phase transitions in the membrane. The presence of the Chitosan interlayer as a water reservoir is essential for both DPPC bilayer formation and stability, favoring the appearance of phase transitions. Our experiments show that the proposed sample preparation from the gas phase is reproducible and provides a natural environment for the DPPC bilayer.

We thank for financial support under FONDECYT grant No. 1100882 and 1141105, and acknowledge a CONICYT scholarship of M.J.R. (Ph.D),

M.A.C. (Master) and S.E.G.M. (Ph.D). U.G.V and T.P.A are grateful to the Anillo Científico Tecnológico ACT1107. S.E.G.M. and T.P.A. acknowledge funding from Programa Basal PFB16 (PIA CONICYT) and Centro Interdisciplinario de Neurociencias de Valparaíso (ICM-Economía P09-022-F). P.H., M.B. M.J.R., and U.G.V. were supported by a bilateral, german-chilean academic exchange project DAAD project no. 56206483 / CONICYT project no. PCCI 044.

10:20am **BI-TuM8 MP-SPR New Characterization Method for Interactions and Ultrathin Films**, Annika Jokinen, N.M. Grangvist, W.M. Albers, J.W. Sadowski, BioNavis, Finland

#### INTRODUCTION

Surface Plasmon Resonance (SPR) has been used already for a few decades for label-free detection and characterization of biochemical kinetics and affinities of many different types of analytes. The physical phenomenon is not limited to biochemistry, but is applicable to other nanoscale characterization of thin films<sup>1</sup>.

#### EXPERIMENTAL METHODS

Aside of the traditional interactions, Multi Parametric Surface Plasmon Resonance (MP-SPR) can be utilized to determine unique refractive index (*R*) and thickness (*d*) of ultrathin (*d* 0.5-100 nm) and slightly thicker films (*d* 300 nm- few  $\mu$ m) without prior assumptions of the RI of the material. These are important properties not only for thin film coating industries and applications, but also for gaining important knowledge in biomaterials. Two methods utilizing MP-SPR to thickness and RI calculations have been introduced, either measuring in two different media (2M) with high *R* difference, such as air and water<sup>1-3</sup>, or at two or more different wavelengths (2W) of light<sup>2,3</sup> in order to characterize properties of the thin films.

#### RESULTS AND DISCUSSION

MP-SPR is suitable for film deposition *in situ* or *ex situ*, which makes it compatible with several deposition methods and thereby makes it applicable to a wide range of surfaces also. Polyelectrolyte multilayer deposition *in situ* was monitored in real-time with MP-SPR. Thickness of each deposited layers was determined utilizing two wavelength method.

Similarly layer thickness and RI was determined also for *ex situ* spin coated cellulose layer. MP-SPR was used not only to determine thickness and RI of the deposited layer but also for real time monitoring of other molecules interaction to the cellulose model surface<sup>4,5</sup>.

Recently, MP-SPR was used also to monitor polymer layer structural changes in real time, such as polymer swelling due to pH or electric potential change<sup>6</sup>. At pH 9 poly (acrylic acid) (PAA) brushes were extended but the brushes collapsed at acidic pH<sup>6</sup>.

#### CONCLUSION

With the ability to characterize both kinetics and nanoscale layer properties, MP-SPR proves to be a versatile tool for nanomaterial, biomaterial and biochemical interactions research, which makes MP-SPR invaluable for multidisciplinary research, where both physical and interaction properties of the materials need to be characterized.

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4. Orelma et al., 12 (12), 2011
5. Kontturi et al., J.Mater. Chem. A, 2013, (ASAP) DOI: 10.1039/C3TA12998E
6. Malmström et al., Macromolecules, 46 (12), 2013

10:40am **BI-TuM9 In-Situ Analysis of Biological and Electrochemical Interfaces Using ToF-SIMS**, Zihua Zhu, X. Yu, Z. Wang, B. Liu, X. Hua, L. Yang, M. Marshall, S. Thevuthasan, J. Cowin, Pacific Northwest National Laboratory

*In-situ* analysis of liquid interfaces using ToF-SIMS is challenging because ToF-SIMS is a high-vacuum technique, but liquids often generate some considerable vapor pressure. For example, the vapor pressure of water is about 20 kPa at room temperature (20 °C), thus handling samples containing water in vacuum is not easily done. We recently developed a self-contained microfluidic device for probing aqueous surfaces and demonstrated its feasibility in ToF-SIMS and SEM.[1,2] The key feature of this device is a small round aperture with a diameter of 2-3 microns, which is opened on top of a microfluidic channel. The aperture is exposed to vacuum and serves as a detection window for ToF-SIMS measurements. Our calculations and experimental data show that vacuum compatibility and possible temperature drop due to water vaporization under vacuum can be well-controlled. Performance of the microfluidic device for *in situ* ToF-SIMS analysis of selected organic molecules at aqueous surfaces has been

tested.[3] This new innovation has been used in *in-situ* study of mechanism of biofilm growth[4] and electrochemical reactions[5] that occur at liquid-solid interfaces. Such *in-situ* chemical information at liquid-solid interfaces is very difficult to be obtained using other techniques.

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11:00am **BI-TuM10 Quantifying ToF-SIMS Depth Profiles and 3D Images for Biological and Organic Materials**, J. Taylor, D.J. Graham, David Castner, University of Washington, USA

To process, reconstruct, and understand the 3D data from complex materials such as multi-component polymers, drug delivery scaffolds, cells and tissues, it is essential to understand the sputtering behavior of these materials. Though much is understood about sputtering characteristics of some organic materials, there is still a general lack of understanding of how organic and biological materials sputter, especially as the complexity of the materials increase. For example, in multicomponent systems each component may have a different sputter rate, resulting in differential sputtering that will distort the reconstructed depth profile. Thus, accurate reconstruction involves accounting for differential sputter rates, complex sample geometries, etc. Polystyrene and PMMA on Si were used as model systems to optimize methods for depth profile reconstruction. Depth profiling of single component and bilayer films was performed using an Ar<sub>1000</sub><sup>+</sup> sputter source and Bi<sub>3</sub><sup>+</sup> analysis beam on an ION-TOF V ToF-SIMS instrument. PMMA sputtered at a significantly higher rate than polystyrene, whilst sputtering of Si can be considered negligible.

Typically the z-axis of depth profiles is converted to depth using an average sputter rate based on measured film thickness and time to remove the film. However, this fails to account for sputter rate variations during the profile, leading to inaccurate film thickness, interfacial position and resolution, and the appearance of penetration into the Si substrate. Applying measured single component sputter rates to the bilayer films, and assuming a step change in sputter rate, yields more accurate film thickness and interface positions; noticeably sharpening the polymer-Si interface. The conversion from sputter time to depth can be further improved by applying a linear change in sputter rate between components across the interface. This further sharpens the interfaces, bringing overall film thickness and interface position more closely in line with expected values. We also have observed a gradual change in sputter rate with mixed polymer blends, possibly due to nanoscale interfacial mixing during sample preparation and storage or induced during the sputter process. Sensitivity analysis performed on variables in sputter rate measurements reveals further scenarios for inaccurate depth profile reconstruction.

This work with a simple laminar system highlights the need for both careful evaluation of component sputter rates and correct application of methods for conversion of sputter time to depth if accurate 3-D reconstructions of complex multi-component samples such as tissue engineering scaffolds are to be achieved.

11:20am **BI-TuM11 In Situ Neutron Scattering Studies of Endothelial Cells Response to Shear Stress**, Jaroslaw(Jarek) Majewski, S. Junghans, Los Alamos National Laboratory, L. Pociwasek, University of Pittsburgh, N. Zebda, G. Birukov, University of Chicago

Neutron reflectivity is very well established experimental tool for obtaining length-scale and density information about well-ordered, layered materials of consistent thickness and high surface occupancy, such as model phospholipid bi- and mono-layers, polymeric thin films, inorganic layered structures, etc. It is much more difficult to obtain any information about poorly stratified samples and samples that incompletely cover the surface. Measuring *living cells* adhesion and response to external stimuli like the fluid (blood) flow provided an interesting challenge because of the complexity, disordered nature, inherent inhomogeneity of the system, a difficulty in controlling and producing samples with consistent surface coverage but also *biological safety requirements*. Despite these challenges, meaningful results can be obtained. I will discuss measurements involving adhesion of human endothelial cells under fluid mechanical shear stress [1]. Understanding of the cell adhesion in dynamic conditions is connected with pathologic buildup of lipids in arterial walls: atherosclerosis. Although

atherosclerosis is responsible for hundreds of thousands of deaths each year from heart attacks and strokes its nature is not fully understood.

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11:40am **BI-TuM12 3D Collagen-Based Biomaterials Assembly: Novel Insights from Advanced Optical Characterization.** *X. Lang, M. Spousta, J. Gigante, A. Vu, Y. Hwang, Julia Lyubovitsky*, UCR

Optical methods are uniquely suited for characterization of complex biological systems due to their generally non-destructive nature. The applications include characterizing biomaterials/devices employed as medical implants or tissue engineered scaffolds. We have been developing advanced optical imaging guided spectroscopy methods to study the structures of 3D collagen-based biomaterials. This talk will summarize the novel insights regarding the physicochemical controls of assembly of collagen biopolymer into the fibers within 3D hydrogels, cross-linking, digestibility and quantification of hydrogels' structural parameters. For example, our recent study indicated that ions strongly affect the aggregation of collagen into the fibers and consequently modulate the length of the fibers that can be prepared. Changing the temperature led to a multilateral response that depended on the type of ion employed. The knowledge obtained can be applied to explore the practically important and complex processes during assembly and dis-assembly of collagen in engineering of functional biomaterials.

## Energy Harvesting & Storage Room: Lehua - Session EH-TuM

### Solar Cells

**Moderator:** Eray Aydil, University of Minnesota

8:40am **EH-TuM3 Understanding and Improving Solar Energy Conversion through Interface Engineering.** *Stacey Bent*, Stanford University, USA **INVITED**

Meeting the world's growing energy needs in a sustainable fashion is one of the most pressing problems of our time. The most abundant source of renewable energy is the sun, which can be converted directly to useful forms of energy such as electricity and fuels by photovoltaics and photoelectrocatalysts, respectively. In this talk, we will discuss the use of nanoscale materials in solar energy conversion, and in particular the role of interface engineering in improving conversion efficiencies. Quantum dots (QDs), which are nanoscale materials typically based on low-band-gap metal chalcogenides, have been widely explored for next generation solar absorbers due to their tunable band gap and high absorption coefficient. Colloidal quantum dot (CQD) solar cells made from lead sulfide (PbS) QDs have achieved a power efficiency of ~ 8%. In these devices, it is important to control the band gap as well the band position of the QDs to efficiently inject electrons and holes into their respective electrodes. We will describe experimental and theoretical studies of the effects of interface engineering through surface ligand modification on the band gap and relative band positions in lead chalcogenide (PbSe<sub>x</sub>S<sub>1-x</sub>) QDs. Multilayer CQD solar cells were fabricated to investigate the effect on carrier collection of QD layers with different relative band positions. We will show that interface engineering can be applied to lead chalcogenide QDs in order to create a favorable band diagram and achieve enhanced photogenerated carrier collection in multilayer CQD devices.

9:20am **EH-TuM5 Understanding Carrier Dynamics in Cu<sub>2</sub>ZnSn(S,Se)<sub>4</sub> Using Time-Resolved Terahertz Spectroscopy.** *G.W. Guglietta*, Drexel University, USA, *K. Roy Choudhury, J.V. Caspar*, DuPont Central Research and Development, USA, *Jason Baxter*, Drexel University, USA

We have used time-resolved terahertz spectroscopy (TRTS) to measure lifetimes and determine recombination mechanisms in Cu<sub>2</sub>ZnSn(S,Se)<sub>4</sub> (CZTSSe) thin films fabricated from nanocrystal inks. TRTS probes photoconductivity on femtosecond to nanosecond time scales that are relevant for recombination in thin film photovoltaics. Terahertz frequencies (0.2-2.5 THz) correspond to typical scattering rates in semiconductors, enabling determination of carrier density and mobility. Ultrafast time resolution permits tracking the evolution of carrier density to determine recombination mechanisms. By manipulating the photoexcitation wavelength and fluence, we can tailor the generation profile of photoexcited carriers to distinguish between surface, Shockley-Read-Hall (SRH), and Auger recombination mechanisms and determine rate constants.

TRTS experiments and modeling were used to understand the role of recombination mechanisms and their contribution to CZTSSe photovoltaic

performance. TRTS photoconductivity shows an instrument-limited onset within 1 ps of an ultrafast pump pulse, followed by a slow decay over nanoseconds. Photoconductivity decay kinetics were fit with a bi-exponential model with two time constants and a weight fraction. The short time constant is typically ~200 ps and roughly corresponds to diffusion to and recombination at the surface. The long time constant is typically ~2 ns and is attributed to SRH recombination. Assignment of these mechanisms is supported by the dependence of kinetics upon excitation fluence and wavelength. Normalized kinetics are independent of fluence over a range of 40x, indicating that no Auger recombination is occurring. Without Auger recombination, we can distinguish between surface and SRH rates by tuning the pump wavelength. As the excitation wavelength is shifted towards the blue, carriers are generated nearer to the front surface and the photoconductivity kinetics are sensitive to the surface recombination velocity. With blue excitation, we see that a larger fraction, ~0.5, of carriers recombine with a short time constant. With redder excitation wavelengths, the carriers are generated more evenly throughout the film and the kinetics are dominated by SRH recombination with the long time constant having a majority of the weight fraction, ~0.8. TRTS provides a pathway to determine performance-limiting recombination mechanisms and measure key parameters like SRH lifetime and surface recombination velocity, helping to direct the design of efficient thin film photovoltaics.

9:40am **EH-TuM6 The CdS/CdTe Solar Cell with the Back Contact Protected by ITO/Mo.** *Juan Peña, V. Rejón*, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, Mexico, *M. Riech*, Universidad Autónoma de Yucatán, Mexico, *N. Hernández-Rodríguez*, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, Mexico

Today CdS/CdTe heterojunction is an important photovoltaic system for conversion of solar energy. Due to the simple techniques used for thin films deposition, it has been brought from laboratory to industrial scale. Although the thin films are deposited by using techniques such as sputtering and CSS, the back contact layers are a challenge in both: the formation of an ohmic contact and that endures a long time. There are several prospects for back contacts using Mo as can be seen in [1]. The solar cell with Cu/Mo as a back contact deposited by using rf-sputtering is reported in [2]. There are few researches that studied how Mo film can be protected against oxidation without adding series resistance. The bilayer Mo/ITO has been used in microelectronics devices [3].

In this work, the CdS/CdTe solar cells that uses Cu/Mo as back contact is investigated. It is shown that the formation of MoO<sub>x</sub> at surface of Mo thin film influences the series resistance. The oxide is formed when the solar cell is used at outdoor conditions without any encapsulation. Here some indoor experiments were made. First, we show how the Mo/Glass film is oxidized when it is annealed at 400 °C in air. Second, how the Mo is degraded at same conditions when it is used on CdTe/CdS cell and annealed at same conditions. Third, how ITO works when it is deposited over of Mo on the solar cell. Preliminary results indicates that the ITO avoids the formation of MoO<sub>x</sub> and mechanical scratching, preserves its electrical properties and the solar cell shows good stability after an annealing at 400 °C.

The films Cu, Mo and ITO were deposited by rf-sputtering. We show evidences that the p-n junction remains working properly and the oxidation of Mo is the main cause of the cell efficiency degradation. By using the thin film of ITO on Mo layer all solar cell characteristics are preserved. The CdTe film was grown by conventional CSS technique. The cells were activated by using CHClF<sub>2</sub>-argon-oxygen gases. DRX spectra and HR-SEM were made for Mo/Glass and ITO/Mo/CdTe structure before and after annealing at 400 °C in air.

#### Acknowledgement

This work has been supported by CONACYT-México under contract FORDECYT-116157, FOMIX-169739 and FOMIX-172298, CeMIE-Sol PY-207450/25. Measurements were performed at LANNBIO CINVESTAV-Mérida, under support from projects FOMIX-Yucatán 2008-108160, CONACYT LAB-2009-01 No. 123913 and CB2012/ 178947.

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10:20am **EH-TuM8 Study of Energy Level Alignment at Electrode Interfaces in Organic Solar Cells.** *Takeaki Sakurai, S. Wang, T. Miyazawa, H. Xia, W. Fu, K. Akimoto*, University of Tsukuba, Japan **INVITED**

Control of electrical properties at organic semiconductor/metal electrode interfaces is one of the significant issues for improving performances of the organic solar cells since it has an influence on carrier extraction and exciton



quenching. In small molecule based organic solar cells, bathocuproine (BCP) is used well as a buffer layer between  $C_{60}$  and metal cathode to improve the device efficiency. Lifetime and the stability of the device with BCP buffer layer, however, are not good for the practical application. To obtain the strategies for the development of the effective buffer layer, we have investigated the electronic structures at the interfaces between  $C_{60}$  and a large variety of organic semiconductors by means of synchrotron based in-situ ultraviolet photoelectron spectroscopy. The  $C_{60}$ /buffer/Ag heterostructures were formed by depositing buffer materials on Ag and subsequently depositing  $C_{60}$  onto buffer/Ag stack layer in a step-by-step way in a vacuum deposition chamber. A series of perylene derivatives (PTCDA, PTCDI and PTCBI), TCNQ derivatives (TCNQ and F4TCNQ) and pyridine based acceptor molecules (BCP, TPBi and TAZ) were applied as buffer layers. For all buffer/Ag stack structures, the LUMO level of buffer layers almost accords with Fermi level of Ag, that is, electron is easily transferred from the Ag electrode to the buffer layers due to the disappearance of the electron injection barrier. In contrast, the electron injection barrier height between LUMO of  $C_{60}$  and LUMO of buffer materials correlates with the work function of the buffer/Ag stack structures ( $\Phi_{\text{buffer}}$ ). We conclude that to select a buffer/Ag heterostructure with low work function is important in order to maintain good electric contact near Ag cathode. The detailed physical mechanism about the energy level alignment will be discussed using charge transfer model.

11:00am **EH-TuM10 n-type Thin Film  $WSe_2$  for use in Homojunction  $WSe_2$  Solar Cells**, *A. Sarkar, Natale Ianno, R.J. Soukup*, University of Nebraska-Lincoln

Previously we have shown that as-grown p-type thin film  $WSe_2$  is an excellent candidate for an earth abundant photovoltaic absorber.<sup>1</sup> The vast majority of thin solar cells are heterojunction devices with a wide band gap n-type window layer. Many of the device issues are centered on the heterojunction interface, making a homojunction more desirable. The problem here is growing n-type material in thin film systems. In this work we present the structural, optical, and electrical properties of n-type thin film  $WSe_2$  grown via the selenization of sputter deposited copper doped tungsten films. We will show that highly textured films with an optical band gap in range of 1.45 eV, and absorption coefficients greater than  $10^5/\text{cm}$  across the visible spectrum can be easily achieved. In addition we will present Hall Effect and carrier density measurements as a measure of film quality. We employ these results to numerically simulate homojunction solar cells based on this material, where we will show efficiencies greater than 20% are possible.

1. Q. Ma, H. Kyureghian, J. D. Banninga and N. J. Ianno, MRS Proceedings , Volume 1670 , 2014. DOI: <http://dx.doi.org/10.1557/opl.2014.477>

11:20am **EH-TuM11 Samarium Sulfide-Cerium Sulfide, A Potential Band Gap Variable Alloy System for Use in Spectrum Splitting Photovoltaic Systems**, *Rodney Soukup, N.J. Ianno, F. Urias-Cordero, C. Berger, A. Sarkar, M. Hilfiker*, University of Nebraska-Lincoln

A new research thrust to obtaining high efficiency photovoltaic systems is spectrum splitting, where the input solar radiation is physically separated via input optics and channeled to a planar array of individual cells, each with a band gap tuned to absorb a specific band width of radiation. This approach allows for simpler device fabrication and a wider breadth of band gaps than the common multi-junction design, in exchange for a complex optics structure to separate the incoming light. Both these approaches require high efficiency cells over a broad range of band gaps. Currently this is met by III-V alloy single crystal cells and while significant advances have been made in reducing the fabrication cost, recent best estimates place their cost at 1-5x single crystal silicon cells. In addition many of these materials contain indium, whose supply may be limited.

In order for the multi-junction and split spectrum designs to fully realize their potential, it is necessary to explore other classes of semiconducting materials with tunable band gap, better crystal abundance and lower production costs. The  $Sm_{2-x}Ce_xS_3$  alloy system with its potentially broad band gap range (0.8-1.9 eV), as grown p-type majority carrier, potentially excellent optoelectronic properties in polycrystalline form and abundance is an excellent candidate. We will present preliminary data on the growth, optical and electrical properties of thin film  $Sm_2S_3$ , and  $Ce_2S_3$  as an initial study of the alloy formation.

## Nanomaterials

**Room: Hau - Session NM-TuM**

## Nano Devices

**Moderator: Joerg Patscheider, Empa, Switzerland**

8:20am **NM-TuM2 Molecular- and Polymer-based Electronic Devices on Rigid and Flexible Substrates**, *Takhee Lee*, Seoul National University, Republic of Korea **INVITED**

Idea of utilizing individual molecules as the electronic components in future ultrahigh-density electronic devices has generated tremendous attention. I will explain recently developed understanding on the electrical transport characteristics through various types of molecular junctions on flat or flexible substrates [1-3]. In particular, obtaining transistor action from molecular orbital control has been the outstanding challenge of the field of molecular electronics nearly since its inception. In this talk, I will demonstrate a direct electrostatic modulation of orbitals in a molecular transistor configuration in electromigration nanogap [1] or in mechanically-controllable break junction (MCBJ) [2]. I will also demonstrate functional devices such as diodes or photoswitches at the molecular-scale on both rigid and flexible substrates [3].

I will also present a brief summary on general characteristics of the materials, device structures, and switching mechanisms used in polymer-based non-volatile memory devices. Strategies for performance enhancement, integration, and advanced architectures in these devices will be presented [4].

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9:00am **NM-TuM4 High-Throughput Nanogap Formation by Field-Emission-Induced Electromigration**, *Mitsuki Ito, K. Morihara, T. Toyonaka, K. Takikawa, J. Shirakashi*, Tokyo University of Agriculture & Technology, Japan

High-throughput nanogap formation is reported for simultaneously fabricating arrays of integrated nanogaps. Using this method, series-connected 10 nanogaps with symmetrical and asymmetrical shapes were integrated. The integration was achieved using electromigration (EM) induced by First, series-connected 10 Ni nanogaps having symmetrical shape were fabricated by electron-beam (EB) lithography and lift-off process. After performing the activation with final preset current  $I_s = 300$  nA into the 10 nanogaps, the separation of the gaps was reduced to less than 10 nm. This tendency is quite similar to that of series connected 10 nanogaps having asymmetrical shape. Therefore, it is indicated that integration of nanogaps using activation method hardly depends on the shape of nanogap electrodes. Furthermore, activation method was also applied into 30 nanogaps connected in series, for the mass production of identical nanogaps. As a result, the distance between the Ni nanogap electrodes was totally and completely controlled by performing the activation. These results clearly suggest that the integrated nanogaps can be simultaneously fabricated by the activation procedure.

9:20am **NM-TuM5 In-Situ AFM Imaging of Structural Change in Metal Nanowires during Feedback-Controlled Electromigration**, *Mamiko Yagi, T. Saito, J. Shirakashi*, Tokyo University of Agriculture & Technology, Japan

We present real time atomic force microscopy (AFM) imaging of structural changes in gold (Au) nanowires during feedback-controlled electromigration (FCE) process. The resistance increases during the FCE process and is associated with drastic changes of the nanowires morphology, suggesting successful control of electromigration (EM) by FCE scheme. Moreover, we find that the AFM images after performing the FCE indicate a matter redeposition along the nanowire in the direction of the anode side. This grains show faceting structures at the anode side. Furthermore, in order to obtain quantitative information on height of structures, cross sections of the nanowire obtained from the AFM images during FCE was investigated. Height evolution of the narrowest part of the wire perpendicular to the electron flow is obtained, resulting that void nucleation and void growth along the grain boundaries, which are located on the border of the nanowire, start in the vicinity of the nanowire constriction at the cathode side. These results imply that *in-situ* AFM technique provides insight into the behavior of EM-induced voids in nanowires during FCE.

9:40am **NM-TuM6 Single Carbon Nanotube Devices for Integrated Photonics**, *Yuichiro Kato*, The University of Tokyo, Japan

Single-walled carbon nanotubes have unique optical properties as a result of their one-dimensional structure. Not only do they exhibit strong polarization for both absorption and emission, large exciton binding energies allow for room-temperature excitonic luminescence. Furthermore, their emission is in the telecom-wavelengths and they can be directly synthesized on silicon substrates, providing new opportunities for nanoscale integrated photonics.

Here we discuss the use of individual single-walled carbon nanotubes for optical devices that could be integrated in silicon photonics. Their light emission properties can be controlled by coupling to silicon photonic structures such as photonic crystal microcavities [1,2] and microdisk resonators [3]. With the strong absorption polarization at the nanoscale, they allow for unconventional polarization conversion that results in giant circular dichroism [4]. More recently, we have found that excitons can dissociate spontaneously [5], enabling photodetection at low bias voltages. Ultimately, it should be possible to combine these results to achieve generation, manipulation, and detection of photons on a chip.

Work supported by SCOPE, KAKENHI, The Canon Foundation, The Asahi Glass Foundation, KDDI Foundation, and the Photon Frontier Network Program of MEXT, Japan. The devices were fabricated at the Center for Nano Lithography & Analysis at The University of Tokyo.

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10:20am **NM-TuM8 Large Scale Confinement Induced Alignment of Gold Nanorods**, *Waqar Ahmed*, COMSATS Institute of Information Technology, Pakistan, *C. Glass, J.M. van Ruitenbeek*, Leiden University, Netherlands

Gold nanoparticles have attracted enormous attention owing to their interesting optical properties arising from the surface plasmon resonance. The plasmon peaks are very sensitive to the size and shape of the nanoparticles. For anisotropic nanoparticles there are multiple plasmon peaks due to the shape anisotropy. For instance, for a rod-shaped gold nanoparticle, there are two plasmon peaks, owing to the difference in resonance frequencies of electrons along the length and width of nanorods. The relative intensity of these peaks can be controlled by controlling the orientation of nanorods with respect to the incident electromagnetic wave's polarization. Therefore, for application purposes, it is crucial to control the orientation of nanorods.

In this work we describe a simple and elegant method to obtain wafer scale alignment of gold nanorods. We have used hydrophilic-hydrophobic contrast patterned substrates to selectively deposit gold nanorods in desired regions of substrate. The gold nanorods were grown in solution and then deposited on the substrate simply by drop casting. As the nanorods were hydrophilic, they only deposited in hydrophilic regions. When the hydrophilic stripe width becomes comparable to the length of the nanorod, the nanorod aligned along the length of the hydrophilic stripe. The degree of alignment increased with decrease in the stripe width. The alignment is influenced by various entropic and energetic forces such as orientational entropy, excluded volume entropy, van der Waals forces and electrostatic forces [1]. We were able to tune the strength of these forces simply by tuning the concentration of nanorods in solution. Our results agree well with the two dimensional Monte Carlo simulations of confined rectangles.

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11:00am **NM-TuM10 Nanodevices for Molecular Detection based on Nanomaterials and Nanogap**, *D.K. Park, C.Y. Lee, A. Kang*, Sungkyunkwan University, Korea, *WanSoo Yun*, Sungkyunkwan University, Korea, Republic of Korea **INVITED**

Singularity dictates a device function at the nanoscale. Dopants or impurities, structural defects, adsorbates, and stray charges can behave as a singularity in certain conditions, either promoting or deteriorating the device function, which frequently is the major concern in the implementation of nanoscale memories and sensors.

In a nanodevice adopting nanomaterials, the control over singular points in the nanomaterials can be regarded as a tuning process of the device property, which may open up a new possibility of its application to the

molecular measurements. In the earlier part of this talk, an example of the property-tuned nanodevice for molecular measurements will be discussed after a short introduction of visualizing the singularities in a nanodevice based on the nanomaterials.

An extreme case of the singularity can be found in a nanogap device which has two electrodes separated by a few to a few tens of nanometers. In the later part of this talk, application of nanogap devices in the electric/electrochemical (bio) molecular detection will be discussed with our recent experimental results along with the way of their simple lab-scale mass production.

11:40am **NM-TuM12 Band Offsets at Zincblende-Wurtzite GaAs Nanowire Sidewall Surfaces**, *P. Capiod, T. Xu, J.P. Nys, M. Berthe*, Institut d'Electronique et de Microélectronique et de Nanotechnologies, France, *G. Patriarche*, CNRS-Laboratoire de Photonique et de Nanostructures, France, *L. Lymperakis, J. Neugebauer*, Max-Planck Institut für Eisenforschung GmbH, Germany, *P. Caroff*, The Australian National University, Australia, *R.E. Dumin-Borkowski, Philipp Ebert*, Forschungszentrum Jülich GmbH, Germany, *B. Grandier*, Institut d'Electronique et de Microélectronique et de Nanotechnologies, France

Recent advances in the growth of nanowires allow the fabrication of complex crystal structures, which otherwise are unstable and hence cannot be achieved in the bulk. In these semiconductor polytype materials, understanding the energetic position of surface states and Fermi level position at the surface is critical, since these parameters might govern the material transport and optical properties. However, the importance of the surface has been put aside so far, due to controversies that already exist for the band alignment in the bulk polytypes. A prototypical material is GaAs, where polytype inclusions consisting of zinc-blende (ZB) and wurtzite (WZ) segments form during the growth of NWs and where the band discontinuities at the interface are strongly debated.

Therefore, we investigated the band structure and the Fermi level pinning at clean and well-ordered sidewall surfaces of zincblende (ZB)-wurtzite (WZ) GaAs nanowires by scanning tunneling spectroscopy and density functional theory calculations. The WZ-ZB phase transition in GaAs nanowires introduces *p-i* junctions at the sidewall surfaces. This is caused by the presence of numerous steps, which induce a Fermi level pinning at different energies on the non-polar WZ and ZB sidewall facets.

## Thin Films

### Room: Makai - Session TF-TuM

## Interfaces in Multilayers & Nanocomposites

**Moderator:** Juan Luis Pena Chapa, CINVESTAV-IPN Unidad Merida, Mexico

8:00am **TF-TuM1 Looking Below the Surface with Photoemission: Standing Waves and Hard X-rays**, *Charles Fadley*, University of California at Davis, USA **INVITED**

I will present some new directions in soft x-ray photoemission (XPS, SXPS) and hard x-ray photoemission (HXPES, HAXPES, HIKE) [1-5], with illustrative examples of applications to a range of sample types. These involve combined SXPS and HXPES studies of buried layers and interfaces in magnetic and transition-metal oxide multilayers [1], as well as semiconductor junctions [2]; solid-gas or solid-liquid interfaces with high ambient pressures [4,5]; and the use of standing waves from multilayer mirrors to enhance depth contrast in spectroscopy [1,3,4,5].

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This work was supported by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231, the Army Research Office, under MURI Grant W911-NF-09-1-0398, the Forschungszentrum Jülich, Peter Grunberg Institute (PGI-6), and the LABEX-PALM, APTCOM project of Le Triangle de Physique, Paris.

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8:40am **TF-TuM3 ToF-SIMS and XPS Characterization of Plasma Polymerized ppAA/Teflon-like Thin Films Interfaces**, V. Spampinato, EC-JRC-IHCP Ispra (ITALY), Italy, C. Desmet, A. Valsesia, P. Colpo, F. Rossi, EC-JRC-IHCP Ispra (ITALY), **Giacomo Ceccone**, EC-JRC-IHCP Ispra (ITALY), Italy

The availability of the high energy cluster sources open new possibilities in the use of surface analysis techniques such XPS and ToF-SIMS to characterize organic films which are important in different application fields ranging from energy to food and medicine (1, 2). In particular the use of molecular depth profiling allows the investigation of the distribution of molecules within the different layers of organic films and nanostructured materials (3).

Plasma polymerization is a well established method to deposit controlled thin films on different substrates and it is applied in many industrial and research activities (4, 5).

In this work we report the analysis of multilayers plasma polymerized polyacrylic acid (ppAA) and teflon-like (PTFE) films using XPS and ToF-SIMS. In particular, XPS has been used to verify the surface composition of the different polymeric films, whilst ToF-SIMS depth profiles have been obtained by means of  $Ar_n^+$  and  $Bi_n^+$  ( $n=1$  and  $3$ ) polyatomic sources. Both single beam and dual beam analysis have been investigated and the different parameters (ion energy, analysis fluence and analysis area) have been studied to evaluate the degree of sample damage (6).

Finally, preliminary data on the use of ToF-SIMS depth profiling technique to identify the presence of nanoparticles at ppAA/PTFE interfaces will be also presented and discussed.

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9:00am **TF-TuM4 A detailed Assessment of Indium Diffusion in InGaAs/high-k/TiN MOS Devices Employing ARXPS**, **Alberto Herrera-Gomez**, O. Ceballos-Sanchez, CINVESTAV-Unidad Queretaro, Mexico, M. Vazquez-Lepe, Universidad de Guadalajara, T. Duong, R. Arroyave, Texas A&M University, A. Sanchez-Martinez, CINVESTAV-Unidad Queretaro, Mexico, F. Espinosa-Magaña, Cimav-Unidad Chihuahua

The electrical performance of InGaAs-based MOS structures is affected by post deposition annealing. A proper characterization of the structural alterations associated with the degradation of the interface and electrical properties is important for understanding failure mechanisms [1]. While most of the results are focused in the control of interfacial passivation [2], phenomena such as diffusion of atomic species from the substrate has not been as widely examined. The samples employed in this study were TiN/high-k/InGaAs MOS structures with different thermal treatments. X-ray spectroscopy (XPS) studies revealed the appearance of an indium peak induced by annealing. Through a robust methodology based on angle-resolved XPS, it was found that the new peak is related to diffusion of indium through the dielectric into the metallic layer. This is the case when the high-k material is alumina [3], hafnia [4] and zirconia [5]. The transport of gallium is only patent in the case of hafnia and zirconia [4,5]. The structure of the samples was characterized employing the MultiLayer Method [6] and the experimental methodology described in Reference 7. Once the structure (thickness and composition) of the various layers constituting the nanofilms were assessed, it was possible to generate the expected angular behavior of the XPS signal from the indium peak under different scenarios. By employing this "scenarios" approach it was possible to robustly show the diffusion phenomenon and to quantify the amount of transported mass. These results, together with density function theory (DFT) calculations, allowed for the assessment of the activation energy for the diffusion of indium through the high-k dielectrics. It was surprising to find that, for all three dielectrics, the transport activation energy of indium is around 0.8 eV.

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9:20am **TF-TuM5 Electric and Thermoelectric Properties of Molecule-Nanoparticle Composite Structures Influenced by Surrounding Gases**, **ShienDer Tzeng**, Y.S. Li, K.T. Chiang, I.C. Ni, National Dong Hwa University, Taiwan, Taiwan, Republic of China

Nanocomposite structures formed by the assembly of nanoparticles with functional surface molecules have many interesting properties [1-3]. We found that these surface molecules at the interface between nanoparticles play very important role on the physical properties (e.g., resistance and Seebeck coefficient reported in this work) of the nanocomposite thin film. For instance, shorter length of surface molecules results in shorter interparticle gap distance and thus increases the electric and plasmonic coupling between nanoparticles. Besides, the barrier height could also be tuned by using different kinds of molecules. Furthermore, the interparticle gap distance or the barrier height of charge conduction could also be influenced by their surrounding gases. In this work, we show that Heme modified nanoparticle assembled films could be used for low water vapor pressure sensing (as shown in Fig. 1). From high vacuum to ~0.01 Torr water vapor, the resistance of Heme device could increase 1%. By contrast, 8-mercaptooctanoic acid (MOA) or 6-mercaptohexanoic acid (MHA) modified nanoparticle assembled films need 1 Torr water vapor to cause 1% resistance change. Besides, we found that the response is proportional to  $P^{\gamma}$ , and the characteristic energy of water adsorbed in the nanocomposite structure could be calculated from the value of  $\gamma$ . Furthermore, the response time of such water vapor sensors could be less than 0.2 sec, much shorter than most known humidity sensors. We also found that the thermoelectric properties of these molecule-nanoparticle composite thin films were very sensitive to surrounding gases (as shown in Fig. 2). For instance, the Seebeck coefficient of MHA-modified gold nanoparticle assembled films was about 12.5  $\mu\text{V/K}$  in high vacuum ( $10^{-5}$  Torr), but became 120  $\mu\text{V/K}$  in 600 Torr  $\text{O}_2$  gas. Such great change in Seebeck coefficient could be explained by the change of density of state contributed by the gas molecules adsorbed on the surface molecules.

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9:40am **TF-TuM6 Laser Lift-Off of Single-Crystal GaAs Thin Films for Low-Cost, High-Performance Photovoltaics, Optics and Electronics**, **Bruce Clemens**, Stanford University, G. Hayes, Stanford University, USA

GaAs and related III-V sphalerite materials offer a wide array of tunable characteristics that lend themselves to many advanced device technologies. However, the cost of GaAs substrates limits their use, specially for photovoltaics. Separating epitaxially-grown layers from a growth substrate can reduce costs, however the current approach, which uses an acid to laterally etch an epitaxial sacrificial layer, is slow and can damage other device layers. Here, we demonstrate laser lift-off as a new approach that is orders of magnitude faster, and that enables more freedom in the selection of other device layers. We grow a structure with a spatially-tuned optical absorption coefficient by growing a small-band-gap, pseudomorphic layer between the GaAs substrate and a GaAs film and device structure. By using InGaAsN with a band gap of 0.9 eV for this layer, we achieve high absorption of 1064 nm (1.17 eV) light from a Nd:YAG nanosecond laser pulse, while GaAs is essentially transparent for this wavelength. Illumination through the back of the GaAs substrate with laser fluences of

about 0.7 J/cm<sup>2</sup> achieves transfer of the GaAs layer to a flexible polymer substrate. Transmission electron microscopy and x-ray diffraction show that the initial InGaAsN layer is coherently strained to match the GaAs substrate, and that the GaAs film is strain-free and free of dislocations, both before and after lift-off. Thermal modeling shows only modest heating outside of the InGaAsN layer, so that the film or device above the InGaAsN layer experiences minimum thermal exposure. Examination of the lift-off interfaces shows evidence of melting and re-solidification. We demonstrate a process using additional InGaP etch layers that allow for quick and easy clean-up of this melted region, resulting in restoration of the original GaAs wafer surface to a condition suitable for re-use. Thus our process can transform the GaAs substrate from a consumable to a manufacturing tool.

10:20am **TF-TuM8 SIMS Depth Profiling and 3D characterization of Organic/Inorganic Surfaces by FIB Crater Wall Imaging and Tomography**, *N.J. Havercraft*, ION-TOF USA, Inc., *Felix Kollmer*, ION-TOF GmbH, Germany, *R. Moellers*, *D. Rading*, *S. Kayser*, *E. Niehuis*, ION-TOF GmbH

Information on the chemical composition, physical properties and the three dimensional structure of materials and devices is of major importance. Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) is known to be an extremely sensitive surface imaging technique which provides elemental as well as comprehensive molecular information on all types of solid surfaces. In the so-called dual beam mode the pulsed analysis beam is combined with a low energy sputter ion beam for the removal of material. This allows depth profiling of multilayers with high depth resolution as well as three-dimensional analysis.

However, the analysis of structures at greater depth (> 10µm) requires long measurement times and the build-up of surface roughness at the crater bottom limits the achievable spatial resolution. Moreover, extremely rough samples, samples with voids, and material that exhibits strong local variations in density or sputter yield are unsuitable for conventional depth profiling. Not only that the initial surface topography is unknown but it is also modified and in many cases even roughened by the sputtering process.

In order to overcome these limitations we used a combined SIMS/FIB setup. Either a Bi cluster beam or a mono-atomic Ga beam is used to FIB mill a crater into the sample. Subsequently, a 2D TOF-SIMS image of the vertical crater wall is acquired. Since the crater wall is hardly affected by the aforementioned roughening problems this approach allows the in-depth distribution of elements to be determined by analyzing a plane perpendicular to the surface at high lateral resolution ( $\Delta l < 50\text{nm}$ ) [1].

Moreover, by serial slicing of the crater wall followed by intermediate analysis steps this approach can be extended in order to provide the full 3D characterization of the analyzed surface. We will present 2D and 3D data of reference material, multilayer samples and technically relevant real world samples such as fuel cells and battery electrodes. For thin multilayer samples the FIB process can be performed under grazing incidence in order to bevel the surface and hence magnify and accentuate thin layers in the plane of the analyzed crater wall.

However, FIB/SIMS approach fails when analyzing organic surfaces since the molecular structure is almost completely destroyed by the sputtering process. We will discuss methods to maintain the molecular structure under high dose sputtering conditions by performing the FIB milling with massive argon clusters.

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10:40am **TF-TuM9 Growth and Characterization of Heteroepitaxial III-N Semiconductor Films using Atomic Layer Epitaxy**, *N. Nepal*, *Virginia Anderson*, *J.K. Hite*, *C.R. Eddy, Jr.*, US Naval Research Laboratory

Aluminum nitride (AlN), gallium nitride (GaN), and indium nitride (InN) semiconductors and their corresponding ternary films, such as InGaN, offer attractive properties, with high breakdown fields and widely tunable direct band gaps. Currently, III-nitrides are primarily deposited with molecular beam epitaxy and chemical vapor deposition. The addition of Atomic Layer Epitaxy (ALE) to the possible growth techniques is driven by the need for ever thinner films integrated into complex heterostructures, something that is increasingly difficult to achieve by conventional techniques. Furthering the attraction of ALE is the promise of lower growth temperatures that allow the deposition of a wider range of indium containing ternary films.

Here we report on ALE in a plasma-equipped Ultratech/Cambridge Nanotech atomic layer deposition system to grow AlN, GaN, and InN at temperatures significantly lower than needed for molecular beam epitaxy (MBE) and metalorganic chemical vapor deposition (MOCVD).[1] In growing epitaxial materials, the substrates and corresponding surface preparation procedures are important. The substrates include silicon(111), sapphire, and MOCVD gallium nitride on sapphire, as well as graphene.[2]

For InN on a-plane sapphire, the expected wurtzite hexagonal phase was heteroepitaxially grown for films deposited in the temperature window of 220 to 260 C, well below the typical minimum 450 C temperature used in MOCVD. At an even lower temperature, 183 C, the heteroepitaxial InN on a-plane sapphire was discovered to be cubic phase with a NaCl structure, a phase of InN that had before been unreported.[3] Heteroepitaxial AlN films were grown on GaN/sapphire at a much lower temperature (500 C) than by MOCVD, typically 1100 C or more. Finally, GaN has been included in ALE deposited ternaries in the relatively low temperature window of 250-400 C even as its optimization continues. The ALE grown III-N films have carbon and oxygen contamination that hinders their immediate use in many applications, and improving the film purity is a major focus. In addition, initial deposition of indium ternaries indicates that more stoichiometries are available by ALE than MOCVD.

The possibilities for greater use of III-nitrides are apparent even at the early stages of progress in atomic layer epitaxy. Further characterization during and after deposition of the films should lead to materials suitable for use in high electron mobility transistors, as well as optoelectronic devices.

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11:00am **TF-TuM10 Controlling Charges States at Nanoscale Schottky Contacts**, *Tae-Hwan Kim*, Pohang University of Science and Technology, Republic of Korea, *H.W. Yeom*, Institute for Basic Science

Metal-semiconductor interfaces have drawn a lot of interest in the field of semiconductor surface and interface science, and have been one of the most essential parts in semiconductor electronic and optoelectronic devices. For example, the Schottky-barrier height experimentally observed at the metal-semiconductor interface appears to be nearly independent of the work function of the metal. Since the time of Bardeen, interface gap states seem to have been a primary mechanism of the Schottky-barrier height causing Fermi level pinning at metal-semiconductor interfaces. Recently, polarized chemical bonds at metal-semiconductor interfaces have been recognized to lead to the apparent Fermi level pinning effect. When these interface bonds are formed underneath thin metal islands grown on a silicon substrate, a spontaneous charge transfer across the semiconductor-metal interfaces occurs as a result of the difference in the Fermi level positions between the metal and the semiconductor. These polarized chemical bonds can form a dipole layer. This dipole layer can play an important role in many areas of technology, for instance, in organic light emitting diodes. However, some of the fundamental aspects of the charge injection process into/from the interface dipole layer at the Schottky contact are yet not explored in any real detail.

In this work, we report the use of scanning tunneling microscopy (STM) to form a double-barrier tunneling junction (DBTJ) with thin metallic nanoislands grown on Si(111) and to control charges of the interface dipole layer formed between the metallic nanoislands and the Si(111) substrate. Reversible hysteric switching in their I-V and differential conductance spectra are observed due to the charging and discharging of the interface dipole layer in a similar fashion to molecular DBTJs. STM images clearly visualize the distinct charge states and scanning tunneling spectroscopy (STS) spectra reveal that quantum well states (QWSs) of the ultrathin islands act as the charging/discharging channels in analogy to the molecular orbitals in the case of the molecular DBTJs. This work demonstrates that the charges of the interface dipole layer at the nanoscale Schottky contact can be controlled by the electron transfer via the QWSs of the metallic islands.

11:20am **TF-TuM11 Enhancement of Contact Properties of Ytterbium Silicide by Alloying with Molybdenum**, *Sekwon Na*, *H. Lee*, Sungkyunkwan University, Korea, Republic of Korea

As scale-down of metal-oxide-semiconductor field effect transistors (MOSFETs) continues, the portion of resistance rising from the contact of total resistance has become burdensome. This has fueled a drive to find a new contact material with a low contact resistance. In particular, rare-earth (RE) metal silicides (Er, Yb, etc.) are promising as source/drain contact materials, since they have a very low Schottky barrier height (SBH) on n-type silicon (0.2~0.4eV).

Among several RE silicides, ytterbium silicide deserves much attention due to its some favorable characteristics for low SBH applications. In this study, we embarked full investigation of Yb silicide by thoroughly analyzing how the formation of the epitaxial silicide layer influences electrical properties including sheet resistance and SBHs. Moreover, we alloyed Yb with Mo to improve oxidation resistance of the material at high temperatures.

Ytterbium and molybdenum were deposited on an n-type silicon (001) substrate with a resistivity of 1-10ohm-cm using a radio frequency (rf) magnetron sputtering system. For the Mo-alloyed sample, the composition

of Mo was found around 20 at. % from EDS analysis. To remove the native oxide of the silicon substrate, the wafer was dipped in 1% HF solution and then rinsed with deionized water. The films were deposited at room temperature and at a working pressure of 9mTorr in Ar ambient. Subsequently, a tantalum nitride (TaN) capping layer with the thickness of 50nm was deposited. To measure SBH, we fabricated Schottky diodes by forming circular dots (diameter: 50 $\mu$ m) of Yb via lift-off. The samples were annealed using rapid thermal annealing (RTA) at various temperatures (300°C ~800°C) for 1 minute in N<sub>2</sub> ambient. For characterization, we utilized transmission electron microscopy and X-ray diffraction. The electrical characteristics were examined using an HP semiconductor parameter analyzer.

Dynamic microstructural evolution of the Yb/Si contact, in which solid-state amorphization between Yb and Si, nucleation and growth of an epitaxial YbSi<sub>2-x</sub> layer, and disruption of the layer due to oxidation occurred successively with the temperature increasing. However, the microstructures of Mo-alloyed samples annealed at high temperatures show that the Mo-rich region is formed above the epitaxial layer, and it fended off oxygen diffusion. Thus, the epitaxial layer remained up to 800°C. While the epitaxial Yb silicide led to low SBHs, oxidation increased significantly SBHs at high temperatures in Yb/Si samples. Protection of epitaxial layer by Mo-segregated region helped to remain low SBHs over a wide temperature range (600~800°C).

# Tuesday Afternoon Poster Sessions

## Biomaterial Interfaces

Room: Mauka - Session BI-TuP

### Biomaterial Interfaces Poster Session

**BI-TuP1 Three-dimensional Conducting Polymer-based Bioelectronic Interfaces for Rare Cell Isolation and Detection, Yu-Sheng Hsiao**, Ming Chi University of Technology, Taiwan, Republic of China, *H.-h. Yu*, Academia Sinica, Taiwan, Republic of China, *H.-R. Tseng*, University of California, Los Angeles, *P. Chen*, Academia Sinica, Taiwan, Republic of China

Here we develop a universal solution-processing approach for producing three dimensional (3D) conducting polymer-based bioelectronic interfaces (BEIs), which can be integrated on chips for rare circulating tumor cell (CTC) isolation and detection. Based on the modified poly(dimethylsiloxane) (PDMS) transfer printing technology and bioconjugation process, the poly(3,4-ethylenedioxythiophene) (PEDOT)-based micro/nanorod array films can be fabricated with topographical and chemical control, respectively. This 3D PEDOT-based BEI film features the advantageous characteristics: (1) diverse dimensional structures (tunable from the microscale to the nanoscale), (2) varied surface chemical properties (tunable from nonspecific to specific), (3) high electrical conductivity, and (4) reversible electrochemical switching, and (5) high optical transparency. Furthermore, we integrated this 3D PEDOT-based BEI onchips, which exhibited optimal cell-capture efficiency from MCF7 cells was approximately 85%; featured highly efficient performance for the cell isolation of rare CTCs with minimal contamination from surrounding nontargeted cells (e.g., EpCAM-negative cells, white blood cells); preserved the cell viability with negligible effect on cells. According to the electric cell-substrate impedance sensing concept, the 3D BEI-based device was also demonstrated as a rapid, sensitive and specific tool for CTC detection. Therefore, it is conceivable that use of this platform will meet the requirements on developing for the next-generation bioelectronics for biomedical applications.

**Keywords:** Poly(3,4-ethylenedioxythiophene) (PEDOT), bioelectronic interfaces (BEIs), circulating tumor cell (CTC), epithelial cell adhesion molecule (EpCAM).

**BI-TuP3 For the Development of Auto-Injection System to Cells: Coating of Inserting Pipettes, Gas-Flow Evaluation Method for Prepared Pipettes, and SPM-inspired Pipette-Top Sensing System, Tomohide Takami**, *J. Uewaki, H. Ochiai*, Hiroshima University, Japan, *M. Koyama, Y. Ogawa, M. Saito, H. Matsuoka*, Tokyo University of Agriculture & Technology, Japan, *Y. Ojiri, K. Nishimoto, S. Ogawa, Y. Takakuwa*, Tohoku University, Japan, *S. Tate*, Hiroshima University, Japan  
Glass nanopipettes have been used as a bridge to connect macro world and micro world.[1] They can be used as an ion-selective probe,[2-6] and as an injector to deposit a small amount of materials onto a surface.[7]

Injection to cell is a hot topic for the statistical experiments on the live dynamics of injected molecules in cell as well as the application to genetic engineering. Several auto-injection systems are already commercially available. However, the fatal problem of these auto-injection systems is the viability of cells after the injection; usually less than 10%.

We have been developing an auto-injection system in which the distance between the injecting pipette tip top and the cell is monitored and the signal depending on the pipette-cell distance is put into the feedback system to achieve the controlled insertion/extraction motion of the pipette to the cell in order to increase the viability of cells. This system is inspired from scanning tunneling microscopy on which the tip-sample distance is well-controlled for the nanoscale observation and molecular manipulation.[8]

Also, we have developed two methods for the auto-injection. One is the coating of the pipette top with chlorobenzene-terminated polysiloxane to reduce the damage to the inserted cell. The other is the gas-flow method to evaluate the inner diameter and the shank length of the pipette before using since the pipettes after the observation with electron microscope cannot be used.

In this paper, we will show our progress to realize the auto-injection system for the use of statistic and quantitative studies. We will demonstrate the ability of manual injection system to show the limit of the manual injection study. We will also demonstrate how the surface science technologies including scanning probe microscopy (SPM), surface coating, and vacuum science can be utilized for the development of the auto-injection system.

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**BI-TuP4 Correlative Imaging of Single Mammalian Cells in their Native Environments, Xin Hua**, *C. Szymanski, Z. Wang, B. Liu, Z. Zhu, J. Evans, G. Orr*, Pacific Northwest National Laboratory, *S. Liu*, Southeast University, China, *X. Yu*, Pacific Northwest National Laboratory

Mammalian cell analysis is of significant importance in providing detailed insights into biological system activities. Due to the complexity and heterogeneity of mammalian cell behavior and the technical challenge of spatially mapping chemical components in a hydrated environment, correlative chemical imaging from multiplexed measurement platforms is needed. Fluorescence structured illumination microscopy (SIM), with super high resolution and visualization of proteins and sub-cellular structures in 3-D, provides more detailed information in cell structure and dynamics. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a unique surface-sensitive tool that provides molecular information and chemical mapping with a sub-micron lateral resolution. However, the understanding of how the spatial heterogeneity and structural difference affect the mammalian cell activities in an unperturbed, hydrated state by ToF-SIMS is severely limited due to the challenge to detect liquids with high volatility in high vacuum using surface sensitive surface techniques.

We recently developed a novel microfluidic reactor enabling correlative imaging of single mammalian cell (e.g., C10 mouse lung epithelial cell) growth by SIM and ToF-SIMS. Cells were introduced in the microchannel, incubated at 37 °C for 24 hr., fed with 5 Nm quantum dots, and then fixed with 4% paraformaldehyde before SIM imaging. In subsequent ToF-SIMS analysis, an aperture of 2 μm in diameter was drilled through the SiN membrane to form a detection window to image biological surfaces directly; and surface tension is used for holding the liquid within the aperture.

SIM images show that cells are successfully cultured on the SiN membrane, and quantum dots are uptaken by cells and dispersed in the cytoplasm. The ToF-SIMS *m/z* spectra were compared among dried cell samples, hydrated cells, and medium solution. Characteristic lipid fragments are identified. Moreover, 2D mapping of representative cell fragments were obtained. In addition, depth profiling was used to provide time- and space-resolved imaging of the single cell inside the microchannel. Furthermore, principal component analysis is conducted to evaluate the intrinsic similarities and discriminations among samples. Our results demonstrate the feasibility for *in situ* imaging of single mammalian cells in the hydrated state using ToF-SIMS for the first time. Correlative imaging using SIM and ToF-SIMS provides much sought-after information across different space scales for investigating cell dynamics. This novel approach has great potential for studying intracellular processes in the future.

**BI-TuP5 Nano-Bio Interfacial Analysis using time-of-flight Medium Energy Ion Scattering, KwangWon Jung**, DGIST, Korea, Republic of Korea, *K.S. Park*, KMAC, Republic of Korea, *W.J. Min*, KMAC, *H.J. Lim, S.J. Moon*, DGIST, Korea, *D.W. Moon*, DGIST, Korea, Republic of Korea

We have developed a TOF-MEIS system using 70-100 keV He<sup>+</sup>. A TOF-MEIS system was designed and constructed to minimize the ion beam damage effect by utilizing a pulsed ion beam with a pulse width < 1 ns and a TOF delay-line-detector with an 120 mm diameter and a time resolution of 180 ps. The TOF-MEIS is a useful tool for interfacial analysis of the composition and structure of nano and bio systems. Our recent applications are reported.

#1) UltraShallow Junction: As doped Si ultra shallow junctions were fabricated with various annealing conditions. We measured the compositional depth profile of 2 x 10<sup>15</sup> atoms/cm<sup>2</sup> As doped silicon (annealed/unannealed) by the random and channelling phenomenon in Si(100) lattice. The result clearly indicates that the As dopant profile depends on the annealing temperature and conditions. Monitoring of As

activated/deactivated ratio in ultra shallow junction by TOF-MEIS will be beneficial to the manufacturing processes of semiconductor industry.

#2) NanoParticles: We measured the quantitative compositional profiling with single atomic layer resolution for 0.5~3 nm CdSe/ZnS QDs with a conjugated layer. We also investigated the effect with Polyaspartic Acid (pAsp) and Osteocalcin on the initial bone growth of calcium hydroxyl apatite on a carboxyl terminated surface. When pAsp is not added to the self-assembled monolayers of Ca 2mM with Phosphate 1.2 mM, the growth procedure of calcium hydroxyl apatite cannot be monitored due to its rapid growth. When pAsp is added to the SAMs, the initial grow stage of the Ca-P can be monitored so that the chemical composition and their nucleus size can be analyzed.

#3) Liquid interface: Using a graphene as a MEIS analysis window, the electric double layer structure of liquid interface was depth profiled with atomic layer depth resolution. The electric double layer of KI solution is reported with discussions on further studies.

**BI-TuP10 Enhancing Protein Adsorption Simulations by Using Accelerated Molecular Dynamics, Herbert Urbassek, X. Muecksch,** Physics Department, University of Kaiserslautern, Kaiserslautern, Germany  
The atomistic modeling of protein adsorption on surfaces is hampered by the different time scales of the simulation ( $\ll 1$  ms) and experiment (up to hours), and the accordingly different 'final' adsorption conformations. We provide evidence that the method of accelerated molecular dynamics is an efficient tool to obtain equilibrated adsorption states. As a model system we study the adsorption of the protein BMP-2 on graphite in an explicit salt water environment. We demonstrate that due to the considerably improved sampling of conformational space, accelerated molecular dynamics allows to observe the complete unfolding and spreading of the protein on the hydrophobic graphite surface. This result is in agreement with the general finding of protein denaturation upon contact with hydrophobic surfaces.

## Energy Harvesting & Storage Room: Mauka - Session EH-TuP

### Energy Harvesting & Storage Poster Session

**EH-TuP4 Synthesis and Hydrogen Properties of Beryllium Intermetallic Compound, Jae-Hwan Kim,** Japan Atomic Energy Agency, Japan, *H. Iwakiri,* University of the Ryukyus, Japan, *M. Nakamichi,* Japan Atomic Energy Agency

Beryllium intermetallic compounds have shown a variety of excellent properties, such as neutron multiplier, refractory function, hydrogen storage, superconductivity and so on.  $\text{Be}_{12}\text{M}$  compounds (M=Ti, V and Zr) have been investigated as neutron multiplier in fields of fusion reactor while  $\text{Be}_{17}\text{M}_2$  compounds have been focused on refractory materials. In addition,  $\text{Be}_2\text{M}$  have been known as a Laves phase which is characterized by an  $\text{A}_2\text{B}$  type compound performing higher  $\text{H}_2$  gas storage potential. Although great interest on hydrogen properties of  $\text{Be}_2\text{M}$  owing to its lower density has been aroused from viewpoints of reactivity with  $\text{H}_2\text{O}$ , trap site of hydrogen and amount of  $\text{H}_2$  gas in this compound, few studies on the  $\text{Be}_2\text{M}$  found and its data base is still unsatisfactory.

In this study, we report on preliminary synthesis of  $\text{Be}_2\text{Ti}$  compound and its properties, such as hydrogen generation due to reaction with  $\text{H}_2\text{O}$  and hydrogen storage. Additionally, first principles calculation of hydrogen trap site in this compound was carried out in order to compare to empirical data.

X-ray diffraction profiles and electron probe micro-analysis results clarify that the preliminary synthesis of  $\text{Be}_2\text{Ti}$  was successful by homogenization treatment and plasma sintering. Hydrogen generation rate of the  $\text{Be}_2\text{Ti}$  by a reaction with 1 %  $\text{H}_2\text{O}$  increased as test temperature increased. High temperature exposure with  $\text{H}_2\text{O}$  leads to formation of  $\text{TiO}_2$  on the surface. In addition, hydrogen storage result of  $\text{Be}_2\text{Ti}$  evaluated by pressure-concentration-temperature curve depicts that  $\text{Be}_2\text{Ti}$  indicated  $\text{H}_2$  gas storage concentration with 1.6 w.t. % at 323 K when the  $\text{H}_2$  pressure increases up to 10 MPa. According to the first principle calculation, there were two hydrogen trap sites, tetrahedron and center of triangle with solidus energies of -0.52 and -0.05 eV, respectively, indicating maximum trap site with 5.4 w.t. %.

**EH-TuP5 Characterization of Real Cyclic Performance of Air Electrode for Li-Air Batteries, DaeHo Yoon, Y.J. Park,** Kyonggi University, Republic of Korea

In this study, we characterized the cyclic performance of an air electrode employing a carbon nanotube (CNT)/ $\text{Co}_3\text{O}_4$  nanocomposite. The lithium anode and electrolyte were replaced every 50 cycles in order to exclude the effect of a corrupted anode and electrolyte and to determine the "real"

cyclic performance of the electrode. The overpotential of the cells increased during the first 50 cycles; however, it almost vanished when the lithium anode and electrolyte were replaced. This result indicates that the increased overpotential of the cells during cycling is highly attributed to the corrupted lithium anode and electrolyte [1, 2]. The cycle life of the cell also significantly increased upon replacement of the lithium anode and electrolyte. This confirms that air electrodes have the ability to maintain their designated capacity (such as  $1000 \text{ mAh} \cdot \text{g}_{\text{electrode}}^{-1}$ ) for much longer cycles if the lithium anode and electrolyte can be made more stable. A polydopamine-coated electrode and a LiI-containing electrolyte were introduced and characterized in order to obtain enhanced cyclic performance of the air electrode.

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**EH-TuP6 Nano-Sized  $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.16}\text{Mn}_{0.56}\text{Co}_{0.08}]\text{O}_2$ /Carbon Composite for Improving Electrochemistry Performance, S.B. Lim,** Kyonggi University, *YongJoon Park,* Kyonggi University, Republic of Korea

Since the commercialization of lithium ion battery, development of cathode materials with high capacity has been one of the important factors for enhancing the performance of that. Lithium rich compounds are promising cathode materials due to their high capacity for satisfying demand of high-capacity batteries. However, they have several disadvantages to overcome for commercialization such as poor rate capability, low cyclic performance, and low stability. In this study, we prepared nano-sized  $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.16}\text{Mn}_{0.56}\text{Co}_{0.08}]\text{O}_2$ /carbon composite for enhanced electrochemical performance such as rate capability. A general method to improve the surface electronic conductivity and enhance the rate capability of cathode is carbon coating. The carbon coating by in-situ carbonization from organic precursors has been successfully applied to  $\text{LiFePO}_4$ . However, it is difficult to apply to Li-rich compounds because they will lose oxygen during carbonization. That is why we introduced composite between cathode and carbon, instead of carbon coating. In this work, super P, a commercial carbon, was composed with nano-sized  $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.16}\text{Mn}_{0.56}\text{Co}_{0.08}]\text{O}_2$ . Nano-sized powders were synthesized by combustion method using surfactants (HPC and Gelatin) to disperse the granule particles [1-3]. The polydopamine pre-coating layer was used as a binding agent between cathode powder and super P [4-8]. Nano-sized  $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.16}\text{Mn}_{0.56}\text{Co}_{0.08}]\text{O}_2$ /Super P composite is expected to exhibit improved rate capability because of dispersed nano-sized lithium rich particles and good electronic conductivity attributed to Super P.

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**EH-TuP8 Fabrication of Structured Organic Solar Cell with Patterned ITO Electrode and Study of Their Effect on Power Conversion Efficiency, Jin-Hyo Boo, J.S. Lee,** Sungkyunkwan University, Korea

In organic photovoltaics (OPVs), there is a competition between the reduction of absorber thickness and the improvement of the probability of carrier collection. To overcome the competition a highly structured interface is highly desirable. However, a solution-based soft-lithography processing resulted in non-uniform structured surfaces. In this report, we proposed and demonstrated a silica-templated soft-lithographical approach for structuring well-defined and controllable transparent ITO layer for enhancing power conversion efficiency (PCE). Also, we focused on the morphological effects of the patterned ITO on optical properties and PCE.

The brief experimental scheme is as follow. First, close-packed PS nanospheres were formed on a cleaned ITO glass substrate by using gas-liquid-solid interfacial self-assembly method and drying for 3days in vacuum desiccator. After that, PS covered ITO glass was etched at 65°C with TIN etching solution. Finally, PEDOT:PSS, P3HT:PCBM, and Al electrode were gradually deposited.

The morphology, optical, electric, and cell properties are investigated by FE-SEM, AFM, UV-VIS spectrophotometer, Haze measurement, and solar simulator.

**EH-TuP9 Supercapacitive Properties of 2D-arrayed Inverse-Opal Nanostructure of Manganese Oxide, Ilhwan Ryu, D. Park, G. Kim, S. Yim, Kookmin University, Republic of Korea**

Supercapacitor has attracted growing attention as an important energy conversion and storage device which basically consists of current collector, electrolyte and active materials. Manganese oxide ( $\text{MnO}_2$ ) is one of the most promising active materials due to its environmentally friendly characteristic and low price. Fabrication of nanostructured active materials has also been widely studied since it can provide large surface area and short diffusion path for ions and electrons, and hence improve the capacitive properties of the supercapacitors. In this work, we fabricated well-ordered  $\text{MnO}_2$  inverse-opal nanostructures using two-dimensionally arrayed polystyrene nanospheres. We also investigated their optical, morphological and electrochemical properties, and compared them with the properties of the device based on the planar  $\text{MnO}_2$  films.

**EH-TuP10 Inorganic-organic Core-Shell Nanowire Solar Cells with Excellent Light-Trapping Properties, Keisuke Sato, Tokyo Denki University, Japan, M. Dutta, N. Fukata, National Institute for Materials Science, Japan**

Development of solar cells using one-dimensional architecture, such as semiconductor nanowires (NWs), have been proceeding rapidly in recent years. The main advantage of such NWs-based solar cells is that they cause greater light absorption (minimal reflectivity) due to incident light-trapping within the NW arrays. This phenomenon is most glaringly apparent in silicon nanowires (SiNWs)-based solar cells, leading to higher absorbance per unit thickness than achieved by commercial crystalline Si solar cells. Thus, the introduction of the SiNW arrays with high light-trapping properties enable lower-cost cell production due to the massive reduction of the consumption of Si materials needed for cell fabrication. We have developed inorganic-organic core-shell NW solar cells in which the vertically-aligned SiNWs were surrounded by organic poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) layer in order to further facilitate the cell fabrication. We report herein on the cell performances of Si-PEDOT:PSS core-shell NW solar cells with excellent light-trapping properties. To investigate the light-trapping capability, the lengths of the core-shell NWs were varied within the range from 2 to 8  $\mu\text{m}$ . In the core-shell NWs with shorter length of 2  $\mu\text{m}$ , the reflectance was suppressed to below 8%, which is extremely lower than the crystalline Si with value of 31%, over a wide spectrum range between 300 and 1000 nm. This suppression is far more effective for longer NW length, resulting in a reflectance of below 4.6% for the core-shell NWs with longer length of 8  $\mu\text{m}$ . These results demonstrate that the longer core-shell NW arrays can extend the broadband anti-reflection effect due to enhanced light-trapping in NW arrays. However, the cell performances of such core-shell NW solar cells closely were intimately related to the NW length-dependent carrier transport efficiency rather than the light-trapping effects. The core-shell NW solar cells with shorter length of 2  $\mu\text{m}$  exhibited the best cell performance with a power conversion efficiency (PCE) of approximately 7%, exceeding those with longer length of 8  $\mu\text{m}$  (PCE of 3.7%). The depression of cell performance with the increase in the NW length was caused by inefficient carrier collection at electrodes due to the enhancement of the carrier recombination, because the transportation distances to electrodes were increased with NW length. Therefore, we suggest that it is important to simultaneously tune the NW length and light-trapping properties to be able to fabricate efficient inorganic-organic core-shell NW solar cells.

**EH-TuP11 Characterization of Zn(O,S) Buffer Layers for Cu(In,Ga)Se<sub>2</sub> Solar Cells, JiHyun Choi, S.M. Hwang, A. Garay Dixon, C.W. Chung, Inha University**

In photovoltaic solar cell, CdS thin films are mostly used buffer layer due to their wide direct band gap (~2.42 eV). The CdS buffer layers which form a p-n junction with absorber layer are deposited by using a variety of deposition methods such as chemical bath deposition (CBD), spray pyrolysis, vacuum-evaporation and sputtering. Among these techniques, chemical bath deposition is widely used method due to its advantage such as easy and inexpensive process. However, CBD technique also has some disadvantages including production of toxic liquid waste containing Cd and ammonia and difficulty in application to mass production scale. In addition, CBD method should be done in liquid phase, so that it can oxidize the absorber layer.

To overcome these disadvantages of CBD method and to apply for large scale deposition, sputtering of Zn(O,S) thin films was proposed. Sputtering method of Zn(O,S) films can reduce the liquid wastes and save the deposition time for fast deposition. It enables all processes for solar cells to be carried out by vacuum processes without exposure to air. In addition, Zn(O,S) thin films can replace the CdS which contains a toxic Cd. Generally, Zn(O,S) thin films can be deposited by sputtering with pure ZnS target by adding oxygen or by co-sputtering using ZnO and ZnS targets.

ZnS itself has very high band gap about 3.6 eV, so that oxygen should be added to control the band gap. Currently, their electrical and optical properties of the sputtered Zn(O,S) films have not been fully studied yet.

In this study, Zn(O,S) thin films are deposited on Cu(In,Ga)Se<sub>2</sub> layer and glass substrate by RF sputtering in O<sub>2</sub>/Ar atmosphere using pure ZnS target. By varying the deposition parameters including O<sub>2</sub> concentration in O<sub>2</sub>/Ar, deposition pressure and RF power, the electrical, optical properties and the morphology of the sputtered Zn(O,S) films were investigated. From this research, the optimal condition for Zn(O,S) buffer layer using sputter method will be obtained.

**EH-TuP12 Formation of CuInSe<sub>2</sub> from Cu-Se and In-Se binary compounds by wet process for solar cell application, Hyungmin Lee, D.-S. Jeong, C. Park, Yeungnam University, Republic of Korea**

CIS was synthesized from binary compound of CuCl, InCl and selenium powder using alcohols as solvent. CIS thin film was prepared by mixing powders of Cu-Se and In-Se binary phase and heat treatment. The binary precursors such as CuSe, InSe and In<sub>2</sub>Se<sub>3</sub> were synthesized using facile chemical route from suitable resources at different stoichiometric ratios. And then, high-quality CIS absorption layer was formed by using three binary compounds. The properties of CIS films were studied and characterized, systematically. The structural and optical properties of CIS films were studied by using X-ray Diffraction, photoluminescence (PL), and UV-Vis. The surface morphological property of the films was also recorded by Scanning Electron Microscope (SEM). The CIS solar cells having the structure of Soda lime glass (SLG) / Mo / CIS / CdS / i-ZnO / Al-doped ZnO (AZO) / Al metal grid was then fabricated. The solar cells' current density-voltage (J-V) characteristics were investigated both in the dark and under AM1.5G illumination by a solar simulator (Keithley 69911). Keywords: CuInSe<sub>2</sub>, Binary compound, Solar cell, Wet process, Photoluminescence Acknowledgment This work was supported by the New & Renewable Energy Core Technology Program of the Korea Institute of Energy Technology Evaluation (No. 20133030011330) and the Human Resources Development Program (No. 20104010100580) Planning (KETEP), granted financial resource from the Ministry of Trade, Industry & Energy, Republic of Korea.

**EH-TuP13 In-situ Investigation of phase Evolution during Cu<sub>2</sub>ZnSnSe<sub>4</sub> Thin Film Photovoltaic Absorber Formation from Various Stacked Cu-Zn-Sn Precursors, Hyeonwook Park, J. Han, W.K. Kim, Yeungnam University, Republic of Korea**

For several decades, chalcopyrite Cu(InGa)Se<sub>2</sub> (CIGS) thin films were considered as a potential candidate for use as light absorbers in high-efficiency thin film photovoltaic cells. Recently, a cell efficiency of 20.9% (Solar Frontier, 2014), which is a little bit higher than multi-crystalline Si cells (20.4%), has been reported. Over the last decade, great attention has been moved to kesterite Cu<sub>2</sub>ZnSn(S,Se)<sub>4</sub> (CZTSSe) as a promising low-cost alternative to chalcopyrite CIGS. In this paper, temperatur-dependent reaction pathways to kesterite Cu<sub>2</sub>ZnSnSe<sub>4</sub> (CZTSe) thin film photovoltaic absorber formation by selenization of various stacked precursor structures including (Cu+Sn)/Zn and (Cu+Zn)/Sn were systematically investigated using in-situ high-temperature X-ray diffraction system, consisting of a PANalytical X'pert Pro MPD diffractometer and an Anton Paar HTK 1200 N furnace. A custom-designed graphite dome was utilized in order to create Se vapor at the elevated temperatures and minimize the loss of vaporized Se. Furthermore, CZTSe films formed by selenization of stacked Cu-Zn-Sn/Se precursors were characterized by X-ray diffraction and raman spectroscopy. The results revealed that the formation temperature of CZTSe and detailed phase evolution would be affected by stacked structure of Cu-Zn-Sn. Furthermore, precursor structure with co-sputtered Cu and Sn (e.g., (Cu+Sn)/Zn and Zn/(Cu+Sn)) could reduce Sn loss effectively during the formation of CZTSe than that with single-layered Sn (e.g., (Cu+Zn)/Sn and Sn/(Cu+Zn))

**EH-TuP14 Feasibility Study on Graphene as Back Contact for Cu(InGa)Se<sub>2</sub> Thin Film Solar Cells, Hee-San Ryu, K. Moon, Yeungnam University, Republic of Korea, Y. Jun, J. Kim, Korea University, Republic of Korea, W.K. Kim, Yeungnam University, Republic of Korea**

Chalcopyrite Cu(InGa)Se<sub>2</sub> (CIGS) solar cells have been considered as the most promising thin film solar cell, holding a record cell efficiency of 20.9% (Solar Frontier, 2014), which is slightly higher than that of multi-crystalline Si solar cells (20.4%). Molybdenum (Mo) is the most common material used as a back contact electrode for CIGS solar cells due to its low cost and electrical suitability with CIGS layer. In this paper, mono- or multi-layer graphene has been explored as an alternative back contact electrode to replace Mo layer. As a back contact electrode, graphene has many attractive properties such as high flexibility, excellent optical transmittance, low resistance, and high mechanical and chemical stabilities. In particular, transparent back contact like a graphene is essential to bifacial



photovoltaic cells that can absorb lights from the front and back sides. In this study, the graphene films produced by chemical vapor deposition process on Cu foil were transferred onto soda-lime glass substrate using a simple wet-based transfer process. Graphene-coated glass was analyzed by tape test, four point probe measurement and UV visible spectroscopy to evaluate adhesion strength, resistance and transparency, respectively. CIGS absorbers were then deposited onto graphene-coated glass by using 3-stage co-evaporation process in a vacuum evaporator. A series of characterizations including X-ray diffraction, scanning electron microscopy and Raman spectroscopy were performed to investigate the effect of number of graphene layers (e.g., 1, 2 and 4 layers) on the formation of chalcopyrite CIGS structure, and compare the characteristics of CIGS absorbers on different back contacts, graphene vs. Mo layers.

**EH-TuP15 SnO<sub>2</sub> Hollow Spheres with Core-Shell Nanostructures of TiO<sub>2</sub> Nanosheets for Dye-Sensitized Solar Cells**, J.Y. Lim, S.H. Ahn, C.H. Park, Jong Hak Kim, Yonsei University, Korea

In this study, SnO<sub>2</sub> hollow spheres were synthesized using sulfonated polystyrene (PS) as template. After sintering at 450°C for removing PS, SnO<sub>2</sub> hollow spheres were dispersed in isopropyl alcohol with amounts of titanium isopropoxide and diethyltriamine followed by transferring to Teflon-lined autoclave. The mixture was heated to 200 °C and maintained for 24 hour, centrifuged, and calcined to obtain a highly crystalline phase. These preformed SnO<sub>2</sub> hollow spheres with core-shell nanostructures of TiO<sub>2</sub> nanosheets were mixed with sol-gel solution of graft copolymer PVC-g-POEM for preparing photoanode of DSSC. The solution was deposited on FTO glasses by doctor-blade method. These core-shell nanostructures were uniformly distributed in the TiO<sub>2</sub> film with large pores, high porosity, and good inter-connectivity due to its relatively low density resulting from high porosity and empty voids inside the shell. Nanostructures of SnO<sub>2</sub> hollow spheres with core-shell nanostructures of TiO<sub>2</sub> nanosheets provide good pore-filling for solid polymer electrolytes, faster electron transfer, and enhanced light scattering, as confirmed by reflectance spectroscopy, incident photon-to-electron conversion efficiency (IPCE), and intensity-modulated photocurrent spectroscopy (IMPS) / intensity-modulated photo voltage spectroscopy (IMVS). DSSC with this material shows a high-energy conversion efficiency of 8.2% at 100 mW/cm<sup>2</sup>. This is one of highest values for N719-based, solid-state, dye-sensitized solar cells.

**EH-TuP16 Effect of MoN Diffusion Barrier on High Temperature Selenization of Cu(In,Ga)**, Min-Su Kwon, H.-G. Kim, S.-H. Kim, C.-W. Jeon, Yeungnam University, Republic of Korea

In commercial manufacturing of CIGS photovoltaic module, the absorber films are usually produced by sputtering and selenization/sulfurization process. During high temperature selenization above 450 °C, the surface of Mo back contact is easily transformed to MoSe<sub>2</sub>, which is beneficial for ohmic contact formation in Mo/CIGS interface.[1] Although MoSe<sub>2</sub> has a high resistance, because it is a semiconductor of having bandgap energy of 1.35–1.41 eV, the thin layer of 100nm or less does not adversely affect the characteristics of solar cell.[2] However, since MoSe<sub>2</sub> may provide a current blocking capability when thicker than 200nm, it is necessary to control the thickness of the MoSe<sub>2</sub>. In this study, Mo/MoxN/Mo multi-layer back contact was selenized to evaluate capability of diffusion barrier of MoxN layer to prevent the excessive MoSe<sub>2</sub> formation. The CIGS absorber films were obtained by solid state selenization, where a sputtered CuInGa alloy film on Mo/MoxN/Mo/glass was subsequently selenized at 460–560 °C for 10 minutes by using Se vapor. Behavior of generated MoSe<sub>2</sub> was analyzed by using XRD, SEM. The conducting compound of MoxN as a diffusion barrier against Se was deposited by a reactive sputtering. The thickness and N content of MoxN was found to be linearly proportional to N<sub>2</sub> gas flow rate, which suggests that MoxN could be easily adjusted by a simple modification of Mo formation process. As a result of selenization, because of the formation of MoSe<sub>2</sub>, thickness of Mo mono-layer precursor was abruptly increased. But the thickness of multi-layered back contact with MoxN was not changed significantly. Therefore, as a diffusion barrier, MoxN was confirmed to be excellent diffusion barrier that is suited for a high temperature selenization process. The effect of MoxN layer on solar cell performance will be discussed. Acknowledgements This research was financially supported by the Ministry of Knowledge Economy(MKE), Korea Institute for Advancement of Technology(KIAT) and Dae-Gyeong Leading Industry Office through the Leading Industry Development for Economic Region. References [1] P.J. Rostan\*, J.Mattheis, G.Bilger, U. Rau, J.H. Werner, Thin Solid Films Volume 480-481, Pages 67-70(2005). [2] SeJin Ahn, Ki hyun Kim, Jae Ho Yun, and Kyung Hoon Yoon, Journal of Applied Physics 105, 113533(2009)

**EH-TuP17 Nano-patterned Pt Counter electrode Enhancing Light harvesting for Dye-Sensitized Solar Cells**, Won Seok Chi, D.J. Kim, J.P. Jung, J.H. Kim, Yonsei University, Korea

Nano-patterning is one of the most simple and effective techniques for efficiently light trapping to boost the energy conversion efficiency. By imprinting with poly(dimethyl siloxane) (PDMS) nanostamp cross-rotate two steps onto thin layered commercial TiO<sub>2</sub> paste, a mesh-shaped (200 nm × 200nm) TiO<sub>2</sub> scaffold electrode with a large area was fabricated. Platinum (Pt) nanoparticles deposited onto TiO<sub>2</sub> pattern by diverse method such as sputtering, thermal deposition and UV-radiation deposition. The Pt nanoparticles distribution as mesh-shaped structure onto counter electrode was characterized by a field emission scanning electron microscope (FE-SEM) and an atomic force microscope (AFM). Moreover, the light trapping ability was measured reflectance by comparison of mesh-shaped patterned and non-patterned counter electrode as a function of angle. For the four cases : 1) patterned Pt counter electrode by sputtering, 2) non-patterned Pt counter electrode by sputtering, 3) non-patterned Pt counter electrode by thermal deposition and 4) patterned counter electrode by UV-radiation deposition were fabricated for all-solid-state dye-sensitized solar cells (ssDSSCs). Among them, patterned Pt counter electrode by sputtering assembled solar cell showed highest solar energy conversion efficiency up to 7.0%. This remarkable result, observed for N719 dye based DSSC, was due to enhanced light harvesting and superior surface area confirmed by incident photon-to current efficiency (IPCE), electrochemical impedance spectroscopy (EIS), and cyclic voltammetry (CV) measurements. More importantly, we believe this approach is universally applicable to a variety of electrochemical cells requiring Pt catalysts such as fuel cells and catalytic chemical reactors. Furthermore, this process could include nano- and micro-sized patterns and can be extended to metal nanoparticles other than Pt.

## Nanomaterials

### Room: Mauka - Session NM-TuP

#### Nanomaterials Poster Session

**NM-TuP1 Electronic Structure of Titanate Nanoribbons Studied by O 1s and Ti 2p X-Ray Absorption and 3-Dimensional Dichroism Measured in a Scanning Transmission X-ray Microscope (STXM)**, Adam Hitchcock, X. Zhu, McMaster University, Canada, C. Bittencourt, University of Mons, Belgium, P. Umek, Jožef Stefan Institute, Slovenia, P. Krüger, Chiba University, Japan

TiO<sub>x</sub>-based nanostructures are being used as active materials in lithium ion batteries, gas sensors, photocatalysts, dye synthesized solar cells, etc. Much effort has been directed toward understanding their electronic properties [1] because they exhibit physical and chemical properties different from their bulk counterparts. They are challenging to study by analytical electron microscopy techniques since they are highly sensitive to radiation damage. Their nano-scale prevents the use of conventional X-ray absorption spectroscopy (NEXAFS) to study individual structures. Scanning transmission x-ray microscopy (STXM) allows studies of the electronic structure of individual nanomaterials with high spatial resolution (30 nm) and high energy resolution (0.1 eV) via NEXAFS spectroscopy and its linear dichroism (spectral variation as a function of the E-vector orientation) [2]. Here we report STXM-NEXAFS studies of individual sodium titanate nanoribbons (NaTiO<sub>x</sub>-NR) prepared by hydrothermal treatment of anatase TiO<sub>2</sub> micro-particles [3]. By measuring the dichroism with the sample at different orientations relative to the X-ray beam, and varying the direction of the linear E-vector by an elliptically polarizing undulator (EPU), the linear dichroism at the O 1s and Ti 2p edges was measured along the 3 principle axes of the anisotropic nanoribbons. Comparison of the spectra and dichroism with high level calculations helps confirm the crystal structure [4] and gives insight into the electronic bonding in these novel layered materials through the orientation dependence of local electronic structure within the crystallite. The methodology for 3D dichroic STXM measurements newly developed in this study is a powerful way to investigate anisotropic nanomaterials.

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**NM-TuP3 VOC Degradation Ability of VO<sub>x</sub>-TiO<sub>2</sub> Mixed Nanoparticles Attached on Glass Fiber in the Flow Chamber Test, Seonmin Kim, KETI, Republic of Korea, Baron. Cho, KETI**

VO<sub>x</sub>-TiO<sub>2</sub> nanocomposite samples made by one-pot synthesis showed the various catalytic activities depending on the calcination temperature. Photocatalytic activity of VO<sub>x</sub>-TiO<sub>2</sub> nanoparticles fabricated at various temperatures were characterized by the degradation of methylene blue in aqueous solutions under UV irradiation. Nanocomposites show significant enhancement of decomposition of methylene blue and the reason is considered by the synergistic effect between two different materials. In this study, the prepared nanocomposite catalysts were attached on glass fiber by cross-linking method and photodegradation abilities were tested by the change of VOC gas concentration in a closed chamber. For the photocatalytic analysis of the prepared nanoparticles, the absorption spectra are measured by UV-visible spectrophotometer and the bandgap analysis are performed by Kubelka-Munk theory. VOC removal abilities are quantified by the variation of p-xylene concentration in the closed chamber. Obtained results show that the as-prepared VO<sub>x</sub>-TiO<sub>2</sub> nanocomposites have different degradation abilities depending on the calcination temperature and vanadium atomic percentage.

**NM-TuP4 Surface Modification of TiO<sub>2</sub> Nanoparticles with Organic Molecule and Their Selective Adsorption Activity Toward Proteins, Xia Zhang, Northeastern University, China**

The nanomaterials have been widely applied in the biomedical area, which play important role in the disease diagnosis and treatment, tissue repair and proteins separation. Nano-TiO<sub>2</sub>, as a biologically inert material, shows good biocompatibility and bonding biological activity of the protein. In addition, the surface modification of TiO<sub>2</sub> can be achieved by the surface bonding between its surface hydroxyl groups and organic molecules. Furthermore, the research on the selective adsorption of proteins on the functionalized nanomaterials has important theoretical significance and application value in the field of protein separation.

In this work, TiO<sub>2</sub> nanoparticles were prepared by improved hydrothermal method, and then some organic molecule, such as silane KH560 and oleic acid were used to modify the TiO<sub>2</sub> nanoparticles. Some means, such as TEM, XRD, TG-DSC, and FT-IR were used to character the functionalized TiO<sub>2</sub> nanoparticles. The results showed that the organic molecules were successfully combined on the surface of TiO<sub>2</sub> nanoparticles via chemical bond and physical weak interaction.

These functionalized TiO<sub>2</sub> nanoparticles were used in the adsorption experiments of bovine hemoglobin (Bhb) and bovine serum albumin (BSA). The effects of different conditions on the adsorption capacity were studied systematically, and the optimum adsorption conditions were determined. Compared with the original nano-TiO<sub>2</sub>, after surface modification, the functionalized TiO<sub>2</sub> nanoparticles showed selective adsorption activity toward Bhb. For example, under optimum conditions ( $c_0$  (Bhb or BSA) = 150 mg/L,  $m$  (TiO<sub>2</sub>) = 0.8 mg/mL,  $t$  = 80 min.), for the pure TiO<sub>2</sub> nanoparticles, the adsorption capacity of Bhb and BSA was 70.6 mg/g and 40 mg/g respectively. Meanwhile, for the KH560 modified TiO<sub>2</sub>, the maximum adsorption capacity of Bhb was 122.8 mg/g and the adsorption of BSA was almost 0.

**NM-TuP5 Spontaneous Oxidation and Exfoliation of Graphene Oxide using Couette-Taylor Reactor, W.K. Park, Hyeonkeun Kim, Korea Electronics Technology Institute, W.S. Yang, Korea Electronics Technology Institute, Republic of Korea**

For the application of reduced graphene oxide to industries, an eco-friendly reduction method and shortening of the pickling and oxidation reaction times in the graphene oxide production process are essential. We dramatically shortened the graphene oxide production time by applying the Couette-Taylor flow, which allows consecutive reactions, to the graphite oxidation process using the modified Hummers method. With a 60-minute oxidation reaction in the Couette-Taylor reactor, the interlayer spacing increased from 0.34 nm to 0.78 nm, and uniform single- to multi-layer graphene oxides were obtained at a high yield of 93%. The properties of fabricated GO was examined by field emission scanning electron microscope, Raman spectra, atomic force microscope, x-ray photoelectron spectroscopy and x-ray diffraction.

**NM-TuP6 Field Emission and Anomalous Light Emission from Isolated ZnO Nanorods Array under Lateral Electric Field Application, T. Hirate, Kanagawa University, Japan, Yu Miura, T. Satoh, Kanagawa University**

We study on electrical and luminescent characteristics of ZnO nanorods array when an electric field is applied in lateral direction to the axis of ZnO nanorods.

ZnO nanorods are grown by chemical vapor deposition after laser ablation of gold on substrate. This growth method was developed by us. Glass

substrates (26 mm x 26 mm) are coated with SiO<sub>2</sub> film of 100 nm thickness by electron-beam deposition. The length of ZnO nanorods is about 1 micron meter and the diameter is from 50 nm to 80 nm. The direction of nanorods is distributed around a vertical axis to substrate surface.

The mean separation between nanorods on the area between electrodes is about 1.5 micron meter, and nanorods are isolated with each other. This is confirmed by SEM images and the measurement of electrical conduction between indium electrodes. Indium electrodes are electron-beam deposited on ZnO nanorods array with 600 nm thick. Shape of anode is rectangular (4 mm x 4 mm) and that of cathode is triangular with 30 degree vertical angle and 3 mm base, and the separation between the side of anode rectangle and the vertex of cathode triangle is 1.5 mm.

DC voltage is applied between electrodes in vacuum. An electrical potential of the metal chamber is same as that of anode. It is gradually increased from 0 volt. When the applied voltage is low, electric current does not flow. When it reaches about 1500 V, however, the current of about 10<sup>-6</sup> [A] initiates abruptly to flow and bluish-white light emission is observed at many points along the cathode edge. These beams of light extend along lines with directions nearly vertical to cathode edge as if the anode electrode did not exist or the voltage was not applied on anode. The intensity of emitted light is very high. It is confirmed experimentally that electrons are field-emitted from ZnO nanorods being at the cathode edges and the light beams correspond to trajectories of the field-emitted electrons. We estimate that the light may be generated by collisions of these electrons with ZnO nanorods, and are studying on this mechanisms.

**NM-TuP7 Carbon Nanotube and Graphene Hybrid Thin Film for Transparent Electrodes and Field Effect Transistors, Ki-Seok An, W. Song, S. Myung, J. Ihm, Korea Research Institute of Chemical Technology, Republic of Korea**

Low-dimensional sp<sup>2</sup> carbon materials including single-walled carbon nanotubes (swCNTs) and graphene have recently received a great deal of attention for potential uses in transparent and flexible nanoelectronics due to their remarkable mechanical, electrical, thermal, and optical properties. Especially, there are many interest in hybrid nanostructures including swCNTs and graphene. Here, we combined swCNTs and graphene hybrid films with complementary properties for use in high-performance transparent electrodes and field effect transistors (FETs). The hybrid films were synthesized by thermal chemical vapor deposition on Cu foil spin-coated with swCNTs. The density and alignment of swCNTs were simply controlled by adjusting the spin-coating speed or swCNT concentration. Evidence for the formation of the hybrid film was provided by the combined G- and 2D-bands intensity and lineshape Raman features of swCNTs and graphene. Based on the transfer characteristics for the hybrid film-based FETs, an improved I<sub>on</sub>/I<sub>off</sub> and on-state current are achieved compared with pristine graphene. Notably, the hybrid film had a sheet resistance of 300 Ω/sq with 96.4% transparency, which was comparable to that of hybrid materials in previous reports.

**NM-TuP9 Electrical Properties of Vertically Integrated Thin Film Transistors using Amorphous-In<sub>2</sub>Ga<sub>2</sub>ZnO<sub>7</sub> Channel Layer, UnKi Kim, S.H. Rha, J.S. Kim, E.S. Hwang, S.J. Lee, Y. Jang, C.S. Hwang, Seoul National University, Republic of Korea**

Recently, serially connected transistors with vertical configuration have received considerable attention in memory applications due to their potential to increase integration density to ultra-high values. In transistors with the vertically integrated configuration, the semiconductor channel material is usually composed of polycrystalline Si (poly-Si). Although the poly-Si channel has revealed feasible functionality as the semiconductor channel, degraded mobility, uniformity and reliability concerns related to the presence of grain-boundaries have not yet been completely resolved. In this regard, the amorphous nature and high carrier mobility of In<sub>2</sub>Ga<sub>2</sub>ZnO<sub>7</sub> (a-IGZO) thin films attract a great deal of attention as the channel material for such applications.

In this study, two serially connected and vertically integrated a-IGZO thin film transistors (V-TFTs) were fabricated using a gate-first fabrication process. The V-TFTs were fabricated with a vertical channel length ( $L_c$ ) of ~500 nm for the top TFT (t-TFT) and ~400 nm for the bottom TFT (b-TFT). Heavily doped p-type silicon was used as the substrate and gate of b-TFT (G<sub>b</sub>). A 100-nm-thick SiO<sub>2</sub> layer was thermally grown as the isolation layer between the t- and b-TFTs. 500-nm-thick poly-Si was deposited by low-pressure chemical vapor deposition to make the gate of the t-TFT (G<sub>t</sub>). Then, the poly-Si/SiO<sub>2</sub>/Si structure was dry etched sequentially to form the gates. Then, a 100-nm-thick SiO<sub>2</sub> layer was deposited by a PECVD as the gate dielectric layer, and an a-IGZO layer was sputter-deposited at room temperature on this structure with a target thickness of 100 nm on the top surface of the sample, which results in a channel thickness of ~40 nm for the t-TFT, and ~50 nm for the b-TFT on the side walls of the SiO<sub>2</sub>. Finally,

the Ti source and drain contacts were fabricated by a lift-off process, as the Ti contact with the a-IGZO is quasi-Ohmic.

The t- and b-TFTs show well-behaved transfer characteristics, with an  $I_{on}/I_{off}$  ratio ( $\sim 10^8$ ) and an SS value of 0.6 V/dec., which are much improved device parameters compared with the previously reported single-layer V-TFT, for which the gate-last fabrication process was adopted. This is due to the favorable distribution of the electric field by the  $V_d$  and  $V_g$  of the TFTs, where the influence of  $V_d$  on the channel can be minimized compared with that from  $V_g$ . While the two serially connected TFTs behave well and rather independently of each other, there were certain cross-influence between them. Details for such cross-talk will be discussed in the presentation. Further study results up to four layer V-TFT will also be presented.

**NM-TuP10 Synthesis and Application of Large-Area Transition Metal Dichalcogenides by Chemical Vapor Deposition.** *Chong-Yun Park, Y.Kim. Kim, J.S.Kim. Kim, S.-H.Park. Park, Y.H.Ko. Ko,* Sungkyunkwan University, Korea, Republic of Korea

Transition metal dichalcogenides ( $MoS_2$ ,  $WS_2$ ,  $WSe_2$ ,  $MoSe_2$ ,  $NbS_2$ ,  $NbSe_2$ , etc.) are layered materials that would exhibit semiconducting, metallic and even superconducting behavior. In the bulk, it is semiconducting and has an indirect band gap. Recently, these layered systems have attracted a great deal of attention mainly due to their complementary electronic properties when compared to other two-dimensional materials, such as graphene (a semimetal) and boron nitride (an insulator). However, these bulk properties could be significantly modified when the system becomes mono-layered; the indirect band gap becomes direct. Such changes in the band structure when reducing the thickness of a  $MoS_2$  and  $WS_2$  films has important implications for the development of novel applications, such as valleytronics. In this work, we report for the controlled synthesis of large-area ( $\sim cm^2$ ) single-, bi-, and few-layer  $MoS_2$  and  $WS_2$  using a two-step process.  $MoO_x$  and  $WO_x$  thin films were deposited onto a Si/SiO<sub>2</sub> substrate, and these films were then sulfurized under vacuum in a second step occurring at high temperatures (750 °C). The synthesized  $MoS_2$  and  $WS_2$  atomic thin films were analyzed by optical microscopy, Raman spectroscopy and TEM, and their photoluminescence properties were evaluated.

**NM-TuP11 Bolometers of Aligned Carbon Nanotubes.** *G. Garcia Valdivieso, HugoR. Navarro Contreras, F.J. González,* Coordinación para la Innovación y la Aplicación de la Ciencia y la Tecnología (CIACyT-UASLP), Mexico, *M. Quintana Ruiz,* Instituto de Física (IF-UASLP), Mexico, *G. Vera Reveles,* Coordinación para la Innovación y la Aplicación de la Ciencia y la Tecnología (CIACyT-UASLP)

The objective of this work is to report on a study on the preparation of bolometers and their characterization, based on parallel linear arrays of carbon nanotubes (CNTs).

The CNTs present good thermal and electrical properties. That is the reason why they may constitute competitive bolometric devices. A bolometer is a device that absorbs energy, in our case infrared radiation, thus varying its temperature (increasing) and electrical resistance (decreasing). The figure of merit of the bolometers is the temperature coefficient of resistance (TCR).

With the objective of obtaining aligned arrays of CNTs we made a solution in water with polymer (PVP), surfactant (SDBS) and CNTs. For a second group Functionalization was also performed with amino groups (Thymine) to induce better alignment, taking advantage of the hydrogen bonds that form between them.

For both sets of prepared CNT's copper was evaporated on them to have proper ohmic metal contacts to characterize the bolometers thus created.

The samples morphology and alignment were characterized by Scanning Electron Microscopy (SEM). Kaiser Test was performed to check on the degree of functionalization. The TCR of the constructed bolometers was electrothermally measured.

The results obtained with SEM were in some case alignments as long as 3 mm in length. The functionalization degree obtained was 1100  $\mu mol/g$ . We obtain values of TCR in the range of -1.7 to -3.0 %  $K^{-1}$  for non-functionalized CNTs and from -0.4 to -5.4%  $K^{-1}$  for functionalized CNT's. These last values are the largest reported for CNTs so far in the literature.

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**NM-TuP13 Mechanical Deformation in Si/Ge Quantum Dots,** *JoséLuis González Arango,* Universidad de Pamplona, Colombia, *P. Freitas Gomes,* Universidade Federal de Goiás, Campus Jataí, Brazil

Mechanical deformation (strain) plays an important role in the electronic, optical and transport properties of semiconductor quantum dots (SQDs). Epitaxial SQDs have a spatial deformation profile caused by the mismatch of the lattice parameters of the materials involved. This deformation creates an elastic energy which is one determinant fact in the SQDs grown on Stranski-Kastranow mode. The deformation also changes the potential profiles experienced by the carriers (electron and hole), requiring consideration of them when one calculates the electronics eigenstates. This shows the importance of the deformation profile on the properties of the nanostructures for future applications in electronic and optical devices.

In this work we show one more tool for the calculation of mechanical deformation on Si/Ge semiconductor quantum dots. We used a numerical simulation package to solve the differential equations for the deformation, using Continuous Elasticity Theory. We studied two systems: capped and uncapped. The cap layer is the Si layer grown above the Ge QDs layer. On the capped system, we observed a larger biaxial deformation on the Ge layer plane, when compared with the uncapped system. We also observed the deformation on the Si layer underneath the Ge layer. Again, on the capped system this biaxial deformation was also larger. With these deformation profile, we can also calculate the stress tensor and the elastic energy profiles.

**NM-TuP14 Synthesis of of Pt-based Bimetallic Nanoparticles using Pulsed Plasma Discharge in Water.** *SangYul Lee,* Korea Aerospace University, Republic of Korea, *S.M. Kim,* Korea Aerospace University, Kora, *J.-W. Kim,* InCheon University, Korea

The synthetic approach for electrocatalysts is one of the most important methods determining the electrocatalytic performance. In this work, we synthesized Pt and Pt-M (M=Cu, Ag, and Pd) bimetallic nanoparticles using a pulsed plasma discharge in water. A morphological investigation revealed that the as-synthesized Pt and Pt-M bimetallic nanoparticles constituted a nanochain network structure interconnected with primary nanoparticles, and the nanochains grew from the primary nanoparticles via the oriented attachment. The Z-contrast, EDX line scanning, and XRD analysis confirmed that the Pt was alloyed with M without elemental segregation or phase segregation. Furthermore, it was found that the composition difference was dependent on the electrode temperature determined by the power density and thermal parameters. The Pt-Pd bimetallic nanoparticles showed the largest electrochemical surface area due to a crystalline size of less than 5nm, whereas the Pt-Ag bimetallic nanoparticles showed superior electrocatalytic activity, stability, and durability with respect to the methanol oxidation reaction, which could be attributed to the downshift of the d-band center via electronic modification.

**NM-TuP15 Crystal Structure and Surface Orientation dependence of Hydrogen Adsorption on Iron Surfaces,** *Yuji Kunisada,* Hokkaido University, Japan, *N. Sakaguchi,* Hokkaido University

#### Introduction

In order to utilize hydrogen as new clean energy resources, we have to realize safe, efficient, and low cost hydrogen transportation and storage. One of the current transport methods is the one with high-pressure hydrogen tanks. However, hydrogen is one of the most important elements in the damage process of materials. Many recent studies have reported that hydrogen atoms absorbed in materials can stabilize vacancies[1], which cause reduction of their ductility. From their point, the atomic- and electronic-scale understanding of hydrogen embrittlement process is necessary to develop new long-life materials for hydrogen transportation and storage.

#### Calculation Methods

In this study, we investigated the adsorption properties of hydrogen isotopes on iron surfaces with the aid of first principles calculations based on spin-polarized density functional theory, in order to understand hydrogen behaviors in commonly-used iron-based materials, for instance, ferritic and austenitic stainless steels. We also adopted the quantum mechanics calculations of hydrogen nuclei, because the importance of delocalization and zero-point energy of hydrogen nuclei has been reported in various papers. [2, 3] Furthermore, we considered hydrogen(H), deuterium(D), tritium(T), and muonium( $\mu^+e^-$ ) as hydrogen isotopes.

#### Results and Discussion

At first, we investigated the potential energy surfaces of hydrogen on bcc-Fe(110) and fcc-Fe(111) surfaces. These surface orientations are the most stable ones for each crystal structure, respectively. Furthermore, in order to reveal the surface orientation dependence of hydrogen adsorption, we investigated the potential energy surfaces of hydrogen on fcc-Fe(100) surfaces. We revealed that the most stable adsorption sites on bcc-Fe(110),

fcc-Fe(111), and fcc-Fe(100) surfaces are the long-bridge, fcc-hollow, and short-bridge site, respectively. The corresponding adsorption energies with these adsorption configurations are 2.99, 2.78, and 2.82 eV, respectively. Thus, we can point that the adsorption energies on bcc-Fe(110) and fcc-Fe(100) surfaces are slightly larger than the one on fcc-Fe(111) surfaces. We also investigated the hydrogen adsorption states on these surfaces by calculating Schrödinger equation for hydrogen nuclei. We found the delocalization of H atoms in the ground state. In addition, we clarified the non-negligible isotope effects in delocalization and zero-point energy of hydrogen isotopes.

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**NM-TuP16 Synthesis and Evaluation of Nanocrystalline Diamond Powder Prepared by Coaxial Arc Plasma Gun, Hiroshi Naragino, A. Tominaga, Kyushu University, Japan, K. Sumitani, Kyushu Synchrotron Light Research Center, Japan, S. Hattori, Kyoto Prefectural Technology Center for Small and Medium Enterprises, Japan, T. Yoshitake, Kyushu University, Japan**

Diamond possesses several superior physical properties including high hardness, wide bandgap, and chemical inertness. Furthermore, it is possible to impart functionalities by doping and surface modification. Nano-sized diamond powder shows different properties from bulk diamond. Nanodiamond has mainly been produced by detonation method so far. However, high-purity nanodiamond powder has been difficult to be fabricated by detonation. Moreover, the functionalization of nanodiamond is made after growth, because of *in-situ* doping being impossible. Our research group has proposed a new novel method that employs a coaxial arc plasma gun (CAPG), which enables us to fabricate nanodiamond crystallites. The specifics to this method are as follows: i) the growth is made using a simple apparatus equipped with a coaxial arc plasma gun, ii) high-purity nanodiamond can be fabricated in principle, iii) doping can be easily made by using doped targets, and iv) the grain size is expected to be changed by controlling the discharge condition of coaxial arc plasma gun. In this work, we experimentally proved the generation of nanodiamond by powder X-ray diffraction (XRD) and transmission electron microscope (TEM) and that the grain size is evidently enlarged with the electric power applied to an arc plasma gun. Moreover, the density of nanodiamond powder was measured using a sink-float method. Nanodiamond powder was fabricated using CAPG (ULVAC, APG-1000) equipped with a graphite target. The inside of the chamber fitted with CAPG was evacuated to  $< 10^{-6}$  Pa and hydrogen was introduced at 5 sccm. The head of the arc plasma gun was pointed at quartz plate heated at 550deg. C. The powder that quickly and automatically exfoliated from the quartz plate was gathered in the collection cell located under the quartz plate. In order to confirm the formation of diamond, the films were structurally investigated by TEM and powder XRD using synchrotron radiation at beamline 15 of the SAGA-LS. The films exhibited diamond-111 and -220 diffraction rings in the electron diffraction patterns and the existence of diamond grains was confirmed from the dark-field TEM images. The XRD patterns also exhibited diffraction peaks due to diamond. The grains size was increased from 2 to 80 nm with increasing electric power applied to an arc plasma gun. From the density measurement, the density of nanodiamond powder was estimated to be approximately 1.77 g/cm<sup>3</sup>. This value is smaller than that of diamond (3.5 g/cm<sup>3</sup>), and indicates that the nanodiamond contains the non-diamond phase such as an amorphous carbon. The details of preparation apparatus and preparation mechanism are explained in the conference.

**NM-TuP17 Surface Structure and Local Valence Electronic States of Si(110)-16×2 Surface after Exposure to Water: XPS and Auger-Photoelectron Coincidence Study, Takuhiro Kakiuchi, S. Nishiura, J. Kawamoto, Ehime University, Japan, S. Nagaoka, Ehime University, K. Mase, KEK, Japan**

Si(110)-16×2 is a favorable candidate for a next-generation semiconductor substrate because it takes a single domain (SD) structure with high hole-mobility, which is larger than that of the other Si crystal faces. Recently, Adatom-Buckling (AB) model has been proposed as the surface structure model for clean Si(110)-16×2 surface [1]. The AB model consists of five Si surface components of SC1: the buckled upper atoms, SC2: the unbuckled atoms and the second layer atoms with dangling bonds (DBs), SC3: the first layer and second layers atoms without DBs, SC4: the adatoms, and SC5: buckled lower atoms. In the AB model, the surface states  $S_1$ ,  $S_2$ ,  $S_3$ , and  $S_4$  with binding energies of 0.2 eV, 0.4 eV, 0.7 eV, and 1.0 eV are reported to be located at specific surface sites of SC4, SC1, SC5, and SC3, respectively [1]. However, the SD structure of Si(110)-16×2 disappears when it is exposed to atmospheric air. In this study, we investigated a water-

terminated Si(110)-16×2 SD surface with XPS and Auger-photoelectron coincidence spectroscopy. Si-2*p* photoelectron spectra indicate that water is dissociatively adsorbed and forms Si-H and Si-OH components after exposure to water of 0.1 Langmuir (L). When Si(110)-16×2 surface is exposed to water from 1.0 L to 5.0 L, there is little change in these Si-2*p* intensity ratio. This result indicates that clean Si(110)-16×2 surface is saturated with water of less than 1.0 Langmuir (L). In addition, water is preferentially dissociative-adsorbed at surface components of the SC1, the SC2, and the SC3 on step edge of SD structure, but is hardly adsorbed at surface components of the SC4 and the SC5 on the terrace of the SD structure. The SD structure of Si(110)-16×2 surface after the exposure to water of 5.0 Langmuir is kept under ultra-high vacuums condition and atmosphere pressure of N<sub>2</sub> gas. This result indicates that Si(110)-16×2 SD surface is inactivated by water dissociative-adsorption. On the other hand, Si-*L*<sub>23</sub>*VV*-Si-2*p* coincidence spectra suggest that the surface states  $S_1$ ,  $S_2$ ,  $S_3$ , and  $S_4$  disappear after exposure to water. The valence band maximum energy of water adsorbed Si(110)-16×2 surface is shifted to deeper binding energy side in comparison with that of clean Si(110)-16×2 surface. The water adsorbed Si(110)-16×2 SD surface may be used as a unique semiconductor substrate.

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**NM-TuP19 Study on Tracking Resistance of Silicone Rubber Nanocomposite under DC Voltage, K.J. Lim, JungHun Kwon, J.S. Park, Chungbuk National University Korea, Republic of Korea**

One of the problems is tracking of outdoor polymeric silicone rubber(SIR) insulation used in HVDC or HVAC transmission lines. These problem are more serious with dc than with ac voltage, due to the electrostatic attraction of airborne contaminants to the insulator surface. In order to improve the tracking resistance of SIR, inclined plane(IP) tracking test similar to IEC 60587 was conducted under positive and negative dc voltages for SIR filled with micro sized silica and nano sized alumina trihydrate(ATH) fillers. The results show that tracking resistance of SIR nanocomposites were more increased than SIR unfilled micro or nano filler. It was also seen that the tracking resistance of SIR showed polarity effect under dc voltage.

**NM-TuP20 Decay Processes of Si 2s Core Holes in Si(111)-7×7 Revealed by Si Auger Electron Si 2s Photoelectron Coincidence Measurements, Kazuhiko Mase, KEK, Japan, K. Hiraga, S. Arai, Yokohama National University, Japan, R. Kanemura, Yokohama National University, Y. Takano, K. Yanase, Y. Ogashiwa, Gunma University, N. Shohata, University of Tsukuba, N. Kanayama, Chiba University, T. Kakiuchi, Ehime University, Japan, S. Ohno, Yokohama National University, D. Sekiba, University of Tsukuba, K. Okudaira, Chiba University, M. Okusawa, Gunma University, M. Tanaka, Yokohama National University**

The filling of an initial core hole by an electron from a higher subshell of the same shell is known as a Coster-Kronig transition, and Auger photoelectron coincidence spectroscopy (APECS), in which Auger electrons are measured in coincidence with photoelectrons with a fixed kinetic energy (KE), is an ideal tool for probing Coster-Kronig transitions because Auger electrons originating from a specific core ionization are detected.

However, studies of Coster-Kronig transitions have mainly been restricted to metal surfaces, even though Si surfaces are crucial for surface science applications and the semiconductor industry. Issues such as the assignments of the Si *L*<sub>1</sub>*VV* Auger peaks, experimental determination of the branching ratio of the Si *L*<sub>1</sub>*L*<sub>23</sub>*V* and Si *L*<sub>1</sub>*VV* Auger decays, and competition between the delocalization of the valence hole and the Si *L*<sub>23</sub>*V-VVV* Auger decay are, to the best of our knowledge, largely unexplored. In this paper, we report on the decay processes of Si 2*s* core holes in a clean Si(111)-7×7 surface studied using coincidence measurements of the Si Auger electron and the Si 2*s* photoelectron.

We measured a coincidence spectrum measured by scanning the ASMA over a KE range of 20–150 eV, with the DP-CMA fixed at a KE of 76.5 eV (Si-*L*<sub>23</sub>*VV*-Si-2*p* APECS spectrum). Distinct Auger peaks are observed in a KE region of 50–92 eV with the maximum peak located at KE = 88 eV. We assigned these peaks to Si *L*<sub>23</sub>*VV* Auger electrons emitted in the decay processes of Si 2*p* holes. Another coincidence spectrum was measured by scanning the ASMA over a KE range of 20–150 eV with the DP-CMA fixed at KE = 26.3 eV, which corresponds to Si 2*s* photoelectrons (Si-Auger-Si-2*s* APECS spectrum). The maximum peak position and shape of the Si-Auger-Si-2*s* APECS spectrum in the AeKE = 50–92 eV region are almost identical to those of the Si-*L*<sub>23</sub>*VV*-Si-2*p* APECS. Therefore, we assigned these Auger peaks to Si *L*<sub>23</sub>*VV* Auger processes. This is direct evidence of Si *L*<sub>23</sub>*VV* Auger processes being induced by Si 2*s* ionization.

The peaks of Si-Auger-Si-2*s* APECS in the AeKE = 20–50 regions were assigned to Si *L*<sub>1</sub>*L*<sub>23</sub>*V* Auger decays, while the peaks of Si-Auger-Si-2*s*

APECS in the AeKE = 100–150 eV regions were assigned to Si  $L_{1VV}$  Auger decays. These results indicate that there are two nonradiative decay processes of the Si 2s core hole. The first is the Si  $L_{1L_{23}V}$  Coster–Kronig transition followed by delocalization of the valence hole and Si  $L_{23VV}$  Auger decay, while the second is Si  $L_{1VV}$  Auger decay. From the integrated intensity of the normalized Si  $L_{23VV}$  and Si  $L_{1VV}$  Auger peaks, we estimated the branching ratio of Si  $L_{1L_{23}VV}$  to Si  $L_{1VV}$  Auger processes to be  $(96.8 \pm 0.4):(3.2 \pm 0.4)$ .

**NM-TuP21 Pulsed Laser Assisted Synthesis of NaLa(MoO<sub>4</sub>)<sub>2</sub>:Ho<sup>3+</sup>/Tm<sup>3+</sup>/Yb<sup>3+</sup> Nanocrystals and their White Upconversion Luminescence, Jeong Ho Ryu, J.-I. Lee, Korea National University of Transportation, Korea**

In recent years, lanthanide ion doped upconversion (UC) luminescence from near infra-red radiation to visible or UV light has received many attention for their various applications in phosphors, solar cell, flat-panel displays, scintillators, solid state lasers and fluorescent bio-medicals. In the fields of industries, it is required that UC luminescent materials should be engineered to emit wide ranges of white colors. Also, high chemical, physical and mechanical stabilities should be achieved through engineering UC materials. Although multi-color UC luminescence with high efficiency was reported using lanthanide doped fluorides emitting bright blue emission of Tm<sup>3+</sup> and green or red of Er<sup>3+</sup> under laser excitation (980 nm), fluorides can decompose easily with moisture in air which makes the application difficult in the fields of industries. Conventionally, solid state reaction, precipitation, hydrothermal and sol-gel methods were used for synthesis of nanocrystalline NaLa(MoO<sub>4</sub>)<sub>2</sub> particles. However, those methods need long processing time and steps for fabrication. Also, chemical additives in procedure may be incorporated to NaLa(MoO<sub>4</sub>)<sub>2</sub> particles as impurities, which results in bad influence to human body clinically. One novel technique for fabrication of NaLa(MoO<sub>4</sub>)<sub>2</sub> nanocrystals is pulsed laser ablation (PLA) in liquid medium. PLA of solid target in liquid has been a promising technique for producing nanocrystals for analytical and bioanalytical applications as well as the rapid synthesis of complex materials because the experimental procedure is simple and above all, chemical additive is unnecessary. However, to date, there is little report on the preparation of upconverting NaLa(MoO<sub>4</sub>)<sub>2</sub> nanocrystals by laser ablation in liquid medium. In this study, we report a novel synthetic approach to produce Ho<sup>3+</sup>, Tm<sup>3+</sup>, Yb<sup>3+</sup> tri-doped NaLa(MoO<sub>4</sub>)<sub>2</sub> nanocrystals using PLA in liquid medium without any surfactant. The fabricated NaLa(MoO<sub>4</sub>)<sub>2</sub>:Ho<sup>3+</sup>/Tm<sup>3+</sup>/Yb<sup>3+</sup> nanocrystals were characterized in terms of their crystallinity, microstructure and white upconverting property. Moreover, the laser ablation process was discussed by a thermally induced explosive ejection mechanism.

**NM-TuP22 DFT Study of Surface Passivation of Silicon Carbide Nanowires by Halogens, Miranda, Universidad Nacional Autónoma de México, Trejo, Instituto Politécnico Nacional, México, Cruz-Irison, Luis A. Pérez, Universidad Nacional Autónoma de México**

The use of silicon carbide nanowires (SiCNWs) as chemical sensors stands out among their many possible applications. At present, SiCNWs are usually coated with SiO<sub>2</sub>. To further extend and customize their applications, surface modification of nanowires (NWs) by different chemical species is one of the feasible ways to achieve it. An insightful understanding of the effects of such passivating functional groups is thus important to understand the electronic properties of surface modified NWs. In this work, by using density-functional calculations, we study the stability and the electronic structure of SiCNWs passivated with halogen atoms such as F, Cl, Br or I, considering different surface covering schemes. We show that the stability of SiCNWs strongly depends on both the passivating element and the percentage of surface covering, in an otherwise fully hydrogen passivated NW. Moreover, when going from the most stable system to the less stable one, the following stability trend is obtained: F-SiCNW > Cl-SiCNW > Br-SiCNW > I-SiCNW > H-SiCNW, which can be attributed to the different electronegativities of the passivating elements considered. Finally, the effects of chemical decoration on the size and nature of the NW band gaps are discussed.

## Thin Films

Room: Mauka - Session TF-TuP

## Thin Films Poster Session

**TF-TuP3 Novel Techniques and Devices for In-Situ Film Coatings of Long, Small Diameter Tubes or Elliptical and other Surface Contours\*,**

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Two devices and techniques that can, via PVD, coat various surface contours or very long small aperture pipes. First 3-axes robotic manipulators controlling separate robotic assemblies resulted in 9-axes of motion combined with conformal shape of the cathodes that can articulate various curved surface contours was developed and successfully used for optically coating aircraft canopies. Second a magnetron mole was developed in order to in-situ coat accelerator tube sections of the Brookhaven National Lab (BNL) relativistic heavy ion collider (RHIC) that have 7.1 cm diameter with access points that are 500 meters apart, for copper coat the RHIC vacuum tube in order to alleviate the problems of unacceptable ohmic heating and of electron clouds. A magnetron with a 50 cm long cathode was designed fabricated and successfully operated to copper coat a whole assembly containing a full-size, stainless steel, cold bore, of the RHIC magnet tubing connected to two types of RHIC bellows, to which two additional pipes made of RHIC tubing were connected. The magnetron is mounted on a carriage with spring loaded wheels that successfully crossed bellows and adjusted for variations in vacuum tube diameter, while keeping the magnetron centered. Electrical power and cooling water were fed through a cable bundle. The umbilical cabling system, which is enclosed in a flexible braided metal sleeve, is driven by a motorized spool. To increase cathode lifetime, movable magnet package was developed, and thickest possible cathode was made, with a rather challenging target to substrate distance of less than 1.5 cm. Optimized process to ensure excellent adhesion was developed. Coating adhesion of 10 μm Cu passed all industrial tests and even exceeded maximum capability of a 12 kg pull test fixture. Details of experimental setup for coating two types of bellows and a full-scale magnet tube sandwiched between them will be presented. Room temperature RF resistivity measurement indicated that 10 μm Cu coated stainless steel RHIC tube has conductivity close to copper tubing. Work is in progress to repeat the RF resistivity measurement at cryogenic temperatures. Plans are to develop techniques for in situ coating of elliptical and other surface contour RF cavities and long beam pipes with thick superconducting films.

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**TF-TuP5 Ultrasound Influence on the Si-SiO<sub>2</sub> System Defects Structure, Daniel Kropman, Tallinn University of Technology, Estonia, T. Laas, Tallinn University, Estonia**

The effect of ultrasonic treatment (UST) on the defect structure of the Si-SiO<sub>2</sub> system by means of electron spin resonance (ESR), selective etching, MOS capacitance technique and secondary ions mass-spectroscopy (SIMS) is presented.[1,2]. The non-monotonous dependence of the defect densities on the US wave intensity has been observed. The influence of the UST frequency on the ESR signal intensity of the defect centres depended on the defects type and may be caused by vibration energy dissipation, which are a function of defect centres type. The influence of the UST on the Si-SiO<sub>2</sub> interface properties depends on the oxide thickness and crystallographic orientation. The density of point defects and absorbed impurities at the Si-SiO<sub>2</sub> interface can be reduced and its electrical parameters improved by an appropriate choice of the UST and oxidation condition. UST is widely used in medicine, not only for diagnostic, but for cancer treatment too. UST influence on inorganic and organic materials have common properties. These allow to suggest that UST may be used in biotechnology for materials properties modification.

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**TF-TuP6 Fabrication of Transparent Superhydrophobic Surface by Single, Multi-Step and Gas Mixture Method Using CH<sub>4</sub>/C<sub>4</sub>F<sub>8</sub>/He Atmospheric Pressure Plasma.** *Duksun Han, S.Y. Moon*, Chonbuk National University, Republic of Korea

Superhydrophobic surface was prepared by CH<sub>4</sub>/C<sub>4</sub>F<sub>8</sub>/He atmospheric pressure plasma. Single step and multi-step processes using CH<sub>4</sub> and C<sub>4</sub>F<sub>8</sub> precursors are performed to investigate evolution of a transparency and wettability. In case of the single step process, a surface modification using C<sub>4</sub>F<sub>8</sub> showed high water droplet contact angle (WCA) relative to the CH<sub>4</sub> plasma treatment due to a difference of surface free energy. On the other hand, the contact angle was remarkably increased to 152°, indicating superhydrophobic property, using sequential multi-step CH<sub>4</sub> and C<sub>4</sub>F<sub>8</sub> plasma treatment. Also, a rapid single-step method using a He, CH<sub>4</sub>, and C<sub>4</sub>F<sub>8</sub> mixture plasma was performed. In this case, WCA was gradually increased to 170° and the transparency was decreased when the gas ratio of C<sub>4</sub>F<sub>8</sub> to the total flow rate was increased. The chemical and physical mechanism responsible for hydrophobicity by atmospheric pressure plasma is discussed through the investigation of chemical composition and surface morphology using a FTIR, XPS, SEM and AFM.

**TF-TuP7 Influence of the Transfer and Chemical Treatment of CVD(Chemical Vapor Deposition) Graphene for Flexible Transparent Electrodes.** *Y. Kim*, Korea Electronics Technology Institute (KETI), Republic of Korea, *H. Kim*, Korea Electronics Technology Institute, *WooSeok Yang*, Korea Electronics Technology Institute, Republic of Korea  
It has become critically important to develop reliable method to transfer chemical vapor deposited (CVD) graphene from its growth substrate to the target substrate without leaving undesired polymer residues on the graphene surface. Here, we have found that for the two different transfer method – wet transfer using poly(methyl methacrylate) (PMMA) and dry transfer using polydimethylsiloxane (PDMS) as support layer, the amount of polymer residues and other impurities left on the graphene surface varies depending on the solvent used to remove those polymers. The exposure of the graphenes to different organic solvents such as acetone and chloroform resulted in different amount of polymer residues and impurities present on the graphene surface, which impact the electronic structure of the transferred graphene. It was found that the graphene obtained using the dry transfer method and acetone as solvent showed a 2D to G (I<sub>2D</sub>/I<sub>G</sub>) intensity ratio of 4.58 and a 2D peak full width-half maximum (FWHM) of 24.66, which was higher than that using the wet transfer method and chloroform as solvent. These results showed that graphene was less affected by the polymer residues and impurities for the dry transfer method rather than the wet transfer method. In addition, using acetone rather than chloroform as solvent in the dry transfer method led to less contaminated graphene.

**TF-TuP8 A Study on Amorphous InGaZnO Thin Film Transistor with Wet Etched Copper/Molybdenum Alloy Electrode.** *JongHyun Seo, J.-H. Jeon, H.H. Choe, J.H. Yoon*, Korea Aerospace University, Republic of Korea, *H.-S. Kim*, Korea Aerospace University

We fabricated the back channel etch type copper/molybdenum alloy/Indium gallium zinc oxide thin film transistors using only wet patterning in phosphoric acid based copper etchant. Compared with pure molybdenum S/D electrode, New Mo alloy electrodes showed better TFT performances both in mobility and on current. The mobility was increased by 50% and on current increased up to 100% compared to those of pure molybdenum electrodes. Little is known about the effect of S/D electrode material on the electrical properties of amorphous IGZO oxide TFTs.

A modeling based on the reduced elastic strain energy by reduction in biaxial elastic modulus of the Mo alloy film is proposed to explain enhanced electrical properties of Cu/Mo alloy/IGZO TFT. The effects of alloy percentage in the alloy, chemical additives on the electrical properties of back channel etch type Cu/Mo alloy/IGZO oxide TFTs were investigated using surface analysis and electrochemical methods.

**TF-TuP9 Synchrotron Radiation Photoelectron Spectroscopy Study on Surface Oxidation of Ge(100) and Ge(111) at Room Temperature.** *Akitaka Yoshigoe*, Japan Atom Energy Agency, Japan, *R. Okada*, University of Tsukuba, Japan, *Y. Teraoka*, Japan Atomic Energy Agency, Japan, *Y. Yamada*, University of Tsukuba, Japan, *M. Sasaki*, University of Tsukuba, Japan

Germanium (Ge) has been interesting as future substitute channel material for metal-insulator-semiconductor field-effect-transistors (MISFETs) because of its high carrier mobility. Although precise controlling of the surface oxide layer of Ge surfaces is important for fabrication of dielectric/Ge interface in Ge-based devices, fundamental aspects of oxidation reaction at Ge single crystal surfaces and nature of the oxide monolayer have not yet been well understood. In this presentation, we report the nature of oxides of Ge(100)-2×1 and Ge(111)-c(2×8) surfaces fabricated with pure oxygen gas (O<sub>2</sub>) at 300 K. Surface oxide and its

evolution from very initial stages to the maximum oxide coverage were measured by real-time photoelectron spectroscopy using synchrotron radiation. All experiments were conducted with SUREAC2000 at BL23SU in Spring-8. We found the saturation oxide coverage on both surfaces is less than one monolayer. We found that initial sticking coefficient of O<sub>2</sub> was much smaller than that for Si(100). SR-XPS measurements demonstrated that the maximum oxidation number of Ge in saturation region was as small as 2+, which exhibits a strong contrast to the case of Si where 4+ state is spontaneously formed. Our results suggest that native oxides layer with Ge<sup>4+</sup> cannot be formed only with pure O<sub>2</sub> gas. Our findings reveal the significant difference between the nature of surface oxides of Ge and Si and can be useful for a precise control of oxide layer on Ge surfaces.

This research was partially supported by grants-in-aid from the Ministry of Education, Cultures, Sports, Science and Technology, for Exploratory Research, No. 26420289. The synchrotron radiation experiments were performed at the BL23SU of Spring-8 with the approval of JASRI (Proposal No. 2007B3802, 2008A3804, 2008B3804, 2009A3804, 2011A3804, 2011B3802, 2012A3802, 2012B3802, 2013A3802, and 2013B3802).

**TF-TuP10 Effect of Al Doping on Crystallization and Electrical Property of CeO<sub>2</sub> Films Deposited by RF Magnetron Sputtering.** *Keiji Ishibashi*, COMET Inc., Japan, *T. Okazaki, H. Kamata, Y. Notani, K. Hara, T. Osawa, K. Aoki, K. Fujiyama*, Hosei University, Japan, *S.-G. Ri, S. Suzuki*, COMET Inc., Japan, *Y. Yamamoto*, Hosei University, Japan

To suppress crystallization of CeO<sub>2</sub> thin films as a gate stack material in MOS devices, Al was doped in CeO<sub>2</sub> films during radio frequency (RF) magnetron sputtering deposition on p-type Si (100) substrates. Deposition was carried out at room temperature in an Ar atmosphere of 5.3 Pa to a typical thickness of 35 nm using a CeO<sub>2</sub> target on which some Al metal plates were bonded. The composition of the resultant deposited films measured by X-ray photoelectron spectroscopy was Ce<sub>0.28</sub>Al<sub>0.06</sub>O<sub>0.66</sub>, equivalent to (CeO<sub>2</sub>)<sub>0.9</sub>(Al<sub>2</sub>O<sub>3</sub>)<sub>0.1</sub> in terms of the molar fraction. The post annealing was performed in air and N<sub>2</sub> in the temperature range from 200 to 600°C. Addition of aluminum oxide with 10% molar fraction into CeO<sub>2</sub> during sputter deposition was effective in suppressing crystallization. The deposited films remained amorphous after annealing up to 500°C from observation of X-ray diffraction and transmission electron diffraction. The interfacial SiO<sub>2</sub> layer was grown after annealing in both ambients of air and N<sub>2</sub>. While after annealing in air the interface consisted of a simple double layer of CeO<sub>2</sub>/SiO<sub>2</sub>/Si, a lower oxide such as Ce<sub>2</sub>O<sub>3</sub> was formed between CeO<sub>2</sub> and SiO<sub>2</sub> in an N<sub>2</sub> annealing ambient. The leakage current measured at the applied electric field of 1 MV/cm (gate voltage=3.5 V) was decreased to as low as the order of 10<sup>-8</sup> and 10<sup>-7</sup> A/cm<sup>2</sup> after annealing at 200°C in air and N<sub>2</sub>, respectively. The C-V hysteresis of the samples annealed in air was broadened with the increase of annealing temperature. Annealing in N<sub>2</sub> reduced C-V hysteresis in contrast to air annealing, but appearance of a kink and gradual slope in the depletion state on its C-V curves suggested the existence of a large amount of shallow states originated from the lower Ce oxide at the interface. The flat band voltage after annealing was shifted toward higher gate voltages due to the fixed negative charge arising from Al oxides. The Al doping in CeO<sub>2</sub> was effective in suppressing crystallization of CeO<sub>2</sub> films, but introduced complicated behavior in I-V and C-V electrical characteristics, while in the non-doped CeO<sub>2</sub> films electrical neutrality of the interfacial lower Ce oxide (Ce<sub>2</sub>O<sub>3</sub>) was maintained and led to relatively simple behavior in electrical characteristics.

**TF-TuP11 Electrical and Crystallization Properties of Al Doped CeO<sub>2</sub> Thin Films Deposited by Reactive RF Sputtering with O<sub>2</sub> Introduction.** *Takashi Osawa, Y. Notani, K. Hara, K. Aoki, K. Fujiyama*, Hosei University, Japan, *K. Ishibashi, S. Suzuki*, COMET Inc., Japan, *Y. Yamamoto*, Hosei University, Japan

Cerium dioxide is one of the materials of interest as a gate stack in metal-oxide-semiconductor (MOS) devices. CeO<sub>2</sub> is likely to crystallize, however, leading to the possible increase of the leakage current. To suppress crystallization of CeO<sub>2</sub> thin films, Al was doped in CeO<sub>2</sub> films during deposition using RF magnetron sputtering using CeO<sub>2</sub> target on which Al plates were bonded with the applied RF power of 50 W at room temperature at a pressure of 5.3 Pa. The deposition was carried out with and without O<sub>2</sub> introduction in order to investigate the influence of oxygen deficiency in the deposited film. The deposition time was adjusted so as to obtain the typical thickness of CeO<sub>2</sub> films of 35 nm since the deposition rate decreased with increasing the O<sub>2</sub> flow rate varying as 0, 2, 5 and 10%. The post annealing was performed in an N<sub>2</sub> atmosphere in the temperature range from 200 to 600 °C.

The electrical properties after annealing were characterized by I-V and C-V measurements using the Hg probe as an electrode. Irrespective of the amount of O<sub>2</sub> introduction, the leakage current at 3 MV/cm was minimized around 1.0×10<sup>-7</sup> A/cm<sup>2</sup> after annealing at 200 °C. After annealing at 400 °C, the leakage current increased by 3 orders of magnitude. For the sample annealed at 600 °C, the leakage current was recovered to the level of the as-

deposited sample. The dielectric constant was increased with increasing amount of introduced O<sub>2</sub>. It tended to increase with increasing annealing temperature, but exceptionally decreased after annealing at 400 °C. The C-V characteristic represented the kink or even the step in the depletion region for sample annealed at 400 °C. The flat band voltage was shifted toward higher gate voltage with increasing annealing temperature, probably due to the fixed negative charge arising from Al oxides. The fact that the C-V hysteresis was broadened with the increase of introduced O<sub>2</sub> implied that the existence of Al oxide in the film enhanced the generation of the interfacial states.

In the X-ray diffraction spectrum, the as-deposited samples represented strong CeO<sub>2</sub> and weak Ce<sub>2</sub>O<sub>3</sub> peaks when the amount of introduced O<sub>2</sub> flow ratio was 0 and 2% while Ce<sub>2</sub>O<sub>3</sub> peaks almost disappeared with the O<sub>2</sub> introduction above 5%. After annealing at 200–600 °C the peak other than CeO<sub>2</sub> was not observed. Judging from the electron diffraction image obtained from the fast Fourier transform (FFT) processing of high resolution transmission electron microscope image, CeO<sub>2</sub> crystalline structure appeared to be destroyed due to the transition to another phase after annealing at 400 °C.

**TF-TuP15 Atomically-resolved Orientational Ordering of C60 Molecules on Epitaxial Graphene on Cu(111), M. Jung, D. Shin, S.-D. Sohn, S.-Y. Kwon, N. Park, UNIST, Hyung-Joon Shin, UNIST, Republic of Korea**

The interaction between molecular adsorbates and graphene is one of the fundamental issues for tailoring the properties of graphene-based molecular devices, because the electronic and structural properties of molecular layers on surfaces are determined by intermolecular and molecule-substrate interactions. Here, we present the atomically resolved experimental measurements of the self-assembled fullerene molecules on single-layer graphene on a Cu(111). Fullerene molecules form a (4 × 4) superstructure on graphene/Cu(111), revealing only single molecular orientation. We can resolve the exact adsorption site and the configuration of fullerene by means of low-temperature scanning tunnelling microscopy (LT-STM) and density functional theory (DFT) calculations. The adsorption orientation can be explained in terms of the competition between intermolecular interaction and molecule-substrate interaction, where strong Coulomb interactions among the fullerenes determine the in-plane orientation of the fullerene. Our results provide important implications for developing carbon-based organic devices using a graphene template in future.

**TF-TuP17 Novel Fabrication of Flexible Graphene-based Chemical Sensors with Heaters using Soft Lithographic Patterning Method, Jongsun Lim, Korea Research Institute of Chemical Technology, Republic of Korea**

We have fabricated graphene-based chemical sensors with flexible heaters for the highly-sensitive detection of specific gases. We believe that increasing the temperature of the graphene surface significantly enhanced the electrical signal change of the graphene-based channel, and reduced the recovery time needed to obtain a normal state of equilibrium. In addition, a simple and efficient soft lithographic patterning process was developed via surface

energy modification for advanced, graphene-based flexible devices, such as gas sensors. As a proof of concept, we demonstrated the high sensitivity of NO<sub>2</sub> gas sensors based on graphene nanosheets. These devices were fabricated using a simple soft-lithographic patterning method, where flexible graphene heaters adjacent to the channel of sensing graphene were utilized to control graphene temperature.

**TF-TuP18 Field-induced Confinement and Quantum Transport in Graphene, Satoshi Moriyama, National Institute for Materials Science, Japan, Y. Morita, Gunma University, Japan, E. Watanabe, D. Tsuya, National Institute for Materials Science, Japan**

**Field-induced Confinement and Quantum Transport in Graphene**

**Satoshi Moriyama<sup>1\*</sup>, Yoshifumi Morita<sup>2</sup>, Eiichiro Watanabe<sup>3</sup>, Daiju Tsuya<sup>3</sup>**

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Graphene consists of a single atomic layer of carbon atoms and has provided a new stage for studying low dimensional physics. The

corresponding energy dispersion adopts the so-called Dirac cone, which leads to a massless Dirac-particle and relativistic quantum physics in a condensed matter. From the application point of view, the ballistic transport and high mobility in graphene make them possible candidates for future nanodevices, such as integrated quantum-dot (QD) devices. However, confining massless Dirac fermions in graphene is difficult due to Klein tunneling and the zero-band-gap electronic structure. Therefore, although attempts have been made to design graphene QD devices, they often suffer from severe design limitations. They basically consist of small QD islands, which confine electrons geometrically, to which narrow graphene-constrictions are connected. We have also demonstrated double QD devices, which exhibits single-electron transport of two lateral QDs coupled in series [1]. In this case, the device performance has been limited due to detailed constriction and edge orientation. It is crucially important to develop other methods of creating graphene nanostructures and control the constrictions.

In this paper, we report an alternative approach to confine the massless carriers in graphene, in which graphene mesoscopic structures are perfectly isolated and metallic contacts are directly deposited onto them without constrictions. We show an experimental demonstration of a magnetic-field-induced quantum confinement in the graphene device. There are several theoretical scenarios for field-induced confinement of massless Dirac fermions, such as the confinement by inhomogeneous magnetic fields. Here, the confinement in our device is induced by both a uniform magnetic field perpendicular to the graphene sheet and an electrostatic surface-potential formed by the metal/graphene junction. Our experimental results indicate that a quantum confinement–deconfinement transition is controlled by the magnetic field [2].

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**TF-TuP19 Enhanced Electrical Properties of Patterned Graphene-Embedded Indium Tin Oxide Transparent Conductive Electrode, Shin Kim, J.K. Kim, J.M. Lee, Sunchon National University, Republic of Korea**

Graphene has attracted a great attention by many researchers in terms of its interesting electrical, optical, and mechanical properties [1]. Furthermore, graphene has showed potential applications such as photovoltaics [2] and optical device [3] as well as transparent electrode[3]. This paper reports the deposition of graphene-embedded indium tin oxide (ITO). Specially, we will show a patterning of graphene which was embedded in ITO will enhance the electrical and optical properties of ITO. ITO films with a thickness of 50 nm were deposited on Corning glass substrate by direct current magnetron sputtering method using an ITO target at room temperature. The graphene samples employed in this work were grown on Cu foils by thermal chemical vapor deposition method. The graphene was transferred to ITO and then patterned with line shape (3um and 12um, respectively) using photoresist. After the dry-etching by using O<sub>2</sub> plasma, ITO was deposited on the patterned graphene again. The sheet resistance and resistivity of the sample were recorded with each fabricating steps. The sheet resistance of ITO film with a thickness of 100 nm showed a 92 ohm/sq. ITO film that the sheet of graphene was embedded in showed a decreased resistance of about 80 ohm/sq. On the other hand, the sheet resistance of ITO films that patterned graphene embedded in was significantly decreased to as low as about 51 and 49 ohm/sq for 3 um and 12 um line shaped graphene embedded ITO, respectively.

In this presentation, we will report the detailed results and mechanism about the enhanced electrical properties of the graphene embedded ITO films.

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**TF-TuP20 Evaluation of Diamond-Like Carbon Films that Enable Observation of Living Cells by Electron Microscopy, Tomotaka Kozuki, Hiroshima International University, Japan, N. Nawachi, Hiroshima Prefectural Technology Research Institute**

In conventional scanning electron microscopy (SEM), the specimen to be observed must be placed in a vacuum. Consequently, observation of living cells has been extremely difficult. In recent years, a method has been proposed to solve this problem and enable observation of samples under atmospheric pressure. In this method, observation in air is accomplished by introducing an electron beam into air from an electron gun located in a vacuum by using silicon nitride (SiN) as an electron transmission film that separates the vacuum and air. However, the resolution is not entirely satisfactory. We therefore noted that diamond-like carbon (DLC) films, in which the primary constituent is carbon, offer both excellent electron transmissivity and sufficient strength to withstand atmospheric pressure.

An electron transmission film that uses DLC was fabricated by forming a DLC film on a silicon (Si) substrate and then etching the Si component from the back side[1]. We compared the electron transmissivity of a DLC

film fabricated by this method with commercial SiN. For a 200-nm-thick DLC film, transmission started at an accelerating voltage of 3 keV, with over 95% of electrons being transmitted at 8 keV. For a SiN film of the same thickness, although transmission started at an accelerating voltage of 4 keV, an accelerating voltage of over 15 keV was required in order to reach a transmissivity of 95%. Furthermore, at an accelerating voltage of 12 keV, the transmissivity was approximately 75% for both a 500-nm-thick SiN film and a 1- $\mu$ m-thick DLC film, showing that a DLC film of approximately twice the thickness of a SiN film could achieve electron transmissivity of 75%.

Next, a 1- $\mu$ m-thick DLC film or a 500-nm-thick SiN film was used as the electron transmission film for observation of a metal mesh by SEM. Although the electron transmissivity was virtually the same at the accelerating voltage of 12 keV, the image obtained when using the DLC film was significantly clearer. This is attributed to the DLC consisting of lighter elements, and thus producing less electron scattering in the film. By using these characteristics of DLC electron transmission films, we succeeded in observing yeast under atmospheric pressure at 10,000 $\times$  magnification by SEM.

By using a DLC film as an electron transmission film, we thus succeeded in obtaining clearer images at lower accelerating voltages as compared with existing electron transmission films. Taken together, the results of this study suggest tremendous potential for the use of DLC films in medicine, particular for biopsy.

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**TF-TuP21 Chemistry of Active Oxygen in RuO<sub>x</sub> and Its Influence on the Atomic Layer Deposition of TiO<sub>2</sub> Films, Woojin Jeon, W. Lee, C.H. An, M.J. Chung, C.S. Hwang, Seoul National University, Republic of Korea**

Atomic layer deposition (ALD) is a highly intriguing thin-film growth technique with self-regulating and self-terminating properties due to the saturated chemical reactions between the adsorption sites and the chemically adsorbing precursor molecules. In such ALD processes, the substrate plays a crucial role by taking part in the ALD-specific chemical reactions. The surface of the substrate must provide the chemical adsorption sites, which would anchor the incoming metal or non-metal precursors via the ligand exchange reactions. There are other cases, however, where the oxygen ions (or atoms) inside the bottom layer film play the crucial role in the film growth. Typical example is Ru (and RuO<sub>2</sub>), which are the material of choice as the capacitor electrode in futuristic DRAM. Recent reports on the inducing of rutile phase formation in the atomic layer deposition (ALD) of TiO<sub>2</sub> films, which have the highest dielectric constant among the binary dielectric oxides, by adopting Ru or RuO<sub>2</sub> as the bottom electrode invokes an even higher interest in this material. While both Ru and RuO<sub>2</sub> electrode have similar electrical properties, the initial stage of deposition of TiO<sub>2</sub> film by ALD exhibited quite different behavior on each substrate due to their different oxygen contents. In this study, the initial growth behavior of ALD TiO<sub>2</sub> film on Ru and RuO<sub>2</sub> substrate with various oxygen contents has been investigated in a greater detail, which has not been explored previously. Ru, RuO<sub>x</sub> (x ~ 1) and RuO<sub>2</sub> films were grown by the cycling pulsed chemical vapor deposition process at a substrate temperature of 230 °C using RuO<sub>4</sub> and H<sub>2</sub>(5%)/N<sub>2</sub>(95%) as the Ru-precursor and reducing agent. The phase control was achieved by controlling the injection time of H<sub>2</sub>(5%)/N<sub>2</sub>(95%) gas for the given RuO<sub>4</sub> injection condition.

It was found that the growth per cycle of TiO<sub>2</sub> at the initial growth stage was drastically increased on RuO<sub>x</sub> (RuO<sub>2</sub>/Ru mixture) compared to Ru and even RuO<sub>2</sub>, although it has been reported that higher oxygen content film (RuO<sub>2</sub>) promotes the initial growth of TiO<sub>2</sub>. This is attributed to the drastic increase in the chemical activity of oxygen in the mixture film of RuO<sub>2</sub>/Ru. The catalytic decomposition of RuO<sub>2</sub> with the help of Ru in the film played the crucial role for the increase in the active oxygen. While RuO<sub>2</sub> and Ru mostly retained their structures during the ALD of TiO<sub>2</sub> or chemical etching using O<sub>3</sub> gas, the RuO<sub>x</sub> film, which was composed of 56% RuO<sub>2</sub> and 44% Ru, drastically changed its phase composition during the ALD of TiO<sub>2</sub> at 250 °C and became almost Ru. Other chemical effects depending on the chemical composition and phase structure were also examined in detail.

**TF-TuP22 Effects of Double Active Layer and Acetic Acid Stabilizer on the Electrical Properties of Solution-processed Zinc Tin Oxide Thin Film Transistor., Jihun Shin, S.J. Kim, S.S. Ha, Y.J. Im, C.H. Park, M.S. Yi, Pusan National University, Republic of Korea**

We investigated the effect of double active layer and acetic acid stabilizer for zinc tin oxide thin film transistor (TFTs) fabricated using solution processes.

Double active layer was composed of two layers made by ZTO solution doped with different Sn concentration (Sn 30 atomic % or Sn 60 atomic %). ZTO solutions were synthesized by dissolving zinc acetate dehydrate and tin chloride dehydrate which were dissolved in 2 different stabilizer

solutions. AA solution was prepared with 2-methoxyethanol added with acetic acid, where ME solution was prepared with 2-methoxyethanol added with mono-ethanolamine. Thus the AA-ZTO films and ME-ZTO films represent ZTO active layer films formed from AA solution and ME solution, respectively.

The bottom-gate TFTs were fabricated on highly doped n-type silicon wafer which is covered with 200nm SiO<sub>2</sub> layer as a gate insulator. Bottom active layer of ZTO film was deposited on the gate oxide layer by spin-coating the solution at room temperature, drying at 300 °C for 10 min, and the top active layer of ZTO film was made on the bottom ZTO film by same method and then annealing at 500 °C for 60 min. Fig. 1 shows the schematics of the double active layer ZTO TFT.

By adding acetic acid into the stabilizer solution instead of commonly used mono-ethanolamine, electrical performance of ZTO TFTs is enhanced. The XPS and TG-DTA(thermogravimetry differential thermal analysis) data shown in Fig. 2 and 3, have demonstrated that acetic acid plays a role in lowering decomposition temperature and reducing hydroxyl groups in the film.

By using double active layer (bottom layer: Sn 60 at. %, top layer: Sn 30 at. %) in ZTO TFTs, the electrical performance is enhanced. We demonstrated that the bottom active layer supplied electron carriers easily from high Sn concentration, and the top ZTO layer suppressed the leakage current of TFTs because it has relatively lower carrier concentration than the bottom ZTO layer.

The best performances were obtained at Sn concentration of 60 at. % in bottom ZTO layer and 30 at.% in top ZTO layer with the added acetic acid as a stabilizer, where the ZTO TFT exhibited an on/off ratio of 1.1 $\times$ 10<sup>9</sup>, a saturation mobility of 5.04 cm<sup>2</sup>/V·s, a subthreshold slope of 0.11 V/decade, and a threshold voltage of 1.6 V. Fig. 4 depicts the transfer curves of the TFTs and the summarized electrical parameters of the ZTO TFTs were shown in Table 1.

**TF-TuP23 Effect of Ge Concentration on Electrical Performance of Ge-doped InZnO thin-film transistor, Yongjin Im, J.H. Shin, S.J. Kim, S.S. Ha, C.H. Park, M.S. Yi, Pusan National University, Republic of Korea**

We fabricated amorphous oxide semiconductor thin-film transistors (TFTs) using GeO<sub>2</sub>-doped InZnO (Ge-IZO) thin films as active-channel layers. The Ge-IZO thin films were deposited at room temperature by radio-frequency (RF) magnetron co-sputtering, and then annealed in air for 1 h at 300°C. Some processing parameters such as sputtering oxygen partial pressure [O<sub>2</sub>/(Ar + O<sub>2</sub>)] and sputtering power for GeO<sub>2</sub> target were changed to investigate what was the optimal amount of Ge in the Ge-IZO active layer.

The cross-sectional schematic of Ge-IZO TFT and a FE-SEM image of Ge-IZO thin film studied in this paper are shown in Fig. 1, and the electrical performance of Ge-IZO TFT is compared with IZO TFT in Fig. 2.

A small concentration of Ge added to IZO by co-sputtering with less than 5W of GeO<sub>2</sub> target power enhanced the saturation mobility  $\mu_{sat}$ . The decrease of  $\mu_{sat}$  at high power of GeO<sub>2</sub> target in Fig. 2 was caused by the increased disorder in case of the high power of GeO<sub>2</sub> target. Threshold voltages (V<sub>th</sub>) in Fig. 2 increases with increase in GeO<sub>2</sub> target power until 20W; thereafter, it decreases. This result should be inversely related to the carrier concentration, which indicates that a small concentration of Ge can lead to retention of its strong bonding with oxygen, thereby suppressing the excessive oxygen vacancies. This is the reason why V<sub>th</sub> increases. Higher Ge-concentration can lead to the greater disorder and this explains why V<sub>th</sub> decreases with increase in Ge concentration.

The device performance was better when low concentration of Ge is incorporated to IZO than with pure IZO or high Ge concentration. In order to optimize the electrical properties of Ge-IZO TFTs, we tried to adjust the processing parameters and the best Ge-IZO TFT was obtained at a co-sputtering oxygen partial pressure of 2% and GeO<sub>2</sub> target power of 10 W.

The fabricated Ge-IZO TFT exhibited an on/off ratio of 3.0 $\times$ 10<sup>7</sup>, a saturation mobility of 13.6 cm<sup>2</sup>/V·s, a subthreshold swing of 0.98 V/dec, and a threshold voltage of -0.8 V. XPS and XRD analyses of Ge-IZO films were performed to investigate the binding energies of atoms in Ge-IZO films and the crystallinity of the films, and a 90% transmittance of visible light was achieved, which makes the technology useful for transparent devices.

**TF-TuP24 Active Multiband Terahertz Metamaterial Spatial Filters Based on Vanadium Dioxide Thin Films, Han-Cheol Ryu, Sahmyook University, Republic of Korea, J.-H. Shin, K.H. Park, ETRI**

This work presents the design, fabrication and terahertz performance of active multiband metamaterial spatial filters based on vanadium dioxide (VO<sub>2</sub>) thin films. VO<sub>2</sub> thin films were deposited on Al<sub>2</sub>O<sub>3</sub> (0001) substrates by the pulsed laser deposition method. Epitaxial relations between VO<sub>2</sub> thin films and Al<sub>2</sub>O<sub>3</sub> (0001) substrates were investigated using X-ray diffraction measurement and transmission electron microscopy observations. The



multiband terahertz metamaterial spatial filters, which are artificial electromagnetic structures, can manipulate electromagnetic response at desired frequency bands. They were designed by electromagnetic simulator and fabricated on VO<sub>2</sub> thin films which are phase transition materials due to their insulator-metal transition at a critical temperature. The terahertz characteristics of the fabricated active filters were controlled by electric bias or temperature variation. The tunable frequency responses of the devices were measured by using terahertz time-domain spectroscopy (THz-TDS) system. The measured tunable characteristics of the active terahertz filters based on VO<sub>2</sub> thin films clearly show the possibility for the various tunable terahertz applications such as modulators, filters, and sensors.

**TF-TuP26 Enhancement of SiO<sub>2</sub>/4H-SiC Interface Properties using ALD Oxides and Nitridation,** *Changhyun Kim, S. Lee, H. Lee, H. Kim, H.J. Kang, H.J. Kim*, Seoul National University, Korea, Republic of Korea  
4H-SiC is a promising wide band gap material which has excellent properties such as high breakdown voltage, high thermal conductivity, and high saturation drift velocity. These characteristics enable 4H-SiC to be used in difficult environments for Si such as processes require high power, high current, high temperature. It also has an advantage in fabrication process because of its native SiO<sub>2</sub> from thermal oxidation. However, carbon components are inevitably produced during oxidation, causing high SiO<sub>2</sub>/SiC interface state density (D<sub>it</sub>) and low channel mobility. The nitridation using NO or N<sub>2</sub>O gas is an effective way to lower D<sub>it</sub> and near interface trap density of a SiO<sub>2</sub>/4H-SiC interface.

In this work, we prepared the atomic layer deposited (ALD) SiO<sub>2</sub> with NO post oxidation annealing (POA) to avoid interface oxidation and improve interface properties. We also compared electrical properties of NO POA treated ALD SiO<sub>2</sub> with thermally grown oxides with/without NO POA. The NO POA treated ALD SiO<sub>2</sub> showed much lower D<sub>it</sub> than thermally grown oxides. Also, the metal-oxide-semiconductor (MOS) field effect transistor (FET) with the ALD SiO<sub>2</sub> showed high field effect mobility, especially in the high electric field region.

But these methods could not reach the sufficient passivation of the interface traps due to reoxidation by oxygen source of NO gas. Therefore, we employed thin ALD SiO<sub>2</sub> layer with NH<sub>3</sub> POA for nitridation without reoxidation. Because the NH<sub>3</sub> POA oxide had low breakdown field (E<sub>b</sub>), we adopted a stacked structure of ALD SiO<sub>2</sub> with NH<sub>3</sub> POA and ALD SiO<sub>2</sub> to exclude oxidation and to improve E<sub>b</sub>, respectively. Inert gas annealing or ozone treatment were used to reduce the defects of upper as-deposited SiO<sub>2</sub>. Oxygen vacancies, a major defect of as-deposited oxide, were effectively reduced by the O<sub>3</sub> treatment. The ALD SiO<sub>2</sub> with NH<sub>3</sub> POA lowered C-V hysteresis and increased the slope of C-V curve, indicating that it reduces the interface defects. It also had low D<sub>it</sub> which might be caused by the suppression of reoxidation. The O<sub>3</sub> treatment increased E<sub>b</sub> effectively, but it did not reach E<sub>b</sub> of thermally grown oxide yet.

In conclusion, ALD oxides with proper nitridation process improved the field effect mobility of MOSFET more effectively than thermal one through decreasing D<sub>it</sub> induced by carbon component at the SiO<sub>2</sub>/4H-SiC interface. The NH<sub>3</sub> POA instead of NO POA showed low D<sub>it</sub> by suppressing of reoxidation, but low E<sub>b</sub> problem remains. The O<sub>3</sub> treated upper ALD SiO<sub>2</sub> increased E<sub>b</sub> maintaining low D<sub>it</sub>.

**TF-TuP27 Molecular Beam Epitaxy and Characterization of Cubic-Phase InN and GaN Films,** *Maximo Lopez-Lopez*, Physics Department, Cinvestav-IPN, Mexico

Group-III nitrides have become one of the most important semiconductor materials in the field of optoelectronic and microelectronic devices. Recently, great interest in III-nitrides with cubic phase has risen due to the absence of built-in electric fields, which can limit the performance of devices. However, the cubic-phase in III-N semiconductors is metastable and can only be grown in a narrow window of conditions. Under non-optimum conditions phase mixing between the metastable cubic (c) and stable hexagonal phases (h) may occur. In this work we present the growth of c-InN films on GaAs(001) substrates using conventional molecular beam epitaxy (MBE) and migration enhanced epitaxy (MEE) techniques. Also, we presented the growth of c-GaN films on GaAs(001) substrates by conventional MBE, using during the nucleation of c-GaN an As overpressure at different substrate temperatures. In order to promote the formation of c-InN, an InN nucleating layer by alternated deposition of In and N was carried out at a growth temperature (T<sub>g</sub>) of 380 °C. After the growth of the nucleating layer, c-InN films were grown using one of the two methods: 1) conventional MBE growth, where the growth surface is exposed simultaneously to both elements In and N and, 2) MEE growth, that proceeds by alternated periods of In and N of 5 s each one. Employing these two methods, different samples were prepared by varying T<sub>g</sub> and the flux of In atoms. On the other hand, we found that the use of an As overpressure during the nucleation of c-GaN plays a very important role in the enhancement of crystalline quality and surface morphology of GaN

films. We present structural and morphological properties of the films and the dynamics of growth analyzed by reflection high-energy electron diffraction (RHEED). We achieved to grow InN and GaN with cubic phase, as confirmed by RHEED, X-ray diffraction and transmission electron microscopy (TEM). For the growth of c-InN the better structural properties and higher cubic phase purity were obtained by the MEE technique. For the growth of c-GaN, we found that the films nucleated at 600 °C present low roughness and the best crystalline quality with a small incorporation of the hexagonal phase, which was identified by reciprocal space maps (RSM) and TEM.

† This work was partially supported by SENER-CONACYT No. 151076

**TF-TuP28 Degradation of Phosphorescent Organic Light Emitting Material by UV Exposure for Cathode Sputtering Process,** *Chan-Jae Lee*, Korea Electronics Technology Institute (KETI), Republic of Korea, *E.J. Um, M.G. Kwak*, Korea Electronics Technology Institute (KETI)

Organic light emitting diodes (OLEDs) have attracted great attention due to its advantages such as light weight, short response time, low power consumption, wide color gamut, wide viewing angle and high brightness in the area of display and lighting.

OLEDs have two electrodes, anode and cathode. Anode is fabricated by sputter and photolithography process but the cathode is deposited by thermal evaporation method with shadow mask. Thermal evaporation process with large size mother glass is difficult to obtain the uniform and high quality thin film. So to improve size and quality of OLED, various sputtering methods for cathode have been suggested.

Sputtering is a process whereby atoms are ejected from a target material due to bombardment of the target by energetic particles. This process can make the prolonged ion, plasma bombardment of a material and ultra violet (UV) radiation. Generally, organic materials are known as the very weak materials under plasma environment. Especially, bombardment has been pointed out a critical issues as it penetrates into the organic layer and breaks off the bonding of molecules. So, some researchers have suggested a facing target sputtering method that is the two targets are facing and substrate is placed in the vertical direction with two facing targets. So it is possible to reduce the damage of organic layer on the substrate, since the direction of the energetic ions can be changed.

Plasma also creates a cause UV radiation, which its influence against organic material is well known as make the quantum efficiency of organic materials to deteriorate. But in the facing target sputtering method, UV influence against emissive organic material is not known clearly yet.

In this study, we analyzed the degradation of phosphorescent emissive materials by UV exposure for cathode sputtering process. To make the environment of UV exposure, we placed the sample in RF sputtering system. And sample with phosphorescent emissive material, 1,3-Bis(N-carbazolyl)benzene (mCP) and tris(2-phenylpyridine)iridium (Ir(ppy)<sub>3</sub>) were placed with different directions and distances from Al target. Farther the distance in the vertical direction of the target, damage is lower by UV. After Al deposition with 100nm thick, PL intensity of organic material by direction deposition is decreased by 70% compared to the sample without Al. But sample that is placed away from the target as much as 1.5 times of the length of the target and in vertical direction to target was reduced by 20% PL intensity. Also we analyzed the critical wavelength of UV radiation against phosphorescent emissive material mCP and Ir(ppy)<sub>3</sub>.

**TF-TuP30 Initial Stage Growth of GaAsSe layers on Sb-terminated Si(110) Surfaces by Metal-Organic Molecular Beam Epitaxy,** *M. Sato, Y. Suzuki, K. Miyazawa, K. Obara, Katsuhiko Uesugi*, Muroran Institute of Technology, Japan

We report on the heteroepitaxial growth of GaAsSe layers on Si(110) substrates by metal-organic molecular beam epitaxy (MOMBE). The growth process of GaAsSe was characterized by reflection high energy electron diffraction (RHEED), atomic force microscopy (AFM), and transmission electron microscopy (TEM).

The dilute HF treated Si(110) substrates were thermally cleaned at 550-600°C for 20 min in a flow of the precursor trisdimethylaminoarsenic (TDMAAs). Atomically flat Si(110) surfaces were successfully fabricated at substrate temperatures as low as 600°C under TDMAAs pressure. After the growth of 10nm-thick GaAsSe layers on TDMAAs-treated substrates, the surfaces were covered with high density dot structures, presumably due to the Stranski-Krastanov (S-K) growth mode. The diameter and density of GaAsSe dots were about 40nm and 8x10<sup>10</sup> cm<sup>-2</sup>, respectively. As the GaAsSe thickness increases, the formation of giant dots and polycrystalline structures due to coalescence of S-K dots was observed. Then we investigate the influence of V/III flux ratio and the effect of Sb surfactant on the initial growth process of GaAsSe on Si(110) substrates. Polycrystallization of GaAsSe layers has been suppressed using the small V/III ratio of about 2. Furthermore, trisdimethylaminoantimony (TDMASb)

treatment of As-terminated Si(110) substrate surfaces at 520°C greatly reduces the three-dimensional island growth due to the surfactant effect of Sb on the Si(110) surface.

**TF-TuP31 Characterization of Diamond-Like Carbon Prepared by High Power Impulse Magnetron Sputtering.** *Norio Nawachi*, West Region Industrial Research Center, Hiroshima Prefectural Technology Research Institute, Japan, *K. Itoh, Y. Isagi*, West Region Industrial Research Center, Hiroshima Prefectural Technology Research Institute, *K. Okamoto*, Toyo Advanced Technologies Co., Ltd., Japan, *T. Nakatani*, Research Institute of Technology, Okayama University of Science, Japan

Diamond-like carbon (DLC) has been considered as a coating for medical devices due to its biocompatibility. In particular, DLC coatings for dental implant made by titanium base alloy are useful as a means of providing high-hardness and a low-friction coefficient. Usually DLC films are deposited by cathodic arc (CA), plasma-enhanced chemical vapor deposition (PECVD), direct current (DC) or radio-frequency (RF) magnetron sputtering (MS). However, the problem is that DLC films deposited by CA show intrinsic growth defects (droplets). On the other hand, DLC films deposited by DC or RFMS can exhibit smooth surfaces, but adhesion strength of the films is a challenging issue [1, 2]. In recent years, a new magnetron sputtering technology named high power impulse magnetron sputtering (HiPIMS) has emerged. HiPIMS allows production of droplet free highly ionized metal flux generated from a sputter source [3, 4].

In this work, the characteristics of DLC films deposited by HiPIMS have been investigated. DLC films were prepared on silicon (Si) by HiPIMS and DCMS for comparison. Depositions were performed from a graphite target (200mm in diameter) operated at maximum power of 3 kW and at chamber pressure of 0.5 Pa. The same experimental arrangement was used for the DCMS depositions. The DLC films were analyzed by various methods.

In the HiPIMS discharge, the target voltage and peak current were approximately -900V and 200 A, respectively, at a repetition frequency of 1 kHz with a pulse width of 50  $\mu$ s. The deposition rate in HiPIMS was approximately 50 % lower (23 nm/min) than that in DCMS. Mechanical properties of DLC films prepared by HiPIMS and DCMS will be presented and discussed.

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**TF-TuP32 UHV-STM Study on the Formation of Si(3 3 7)-4x1.** *Q. Quan, S. Song, Z. Zhang, L. Li, Yong-Zhe Zhu*, Department of Physics, Yanbian University, Yanji city, 133000, China

In the process of one-dimensional metal wire growth on the Si(5 5 12) surface with ultra-high vacuum scanning tunneling microscopy, Si(3 3 7)-4  $\times$  1 structure is discovered. It is found that Si(3 3 7)-4  $\times$  1 is a ultra stable structure with low defect density. It can be expected as a good template for nanostructure growth. However, up to now, there is no routine method to fabricate Si(3 3 7)-4  $\times$  1. Therefore, it is necessary to study the formation reasons of Si(3 3 7)-4  $\times$  1 surface and then fabricate this structure. The possibility is considered in two aspects: Firstly, is it induced only by high temperature annealing? Secondly, is it due to the residual C existed in the UHV-STM chamber? For this purpose, results from four experimental studies are analyzed: One is heating several kinds of Si(5 5 12) vicinal surface at high temperatures, and the others are adsorbing Ge, C<sub>2</sub>H<sub>2</sub>, and O<sub>2</sub> on Si(5 5 12)-2  $\times$  1 surface, respectively. The orientation dependence of this kind of structural phase transition from Si(5 5 12)-2  $\times$  1 to Si(3 3 7)-4  $\times$  1 has been studied as well. To achieve this structural phase transition, an energy barrier needs to be overcome, and a large amount of atoms must be moved to meet the orientation difference, which is performed by surface melting process via high temperature annealing. This phase transition has the orientation dependence but is not induced by the adsorption of carbon. This research was supported by the National Natural Science Foundation of China (Grant No. 10964014).

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**TF-TuP33 Etch Characteristics of Co<sub>2</sub>MnSi Thin Films in CH<sub>4</sub>/O<sub>2</sub>/Ar Plasmas.** *SuMin Hwang, A. Garay Dixon, J.H. Choi, C.W. Chung*, Inha University

In the semiconductor memory device field, for the next generation it is a big challenge to develop a memory device that has fast speed of read and write, high density of memory storage and non-volatility. Nowadays, Magnetic random access memory (MRAM), one of the possible candidates for non-volatile random access memory (NVRAM), has a received great deal of attention due to its several advantages.

Magnetic random access memory (MRAM) is a hybrid technology between a spintronic device and standard silicon-based microelectronics. Compared to commercial memory devices such as DRAM, SRAM and flash memory, based on charge storage, MRAM devices store data by employing the magnetoresistance effect. MRAM consists of a magnetic tunnel junction (MTJ) stack and a complementary metal-oxide semiconductor (CMOS). MTJ stack is an important part of the MRAM and it is composed of various magnetic materials, metals, and a tunneling barrier layer.

The etching of magnetic materials such as NiFe, NiFeCo, CoFe, CoFeB and FePt using halogen containing gas have been widely researched. However, halogen gases chemistries tend to produce non-volatile etch by products that can cause the corrosion of the magnetic materials after etching. Recently, Co<sub>2</sub>MnSi co-heusler alloy was used as a magnetic material because of high spin polarization and a high Curie temperature (~985K). Furthermore, several researches have reported that the etching of magnetic materials by C, H, O containing gases can produce a vertical etch profile with no post etching redeposition. Therefore, the etch characteristics of Co<sub>2</sub>MnSi thin films using C, H, O containing gas should be developed.

In this study, the etch characteristics of Co<sub>2</sub>MnSi thin films have been investigated in CH<sub>4</sub>/O<sub>2</sub>/Ar gas mixtures using an inductively coupled plasma reactive ion etching (ICPRIE). TiN thin films were applied as a hard mask to enhance the etch selectivity. The etch rates were obtained using surface profilometer and etch profiles were observed by using the field emission scanning electron microscopy (FESEM). The condition of plasma during process was employed by optical emission spectroscopy (OES).

**TF-TuP36 Crystallization of Biodegradable Poly-[(R)-3-Hydroxybutyrate] Ultrathin Films revealed by Surface-sensitive X-ray Diffractions: Effect of Small Amount of Biodegradable Poly(L-lactide)s with Different Molecular Weights.** *Naotaka Torimoto, N. Shimatani, R.R. Kumetha, I. Takahashi*, Kwansai Gakuin University, Japan

Biodegradable polymers synthesized by bacteria are environmental-friendly material. Poly-[(R)-3-hydroxybutyrate] (PHB) is one of the most intensively studied biological polymers and is also used to many applications. We investigated a new confinement effect of biodegradable poly(L-lactide) (PLLA) on crystallization of PHB ultrathin films with surface-sensitive X-ray diffractions in which PLLA with large molecular weight can reduce the crystallinity of PHB thin films effectively, although its mechanism is still not fully-understood. [1] In the present study, we expand our research in a wider range of molecular weight of PLLA as well as that of PHB, since controlling crystallinity, orientation of crystallographic axes with respect to the films surface and surface morphology of PHB thin films should be a key to controlling physical properties including thermal plasticity, brittleness and piezoelectric constant of PHB, that is quite favorable for a wider range of applications. Grazing incident X-ray diffraction (GIXD) and X-ray reflectivity (XR) are used to estimate degree of crystallization, thickness, electron density and surface roughness of polymer blend of PHB and PLLA spin-coated films deposited on silicon 100 wafers isothermally. Molecular weights of PHB were 1,000 and 650,000 g/mol, and those of PLLA were 2,000, 50,000, 100,000 and 300,000 g/mol, respectively for films with typical thicknesses of 30 nm.

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Keywords: biological polymer, polymer blend, crystalline polymer, X-ray surface diffraction, surface and thin films

**TF-TuP37 P3HT-based Multilayer Ultrathin Films Characterized with Surface-Sensitive X-Ray Scatterings –temperature and substrate dependence of crystalline structure-** *Yusuke Shima, R. Iseiki, J. Takemoto, I. Takahashi*, Kwansai Gakuin University, Japan

Regioregular poly(3-hexylthiophene) (P3HT) has attracted significant interest as one of the promising materials for organic field effect transistors

(OFETs) and organic photovoltaics (OPV) to behave a p-type semiconductor with high charge mobility due to its high crystallinity. The organic thin film devices basically consist of conductive polymer films and insulating polymer films. However, maintaining well-defined interface structures is difficult when the temperature of confined system is raised by Joule's heat. Therefore, any information on temperature dependence of interface structure of organic thin films is very important for applications. We study molecular chain orientations, crystallinity and surface morphology of P3HT thin films prepared on several different substrates at high temperatures with grazing incident X-ray diffraction (GI-XD), X-ray reflectivity (XRR), grazing incident wide angle X-ray scattering (GI-WAXS) and atomic force microscopy (AFM). The substrate we have investigated are SiOH, SiO<sub>2</sub>, C surface of SiC(0001) and Si surface of SiC(0001), and poly(4-vinylphenol) (PVPh). We found that substrate greatly affects the crystal growth of P3HT even for films thicker than 25 nm. Keywords: Poly(3-hexylthiophene) (P3HT), X-ray surface scattering, thin film, conductive polymers

**TF-TuP38 Electrical Transport Properties and Photodetection Performances of n-Type NC-FeSi<sub>2</sub>/i-UNCD/a-C/p-Type Si Heterojunction Photodiodes at Low Temperatures, *Nathaporn Promros*, King Mongkut's Institute of Technology Ladkrabang, Thailand, *K. Hanada*, Kyushu University, Japan, *P. Sittimart*, King Mongkut's Institute of Technology Ladkrabang, Thailand, *M. Takahara*, *T. Hanada*, *L. Chen*, *T. Yoshitake*, Kyushu University, Japan**

n-Type nanocrystalline iron disilicide (NC-FeSi<sub>2</sub>)/intrinsic ultrananocrystalline diamond/amorphous carbon composite (i-UNCD/a-C)/p-type Si heterojunctions have been successfully fabricated and their current - voltage characteristics were measured at low temperatures range from 300 down to 60 K. i-UNCD/a-C and n-type NC-FeSi<sub>2</sub> layers were deposited by coaxial arc plasma deposition and pulsed laser deposition, respectively. We investigated their carrier conduction mechanism on the basis of thermionic emission theory and their near infrared photodetection using a 6 mW, 1.31 μm laser. The predominant conduction mechanism through the heterojunctions at 300 - 200 K and 200 - 60 K are recombination and tunneling processes, respectively. At 60 K, the ratio between photocurrent and dark current became three orders of magnitudes. The detectivity is  $8.8 \times 10^{11}$  cmHz<sup>1/2</sup>/W at -1 V, which is comparable with the values of existing NIR photodiodes at the same temperature.

**TF-TuP40 The Effects of Plating Applied on Thin Film Process to the Stress Analysis of Silicon Substrate by Simulation, *Sang-Hoon Lee*, *C. Park*, Yeungnam University, Republic of Korea**

Crystalline silicon is a great, low cost, cheap material and the most widely used for solar cells application. Crystalline silicon solar cells are modules built using crystalline silicon (c-Si), developed from the microelectronics technology industry. Crystalline silicon solar cells have high efficiency. To reduce the cost of manufacturing process, the plating process is analyzed by using the simulation of stress applied on the silicon substrate. In this study, the occurring of metal-silicon interface was modeled to predict the quantitatively of stress affected inside the silicon substrate. We predicted through the changing of simulation what the factors will give a large effect on the value of the results. The stress characteristic factor was found as major factor of the substance to be plated. Mechanical properties of plating materials were changed as density, Young's modulus, and Poisson's ratio. Thermal properties are not considered as parameters because the plating system is became the progress to isothermal process. The density and Poisson's ratio are not expected to give greater effecting on the stress, so Young's modulus is main factor. It was affected sensitivity on the stress of silicon substrate. Controlling the Young's modulus can be adjusted stress in the silicon substrate.

# Tuesday Afternoon, December 9, 2014

## Energy Harvesting & Storage

Room: Lehua - Session EH-TuE

## Batteries, Capacitors & Storage Materials

Moderator: Stacey Bent, Stanford University, USA

5:40pm EH-TuE1 **Electrochemical Deposition of Organic-inorganic Composites for Supercapacitors**, M. Bai, Xiaoxia Liu, Northeastern University, China

### Electrochemical Deposition of Organic-inorganic Composites for Supercapacitors

Ming-Hua Bai, Xiaoxia Liu\*

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Electrochemical capacitors (supercapacitors) are widely recognized as an important class of energy storage devices. Development of high performance supercapacitors is highly desirable to meet the increasing demand for energy storage devices. Conducting polymers, including polyaniline (PANI) and polypyrrole (PPy) have promising applications in a variety of technological fields, including supercapacitor. One-dimensional (1D) growth control of conducting polymer, directing to polymer nanofibers, has aroused great interest because an ordered arrangement of the polymer chains favours higher conductivity and better performance in charge storage. The growth of nanofibers is known to be intrinsic to PANI, however heterogeneous nucleation on the initially-formed PANI nanofibers would result in irregularly-shaped PANI particles. The suppression of this overgrowth on the surface active sites of initially-formed PANI nanofibers has been achieved by some chemical polymerization methods, including aqueous/organic interfacial polymerization, rapidly-mixed reactions, which led to the formation of nanofibrous PANI. However, only nonfibrous, granular powder PPy can be yielded by these methods since fibrillar structure is not intrinsic for PPy and so it is very hard for PPy to grow one dimensionally. Electrochemical deposition is very attractive due to the ability to anchor the product onto substrate materials in the desired quantity, shape and size in one single step, enabling the final application to be performed easier.

In this work, we will present the one-dimensional growth of conducting polymer through electrochemical co-deposition with inorganic oxide. Pseudocapacitive properties of the obtained composite films are studied as well. The local environment at the electrode surface for polymerization was tried to be controlled by the electrodeposition of inorganic oxide from their precursors like  $\text{VO}^{2+}$ , in which process proton may be released and some of the anodic charges may be consumed. Composites with improved electrochemical performance were obtained through 1D growth control of the conducting polymer, leading to increased surface area and organic-inorganic synergistic effect.

### Acknowledgements

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6:20pm EH-TuE3 **Soft X-ray Operando Spectroscopy for Polymer Electrolyte Fuel Cells and Li Ion Batteries**, Masaharu Oshima, The University of Tokyo, Japan **INVITED**

In order to meet strong demands for electronic structure analysis of green devices, namely 1) power generation devices such as polymer electrolyte fuel cells (PEFC), 2) power efficient devices such as graphene FET and Resistive RAM, and 3) energy storage devices such as Li ion battery (LIB), we have developed two soft X-ray nano-spectroscopy systems at the Spring-8 University-of-Tokyo (UT) outstation. One is *operando* soft-X-ray emission spectroscopy (XES)<sup>1)</sup> for PEFC cathode catalysts and Li ion battery, and the other is scanning photoelectron microscopy with 70 nm spatial resolution<sup>2)</sup>, which has been used to analyze graphene FET and organic FET *in operando*.

First, we analyzed electronic structures of carbon-related catalysts alternative to Pt for PEFC in order to elucidate the oxygen reduction reaction (ORR) mechanism. We prepared metal phthalocyanine-based carbon catalysts with 1-2% nitrogen and less than 1 % of Fe for PEFC. Photoelectron spectroscopy and first principles calculation revealed that zigzag edge carbons with neighboring graphite-like nitrogen are ORR active sites. Based on these analyses, we fabricated fuel cell stack for PEFC which showed comparable performance to Pt catalysts. Furthermore, we

have taken *operando* XES spectra of Fe 2p-3d transition during power generation, revealing that Fe impurity may act as an ORR catalyst<sup>3)</sup>.

Next, we analyzed the change of Fe 3d states accompanied with the Li intercalation/ deintercalation process by resonant photoemission spectroscopy. Since the battery voltage should reflect the energy difference between Li 2s and Fe 3d down-spin state, we measured the change in Fe 3d down-spin states for  $\text{LiFePO}_4$  (3.4V) and  $\text{Li}_2\text{FeP}_2\text{O}_7$  (3.6V) and found that 0.2 eV shift from  $\text{PO}_4$  to  $\text{P}_2\text{O}_7$  poly-anions directly reflects battery voltage. Furthermore, the *operando* XES method was applied to cathode materials  $\text{LiMn}_2\text{O}_4$  in Li ion battery to reveal the electronic structure change of Mn with changing OCV (open circuit voltage). It was demonstrated that the  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  states are successfully distinguished using high-energy-resolution resonant XES<sup>4)</sup>. Multiplet calculations<sup>5)</sup> have been performed to determine the electronic structures in comparison with *operando* XES spectra for both Fe and Mn chemical states in FC and LIB, respectively.

This work has been done in collaboration mainly with Y. Harada, H. Niwa, T. Aoki, Y. Nabae, Y. Nanba and D. Asakura.

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7:40pm EH-TuE7 **Water as Promoter and Catalyst in Di-Oxygen Reactions at Aqueous and Organic Electrified Interfaces**, Nenad Markovic, Materials Science Division, Argonne National Laboratory, Argonne, IL 60439, USA

Understanding the role of water in di-oxygen electrochemistry at atomic and molecular levels is the key to driving technological innovations that are urgently needed to deliver reliable, affordable and environmentally friendly energy [1-4]. Surprisingly, all previous studies have treated the water molecule as reactants needed to satisfy the stoichiometry of the reaction, rather than as vital hydrogen-donor molecules that can promote the rates of transformation of oxygen intermediates to final products. It is the impact of water on di-oxygen electrochemistry that constitutes the focus of our paper. First, we introduce a universal model that is capable of rationalizing, and ultimately understanding, electrocatalysis of the oxygen reaction in aqueous media, as well as in Li-O<sub>2</sub> electrochemistry in organic environments. The model is based on the formation of  $\text{HO}_{ad}\cdots\text{H}_2\text{O}$  (alkaline) and  $\text{LiO}_2\cdots\text{H}_2\text{O}$  (organic solvents) complexes that place water in a configurationally favorable position for proton transfer to  $\text{O}_2^-$  and  $\text{HO}_2^-$  intermediates that are formed on neighboring active sites. We propose that monometallic electrodes modified by omnipresent oxygenated spectators such as  $\text{OH}_{ad}$  and  $\text{LiO}_2$  are, in fact, bifunctional catalysts capable of facilitating different parts of the overall multi-electron process: providing adsorption sites for the formation of complexes as well as bare metal sites to facilitate the electron transfer to  $\text{O}_2$ ,  $\text{O}_2^-$  and  $\text{HO}_2^-$ .

Moreover, we demonstrate that water plays a dual role in Li-O<sub>2</sub> electrochemistry, acting simultaneously as a promoter in the production of  $\text{Li}_2\text{O}_2$  and also as a *catalyst*, regenerating itself through a sequence of steps that include the recombination of  $\text{H}^+$  and  $\text{OH}^-$  back to water. Water acting as a catalyst has not, to the best of our knowledge, previously been reported for any electrochemical reaction.

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8:20pm EH-TuE9 **Electrochemical Reduction of CO<sub>2</sub> as a Way to Store Energy from Intermittent Sources**, Paul Kenis, University of Illinois at Urbana-Champaign

The desire to increase the utilization of sustainable energy sources such as solar and wind is hampered by their intermittent nature. Large scale energy storage capacity is needed to maximize utilization of these sources,

specifically to avoid large amounts of renewable energy being wasted when their supply exceeds demand.

Over the last years we have studied the electrochemical reduction of CO<sub>2</sub> to various value-added chemicals such as carbon monoxide (CO), formic acid, and methane. When coupled to renewable energy sources such as wind and solar, this process can produce carbon-neutral fuels or commodity chemicals, possibly providing a method for storage of otherwise wasted excess energy from intermittent renewable sources [1].

For this process to become economically feasible, more active and stable catalysts as well as better electrodes are necessary such that CO<sub>2</sub> electrolyzers can be operated at sufficient conversion (current density >250 mA/cm<sup>2</sup>), reasonable energetic efficiency (>60%), and sufficient product selectivity (Faradaic efficiency >90%). For CO production, a key reactant in the Fischer-Tropsch process, the best performance reported to date is current densities on the order of 90 mA/cm<sup>2</sup> and energy efficiencies up to 45%, when operating at ambient conditions [2]. This presentation will focus on new catalyst systems for efficient conversion of CO<sub>2</sub> to CO: (i) Ag nanoparticles supported on TiO<sub>2</sub> [3]; (ii) Au nanoparticles supported on multiwall nanotubes; and (iii) metal-free N-doped carbons. These catalysts have been characterized in a 3-electrode cell and in an electrolyzer. Current densities of between 100 and 250 mA/cm<sup>2</sup> as well as energy efficiencies of up to 70% were obtained. The electrodes in all these cases are prepared using automated airbrushing [2], which reduced catalyst loadings to 0.75 mg/cm<sup>2</sup> for Ag and 0.17 mg/cm<sup>2</sup> for Au. These performance levels, together with the lower cost due to low precious metal loading (due to the use of catalyst supports), or even the elimination of precious metals altogether (N-doped carbons), brings electrochemical reduction of CO<sub>2</sub> to CO closer to economic feasibility.

We also performed an economic / life-cycle analysis of this process, to determine whether this technology can become, economically viable for large scale application in the storage of energy from renewable sources, and/or in the reduction of greenhouse gas emissions.

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## Nanomaterials

Room: Hau - Session NM-TuE

### Nanomaterials Characterization & Reactivity II

Moderator: Katsuyuki Fukutani, University of Tokyo, Japan

5:40pm **NM-TuE1 High Spatial/Energy Resolution Cathodoluminescence Spectroscopy: Powerful Tool for Precise Characterization of Nanostructures, Dapeng Yu, Peking University, China** **INVITED**

Nanowires have been a top-five focused research topics in physics, and stimulated intensive interests world-wide. This talk composes of two major parts. In the first part, I will give a brief summary of our contributions to the world-wide nanowire research. In the main second part, I will extend to show the advantage of both high spatial and energy resolution cathodoluminescence (CL) in characterization of the fine structures of the nanomaterials. In particular, I will demonstrate that the high special resolution of the CL at ~ 5.5 K enable us to address the significant strain modulation of the optical emission and electronic structures of semiconductor nano/micro wires[1-5]. In contrast, the high energy resolution of the CL makes it possible to "see" directly the resonant SPP modes that are confined to the metal nanocavity.

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6:20pm **NM-TuE3 Quantum Many-Body Effects in Light Emission from Molecular Exciton and Plasmon Induced by Scanning Tunneling Microscopy, K. Miwa, RIKEN, Japan, Mamoru Sakaue, H. Kasai, Osaka University, Japan**

Luminescence from the systems consisting of metal nanostructures (NSs) and adsorbed molecules can be strongly influenced by quantum many-body effects which arise from the interplay between dielectric response of metal NSs and intra-molecular electronic/vibrational excitations. In light emission induced by the tunneling current of a scanning tunneling microscope (STM) from molecule-covered metal surfaces, interface plasmons localized near the tip-substrate gap region play important roles in electronic excitations and radiative decays of the molecule. Recent experimental results have also suggested that the dynamics of molecules (e.g., luminescence and energy absorption) have an influence on the luminescence-spectral profiles of interface plasmons [1]. Since the dynamics of molecules and interface plasmons have influence on each other, quantum many-body effects resulting from interplay between these dynamics are expected to occur. To unveil these effects from a microscopic point of view, there is a need to investigate the dynamics of the molecule and interface plasmons within the framework of quantum many-body theory. In this study, we develop the effective model of the system and investigate the effects of coupling between molecular exciton and interface plasmon (exciton-plasmon coupling) on the luminescence properties using the nonequilibrium Green's function method [2-5]. It is found that in addition to the dynamics of the molecule, the dynamics of interface plasmons plays an essential role in determining the luminescence spectral profiles of interface plasmons. Prominent peak and dip structure observed in recent experiments are interpreted by the developed theory. The details of exciton-plasmon coupling on the luminescence properties will be discussed.

#### References

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6:40pm **NM-TuE4 Imaging Three-Dimensional Surface Objects with Submolecular Resolution by Atomic Force Microscopy, Tomoko Shimizu, C. Moreno, O. Stetsovych, O. Custance, NIMS, Japan**

Submolecular imaging using atomic force microscopy (AFM) has recently been established as a stunning technique to reveal the chemical structure of unknown molecules, to characterize intramolecular charge distributions, and bond ordering, as well as to study chemical transformations and intermolecular interactions. So far, most of these feats were achieved on planar molecular systems because high-resolution imaging of three-dimensional (3D) surface structures with AFM remains challenging. Here we present a method for high-resolution imaging of non-planar molecules and 3D surface systems using silicon cantilever based AFM. We demonstrate this method by resolving the step-edges of the (101) anatase surface at the atomic scale, by simultaneously visualizing the structure of a pentacene molecule together with the atomic positions of the substrate, and by resolving the contour and tip-surface force field on a C<sub>60</sub> molecule with intramolecular resolution. The method holds substantial promise for the study of 3D surface structures such as nanotubes, clusters, nanoparticles, polymers, and biomolecules using AFM with unprecedented resolution.

7:00pm **NM-TuE5 Spatial Mapping of Exciton Lifetimes in Single ZnO Nanowires, Frank Güell, Universitat de Barcelona, J.S. Reparaz, Institut Catala de Nanotecnologia, G. Callsen, Technische Universität Berlin, M.R. Wagner, Institut Catala de Nanotecnologia, A. Hoffmann, Technische Universität Berlin, J.R. Morante, Institut de Recerca en Energia de Catalunya**

The quest for novel semiconductor materials with improved optoelectronic performance has triggered intense research activities to exploit the great diversity of effects offered by low dimensional systems. In this work, we demonstrate that the recombination dynamics of excitons in ZnO nanowires can be well understood within the concept of optical nanocavities. We investigate the spatial distribution of the lifetimes of the near-band-edge and bound-exciton emissions in single ZnO nanowires with different dimensions by means of temperature dependent and time-resolved spectroscopy. We demonstrate that the lifetime of the excitons is systematically reduced by 30% at the tips of the nanowires with respect to their maximum value at the center, which originates from the combined effect of the cavity-like properties of these nanostructures with the Purcell

effect. In addition, show that the model of Rashba and Gurgenishvili is valid even at the nanoscale, i.e. the lifetime of the bound excitons is proportional to the localization energy (E<sub>loc</sub>) to the power of 3/2. This result provides a means to understand the spatial dependence of the lifetimes of the near-band-edge emission (NBE), which is not intuitive due to their spatially extended nature. Finally, the temperature dependence of the photoluminescence and lifetimes of the excitons in single nanowires is also briefly discussed in comparison to bulk ZnO samples.

7:40pm **NM-TuE7 What is New in Thin Film and Interfaces Characterization, Miguel Jose Yacamán**, University of Texas San Antonio, USA **INVITED**

Electron Microscopy methods to characterize Thin films and interfaces have advanced very substantially during the last decade. In particular two methods are some of the most significant: Aberration corrected TEM-STEM images and Precession Electron Diffraction. In this paper we describe this methods and apply them to the characterization of gold thin films. It is possible to obtain atomic images of the interfaces using STEM-HAADF which yield reliable information about the atomic positions. When we combine this with single grain diffraction we can obtain a very complete description of the grain structure.

We present the case of polycrystalline Gold thin films grown at different temperatures. We discuss the distribution of most likely boundaries present and its frequency as a function of the temperature. In addition by using STEM-HAADF it is possible to obtain the surface topography evolution as function of the temperature.

8:40pm **NM-TuE10 Double Dressing for Efficient Manipulation of the Optically Active Frequency Bands in Nanostructured Artificial Atoms, Hanz Ramírez**, Grupo de Física Teórica y Computacional, Escuela de Física, Universidad Pedagógica y Tecnológica de Colombia, Tunja, Boyacá, Colombia

In this work, a model to study the coupling between a semiconductor qubit and two time-dependent electric fields is developed. By using it in the resonantly monochromatic double dressing regime, control of the local density of optical states is theoretically and numerically demonstrated for a strongly confined exciton.

As a main result, tailored manipulation of the optical density of states in semiconductor quantum dots is proved. It is shown that by coupling a nanostructured qubit simultaneously to two distinguishable lasers whose frequencies match the exciton transition, a discrete eigenstate turns into an energy subband in a process closely analogous to band formation in solid state physics.

Such strong changes in the local density of optical states, controllable through the ratio between the driving laser intensities, open new possibilities for on-demand photon emission from artificial atoms.

The presented results are in remarkable qualitative and quantitative agreement with experimental measurements.

## Thin Films

**Room: Makai - Session TF-TuE**

### Thin Film Synthesis & Characterization I

**Moderator: Ivan Petrov**, Linköping University, Sweden, University of Illinois at Urbana-Champaign

5:40pm **TF-TuE1 Sputtering Growth of ZnO-based Semiconductors with Band Gap Tunability Over the Entire Visible Spectrum, Naho Itagaki**, Kyushu University, Japan **INVITED**

ZnO is a remarkable multi-functional material with a distinctive property set and a huge range of existing applications. Recently, some research has been directed towards development of ZnO based materials with smaller band gap (E<sub>g</sub>), which allow light emission/absorption over a broad spectrum from the UV to the visible region. One of the most promising means to narrow the band gap is to alloy ZnO with CdO that has small direct band gap of 2.3 eV. However, there are technological challenges for the growth of high-cadmium-content CdZnO because of the crystal phase segregation between wurtzite ZnO and rocksalt CdO.

In this context, we have developed a new compound, ZnInON (ZION), which is a pseudo-binary alloy of ZnO with InN. Since both ZnO and InN have the same wurtzite crystal structure and different band gaps (ZnO: 3.4 eV; InN: 0.7 eV), the alloy may possess band-gap tunability in a wide range. Here, we first demonstrate the sputtering synthesis of ZION and the band gap tuning by changing the chemical composition ratio. The detailed analysis on the crystal structure as well as the photo-electric properties of

this new material are then conducted. Finally, we discuss the advantages of ZION as light-absorbing layers of multi-quantum well (MQW) solar cells, the theoretical efficiency of which exceeds 50%.

From the analyses of wide-range reciprocal space mapping of XRD spectra, we found that ZION has the same crystal structure as wurtzite ZnO and InN. The lattice constant of ZION is in between ZnO and InN, and decreases continuously with decreasing [Zn]/([Zn]+[In]), which indicate that ZION is a pseudo-binary system of ZnO and InN. The transmittance spectra reveal that the optical absorption edge is shifted continuously toward longer wavelengths with decreasing [Zn]/([In]+[Zn]). The band gap of ZION films, being determined by Tauc's plot, changes from 3.4 eV to 1.5 eV, which covers entire visible spectrum. The analyses of transmittance spectra indicate that ZION is of direct band gap, and thus it has high absorption coefficient around 10<sup>5</sup> cm<sup>-1</sup>. Furthermore, we found significant advantages of ZION in terms of applications in multi-quantum-well (MQW) solar cells. The lifetime of photo-generated carriers in QWs is increased by a few orders of magnitude when ZION is used as a MQW material instead of conventional GaAs-based materials, owing to the large piezoelectric field (several MV×cm<sup>-1</sup>) that separate electrons and holes. These results indicate that ZION is a promising material that opens new pathways for realizing new generation solar cells with very high efficiency.

6:20pm **TF-TuE3 Improvement of Thermal Stability of p-ZnO:(Al,N) Thin Films by Oxidizing Amorphous Zn<sub>3</sub>N<sub>2</sub>:Al Thin Films, Bingsheng Li**, Harbin Institute of Technology, China

ZnO has attracted much more attention as a potential candidate for more efficient UV-lasers due to its wide band gap of 3.374 eV and a large exciton binding energy of 60 meV. However, the problem associated with the preparation of stable p-type ZnO with high hole density hinders the ZnO-based device application as UV-emitters. Although substantial studies have been focused on this challenging issue, there are, so far, no efficient and practical doping methods to prepare stable p-ZnO with high hole density. The n-type conduction with high electron density (10<sup>21</sup> cm<sup>-3</sup>) have been achieved by doping ZnO with group-III elements (Al, and Ga). On the other hand, although extensive studies have been focused on the p-type doping issue of ZnO, the ZnO-based optoelectronic devices fabricated from p/n junction still suffer from p-type ZnO problem. P-type conduction has been reportedly realized with chemical doping. However, the low hole density and instability in electronic behavior become the bottleneck to improve the ZnO-based device performance.

For improving the thermal stability of p-ZnO, we introduce Al to capture the N by forming Al-N chemical bonds. The bond dissociation energy, ΔH<sub>298</sub>, of Al-N is 297 kJ·mol<sup>-1</sup>, is much larger than the Zn-N (ΔH<sub>298</sub> = 160 kJ·mol<sup>-1</sup>). Theoretical calculations suggested the possible approach to the p-type doping in ZnO with III-V Ga-N co-doping or cluster-doping, which can increase the solubility and stability of N in ZnO. Here, we use Al to stabilize the N-doping, because the corresponding bonds with N and O are stronger for Al than for Ga. For stabilizing N in p-type ZnO, the key issue is to reduce the compensation of single Al doping due to the formation of only Al-O bands. Another crucial point is to make sure the Al captures more than one N-atoms to form AlN<sub>2</sub>, AlN<sub>3</sub>, and AlN<sub>4</sub> in ZnO. To realize that, we prepared Zn<sub>3</sub>N<sub>2</sub>:Al and convert it to ZnO by an oxidation procedure. For Zn<sub>3</sub>N<sub>2</sub>:Al, p-ZnO appears around 600 °C and do not convert back to n-type with further increase of annealing temperature. However, for Zn<sub>3</sub>N<sub>2</sub>, we did not obtain p-type ZnO. A reasonable explanation is that the Al will stabilize the N during the reaction to form ZnO from Zn<sub>3</sub>N<sub>2</sub>. Comparing with previous reports, the thermal stability is improved. However, the hole density is still low and needs further improvements. More details about the structural, optical, and electronic properties of the samples will be given in the presentation.

We will optimize the concentration of Al dopant in Zn<sub>3</sub>N<sub>2</sub>:Al. The dependence of the hole density in ZnO, oxidized from Zn<sub>3</sub>N<sub>2</sub>:Al, on the Al concentration in Zn<sub>3</sub>N<sub>2</sub>:Al will be studied.

6:40pm **TF-TuE4 Well-Ordered Monolayers of Alkali-doped Coronene and Picene, Yoichi Yamada, M. Yano, M. Endo, E. Shimizu, Y. Hasegawa, M. Sasaki**, University of Tsukuba, Japan

Although the electronic modifications of the organic thin films by means of the chemical doping have been widely investigated, the structural properties of the doped organic materials have been poorly understood. This is generally due to an inhomogeneity of the doped materials, hindering the detailed understanding of the structure. However, structural information is inevitable for understanding the mechanism of the doping. For the basic investigation on the doping of the organic materials, we utilize well-defined monolayers of organic materials. We model the doping by depositing the dopant onto the monolayer. When the substrate is inert enough, self-organization of the dopants and host materials will be facilitated and well-ordered doped monolayer will be obtained. We focus mainly on so-called "metal-intercalated aromatic superconductors" discovered in 2010 in K-

doped picene [1]. Since its discovery, electronic properties of these materials have been investigated by means of the photoemission spectroscopy. However, contradicting results, deviating from a metallic to an insulating ground state, have been obtained. It is speculated that there exists notable variation of the structures in the thin films used in the photoemission studies. The theoretical reports have also reached contradicting results and have suggested that the electronic states are quite sensitive to the molecular arrangements. Therefore it is demanded to realize the well-ordered samples of these materials. Here we demonstrated the fabrication of the well-defined monolayer of the metal-intercalated aromatic superconductors, such as K-doped picene and coronene. These systems enable us the systematic investigations of the relation between structure and electronic properties. It is found that the alkali-doping causes a rearrangement of the host monolayers, based on the scanning tunneling microscopy and the X-ray absorption spectroscopy. Upon the reconstruction, electronic states of the host molecules also change drastically, suggesting the charge transfer from alkali metals to the molecule, revealed by means of the photoelectron spectroscopy. These observations confirm that the well-ordered monolayer, as realized in this study, can properly model the doping process [2,3].

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#### 7:00pm **TF-TuE5 Electrochromic Thin Film Synthesis, Understanding and Performance Enhancement**, *Yi Ren, S.Y. Chiam, J. Liu*, Institute of Materials Research and Engineering, Singapore

Electrochromic (EC) thin films are important for enabling technologies such as smart windows and non-volatile displays. To date, various organic EC films have been shown to possess high coloration efficiency and many color variety, while inorganic films have demonstrated excellent optical modulation and cycling stability. In addition, flexible EC devices that are retrofittable to existing windows can also be achieved by utilizing organic or porous inorganic films, and this poses new challenges in device integration and performance enhancement. In this presentation, I will first talk about various synthesis methods used by us for EC thin film deposition. Solution-based methods which target for low-cost and large-scale fabrication will be emphasized. Besides chemical bath deposition and electroplating, an innovative dip coating method with better thickness control will be introduced. Materials covered range from inorganic metal oxides (such as nickel, tungsten, molybdenum and tantalum oxide) to organic polymer electrolytes. We found that different synthesis methods result in films with different structure, phase and defect density. These differences in turn significantly affect the electrochromic performance of the material. Therefore, in the second part of the presentation, I will focus on characterizing and correlating the physical and electrochromic properties of the synthesized films. As an example, layered nickel oxide/hydroxide will be discussed in details. With different synthesis methods and post treatments, we are able to investigate the electrochromic performance of films with different structures (compact, porous and nanostructured), phases ( $\alpha$  and  $\beta$  phase), defect density (amount of  $Ni^{3+}$  sites) and intercalated species (water and anions). By changing electrolyte, we can also study the role of different ions in causing the color change, in particular,  $H^+$ ,  $OH^-$  and  $Li^+$ . Recently, we have successfully identified the causes of the activation and degradation phenomenon observed in oxide material. We have also proved the importance of having existing reaction sites such as defects for improved electrochromic reaction involving  $Li^+$ . The above knowledge can be extended to other layered material such as tungsten and molybdenum oxides. Last but not least, our ongoing work also focuses on synthesizing and characterizing thin films that can be functioned as solid electrolyte in electrochromic device. Besides the organic polymer electrolyte, we also look at emerging inorganic metal oxide electrolyte such as tantalum oxide. Their synthesis and ion conducting properties play significant role in device integration and performance.

#### 7:40pm **TF-TuE7 Thin Film Synthesis via Nanogrinding**, *Chris Papadopoulos*, University of Victoria, Canada

Thin films composed of nanoscale particles possess unique and varied electrical, optical and mechanical properties, which can be used to create advanced functional materials and nanostructured composites for devices. Such thin films find applications in electronics, optics, photovoltaics, energy storage, biomedicine, etc.

Here we describe a general approach to nanoparticle thin film synthesis based on *colloidal* or *nanogrinding*. Nanogrinding can produce large amounts of nanoscale particles in an appropriate solvent without the use of complex chemical or physical processing. The nanogrinding method typically employs planetary ball milling to grind a starting bulk powder into a nanoscale colloidal suspension suitable for thin film coating. Ball milling uses the rotary motion of a grinding jar containing the sample, grinding

beads and a liquid medium, which is arranged eccentrically on a so-called sun wheel. The efficient energy transfer during planetary ball motion leads to nanogrinding being a fast and inexpensive process for the creation of nanostructured thin films. In addition, nanogrinding is very flexible allowing the formation of semiconducting, metallic or insulating particles and films. These unique advantages combine to create a general solution-based processing approach for thin film surface coatings and devices (including non-planar geometries).

Results of nanogrinding trials using high-purity bulk materials (Si, silicides, oxides) and characterization of the nanoparticles and films via electron microscopy, scanning probe methods, Raman spectroscopy and elemental analysis are presented. Zirconia grinding vessels and either zirconia or silicon nitride beads are used in a planetary ball mill to grind readily available high-purity powders initially consisting of ~10-50 micron particles dispersed in solvent. Grinding speeds and times are varied between 200-1000 rpm and 10-500 minutes, respectively. After milling, the resulting colloidal dispersions are optionally filtered and deposited on a substrate for further analysis. As grinding time is increased, the resulting particles and films display good uniformity with sizes below 100 nm. Atomic force microscopy of the particles showed that diameters down to ~2-4 nm could be achieved. Elemental analysis indicates that contamination from the grinding tools is minimal.

Nanogrinding is an efficient route to directly creating nanoparticles suitable for thin film deposition of various materials from solution. By adjusting the grinding parameters, the size and dispersion of the particles can be controlled and their properties optimized for applications, including thin film electronic and optical devices.

#### 8:00pm **TF-TuE8 Effect of Annealing on Current Conduction Mechanism in High-k Dielectric Thin Films Deposited on Silicon Substrates**, *Anil Khairnar, P.A. Deshmukh, V.S. Patil, K.S. Agrawal, A.M. Mahajan*, North Maharashtra University Jalgaon, Maharashtra, India-425001, India

##### **Abstract:**

The ever increasing demand for functionality and speed for semiconductor applications requires enhanced performance, which is achieved by the continuous miniaturization of CMOS dimensions. However, as we further reduce the device dimension, transistor with conventional structure and material is attaining its fundamental scaling limit. Beyond the 22 nm node fundamental as well as practical constraints will limit the maximum performance achievable by these scaled transistors. The integration of high-k gate dielectric provides a promising solution to continue improving the device performance, as their higher k-value allows a physically thicker layer while aiming the same capacitance and Equivalent Oxide Thickness (EOT). This study primarily focused on studying the electrical properties of high-k MOS capacitors with metal gate electrodes. In this work, we have deposited  $HfO_2$  and  $Al_2O_3$  thin film deposited on silicon substrate by RF sputtering technique and Plasma enhanced atomic layer deposition system (PEALD) respectively. The deposition of  $HfO_2$  is confirmed by FTIR measurement. Current density vs voltage characteristics have been studied by I-V measurement further comparative study of current conduction mechanisms is done. In MOS structure due to the charge trapping and interface characteristics of dielectric films causes leakage current in dielectrics. The density of leakage current has been investigated and analyzed, by current-voltage and conduction mechanisms. Among the various conduction mechanisms  $HfO_2$  and  $Al_2O_3$  film on Si follows the Fowler Nordheim (FN) tunneling. The Poole Frenkel (PF) emission, Schottky emission (SE) and Trap assist tunneling (TAT) also studied. The barrier height ( $\phi_B$ ) is calculated of experimental work through Fowler Nordheim tunneling mechanism.

**Keywords** -  $HfO_2$ ,  $Al_2O_3$ , high-k, leakage current density, FN tunneling.

#### 8:20pm **TF-TuE9 Effects of Very High Frequency $O_2$ Plasma Reactant on High-k Film Properties Deposited by Atomic Layer Deposition**, *Gilsang Yoo, I.K. Oh, C.W. Lee*, Yonsei University, Republic of Korea, *T.H. Kim, G.Y. Yeom*, Sungkyunkwan University, Korea, Republic of Korea, *H.B.R. Lee*, Incheon National University, Republic of Korea, *H.J. Kim*, Yonsei University, Republic of Korea

High permittivity (high-k) dielectrics have been explored for an alternative gate insulator to conventional  $SiO_2$  in the metal oxide semiconductor field effect transistor (MOSFET) technology. Among various high-k deposition techniques, atomic layer deposition (ALD) appears to be one of the suitable methods due to its excellent process controllability for extremely thin high-k films. Plasma-enhanced atomic layer deposition (PE-ALD) using plasma reactant has been spotlighted because of its several benefits over conventional thermal ALD using gas reactant, such as lower process temperature and improved film properties by the reactive radicals of reactants. However, use of plasma reactants negatively influences electrical properties of high-k films in MOSFET since ion bombardment of energetic

radicals generates defects in films. Instead of radio frequency (RF) plasma which is usually used for plasma assisted processes, very high frequency (VHF) plasma for chemical vapor deposition (CVD) process was reported. The negative effects of plasma on film properties were reduced in VHF plasma process due to its lower ion kinetic energy and higher plasma density than RF plasma. Therefore, VHF plasma is expected to be a better plasma reactant for PE-ALD than RF plasma in the context of high growth rate and low ion damage. However, there has been no report on PE-ALD using VHF plasma reactant.

For this study, Al<sub>2</sub>O<sub>3</sub> PE-ALD were developed using Trimethylaluminum (TMA) precursor and O<sub>2</sub> plasma reactant on Si substrate. O<sub>2</sub> plasma reactant was generated using two different frequencies, 13.56 MHz and 60 MHz for RF and VHF, respectively. The processes exhibited ALD mode with good self-saturation behavior and linear growth as a function of growth cycles. To investigate the characteristics of plasma density and electron temperature, a Langmuir probe was installed in the chamber. The thickness and density of the films was analyzed by spectroscopic ellipsometry and X-ray reflectivity (XRR), respectively. By using VHF plasma, better film properties were observed compared to RF plasma. The growth rate of VHF plasma (2.7 Å/cycle) was higher than that of RF plasma (2.3 Å/cycle). In addition, the VHF PE-ALD film was denser than RF PE-ALD film (3.26 for VHF and 3.11 g/cm<sup>3</sup> for RF plasma), since ion and radical density generated by VHF is higher than those by RF. The VHF PE-ALD provides improved film qualities, such as low leakage current and low interface trap density, compared to RF PE-ALD grown film. The VHF plasma reactant for PE-ALD has potentials for various applications which require very thin and dense films in nanoscale regime.



# Wednesday Morning, December 10, 2014

## Biomaterial Interfaces

Room: Milo - Session BI-WeM

## Biomaterials, Interfaces, and Cells

Moderator: Keith McLean, CSIRO, Australia

8:20am **BI-WeM2 Self-Assembly of Macroscopic RNA Membrane**, *Y. Park, H. Kim, Jong Bum Lee*, University of Seoul, South Korea

DNA and RNA have gained attention as powerful materials for biotechnology. Although, a variety of DNA structures have been developed, structures based on RNA are extremely rare. Here, we developed the robust and free-standing RNA membrane using an enzymatic synthetic method. This macroscopic RNA structure was fabricated by following two steps, complementary rolling circle transcription (cRCT) and evaporation-induced self-assembly (EISA). In addition, properties of the membrane can be controlled by adjusting base-pairing of RNA strands and the concentration of template circular DNA. In this research, we fabricated three types of RNA membranes and used these membranes for controlled drug release systems.

8:40am **BI-WeM3 Cytocompatible Mineralization on Jurkat T Cell Surfaces with Titania Composites**, *EunHyea Ko*, KAIST, Republic of Korea, *W.G. Youn*, KAIST, *I.S. Choi*, KAIST, Republic of Korea

The artificial shells of organic/inorganic materials on living cells would give new properties to the encapsulated cells. For example, the encapsulate cell could live against physical deformation and chemical hazards, and control the cell division. Also, functionalization would be easier than native cell surface. Recently, our paper said that the  $(RKK)_4D_8$  peptide had both the  $TiO_2$ -inducing and cytocompatible units for *Chlorella* cell. However, due to the fragile property of mammalian cells, there are few studies on the mammalian cell encapsulation.

In this work, individual Jurkat T cells were encapsulated within peptide/ $TiO_2$  composite shells by layer-by-layer assembly and bioinspired mineralization. The cell viability and shape were maintained during the encapsulation processes, and the division of the encapsulated cells was changed by the artificial  $TiO_2$  shell. There are cluster of differentiation 3 (CD3) antigens on the Jurkat T cell surface. After encapsulation, anti-CD3 antibody was hindered to bind CD3 antigens on the cell. For the functionalization of cell surface,  $TiO_2$  composites made it possible to anchor the ligands of interest to the shell. After formation of the  $TiO_2$  shells on cell surfaces, the shells were functionalized via catechol chemistry in a cytocompatible fashion. We believe that these new properties on the Jurkat T cell surface could be applied to cell-based sensors and assays as well as for fundamental studies such as immunology.

9:20am **BI-WeM5 Selective Cell Adhesion to Surface Nanotopography**, *Elena Liang*, MN, *Dickson*, N. *Vollereaux*, AF. *Yee*, University of California, Irvine

Understanding cell interactions with material surfaces is critical to the performance of medical devices. Of particular interest to our research, such understanding could lead to simple and durable ways to control cell adhesion without chemically modifying the surface of biomaterials used in implantable devices. Recently, it was found that the nanopillar structures on cicada wings are inherently antibacterial irrespective of surface chemistry (Ivanova *et al.* Small. 2012). Such nanostructures can eventually be incorporated on surfaces of medical devices, but first, we need to ensure that patient's own cells would not be adversely affected by these structures. Hu *et al.* showed that nanopillars of widely varying aspect ratios and surface energies had strong effects on cell morphology, discouraging cell spreading (Hu *et al.* 2010). Kong *et al.* discovered that human embryonic stem cells grown on nanopillar structures have a significantly reduced number of focal adhesions per cell and concordantly exhibit increased cell motility on the nanopillars (Kong *et al.* 2013). Based on these findings, we hypothesized that the pillar nanostructures on the cicada wing would prevent cells from adhering. To show this, we first created a library of nanostructures, beginning with a biomimetic cicada wing replicate. We molded a negative hPDMS stamp of the cicada wing and pressed the stamp into polymethylmethacrylate and polystyrene films to create the polymer replicates. We also fabricated pillar arrays of different spacings from commercially available silicon molds using nanoimprint lithography. To evaluate cell adhesion, we counted the number of fibroblasts adhering to flat polymer and the nanopillars, and we determined the number of focal adhesion sites from immunostaining for vinculin, a major protein in the focal adhesion complex. In addition, we examined cell morphology on the various surfaces. After 24 hours, we observed that the cells adopted

different cell morphologies, possibly indicating changes in adhesion dynamics. Fibroblasts showed a spread-like morphology on the flat film while the cells on pillars were more equiaxed. Our study has shown that nanostructures in the 100-500 nm-size range do affect cell adhesion dynamics. We found that structure dimensions modulate the adhesion of cells, which may provide researchers a useful means of controlling cell adhesion on material surfaces.

9:40am **BI-WeM6 Polysaccharide Films at an Air/Liquid and a Liquid/Silicon Interface: Effect of the Polysaccharide and Liquid Type on their Physical Properties**, *Cathy McNamee*, Shinshu University, Japan, *Y. Taira*, Tohoku University, Japan

Chitin and chitosan show biocompatibility, biodegradability, and non-toxicity, and are therefore used in pharmaceutical and biomedical applications. The successful applications of chitin and chitosan require the ability to create well-defined films that display the required properties in the working environment. This ability requires an in-depth understanding on the physical properties of the films created using chitin or chitosan and the way to control these properties in different environments. The polysaccharide type, its conformation and packing in the film, and the surrounding liquids in the working environment contribute to the forces and friction of the system, which affect the properties of the polysaccharide films. We investigated the effect of the polysaccharide type, the subphase on which the chitin or chitosan Langmuir monolayers were prepared, and the liquid in which the properties of the transferred monolayers were measured on the physical properties of the polysaccharide films at an air/aqueous interface and at a liquid/silicon substrate interface, and the forces and friction of the polysaccharide transferred films when measured in solution against a silica probe.

Chitosan was modified with a silane coupling agent to make chitosan derived compounds with a low and a medium molecular weight. Chitin and the chitosan-derived compounds were used to make Langmuir monolayers at air/water and air/pH 9 buffer interfaces. The monolayers were transferred to silicon substrates via a Langmuir-Blodgett deposition, and the chitosan-derived compounds subsequently chemically reacted to the silicon substrates. Atomic Force Microscope force and friction measurements were made in water and in the pH 9 buffer, where the water and the pH 9 buffer acted as a good and a bad solvent to the polysaccharides, respectively.

The polysaccharide type affected the friction of the polysaccharide film, where the physically adsorbed chitin gave the lowest friction. The forces and friction of the polysaccharide films changed when the subphase on which the Langmuir monolayers were formed was changed or when the liquid in which the properties of the films adsorbed at the silicon substrate were being measured was changed. The friction increased significantly when the liquid was changed from water to the pH 9 buffer.

10:20am **BI-WeM8 Engineered Surfaces for Stem Cell Expansion**, *Laurence Meagher*, CSIRO, Australia **INVITED**

Control over biomolecule-material and cell-material interactions is critical to the performance of designed surface coatings in a broad range of applications including cell culture materials, implantable biomedical devices and biosensors. Three key design features for materials used in the expansion of cells is that the materials should have very low non-specific protein adsorption, the coatings should be covalently attached to the substrate and should contain covalently attached, highly specific ligands to mediate cell attachment. For cell therapy applications, these materials should be able to function effectively in cell culture media which is chemically defined and animal product free (i.e. serum-free). We have developed a platform coating approach<sup>1</sup>, which in one step, results in coatings with very low non-specific protein adsorption, i.e. no initial chemical functionalisation or priming steps are required. In addition, the coatings also contain functional groups onto which cell attachment ligands such as peptides can be chemically attached. The approach can be used to produce coatings on many different formats of interest, such as multiwell plates, tissue culture flasks and microcarrier particles. Microcarrier particles are particularly attractive for application in stirred tank and wavebag-type bioreactors

In this study we have prepared a number of synthetic polymer coatings using a platform grafting from approach to produce materials for the culture of cells. Coatings were formed using a grafting from approach from a monomer feed comprising 10 mole percent acrylic acid and 90 mole percent acrylamide. Coatings were found to be similar in composition to the monomer feed ratio, highly swelling. Characterisation was carried out using X-ray photoelectron spectroscopy and atomic force microscopy. Coupled to these coatings was a cyclic peptide (cRGDFK) which interacts in a highly specific manner with  $\alpha\beta3$  integrins only. These surfaces were found to be

highly suitable for the attachment and growth of murine L929 fibroblasts, bone marrow derived human mesenchymal stem cells (hMSCs) and human embryonic stem cells (hESCs). Furthermore, in the case of hMSCs the surfaces were used to expand the cells over three passages in three different media (two were serum free). The hMSCs were characterised by their ability to differentiate into adipocytes, osteocytes and chondrocytes as well as maintenance of cell surface markers typically used to define hMSCs.

#### References

<sup>1</sup>. Ameringer, T., Meagher, L., Thissen, H., Pasic, P., Styan, K., Process for Modifying a Polymeric Surface, WO 2014/000052 A1, 3January 2014

11:00am **BI-WeM10 Why Biointerface Science is Important for Stem Cell Research**, *Kevin Healy*, University of California, Berkeley, USA  
**INVITED**

Highly regulated signals in the stem cell microenvironment such as ligand adhesion density, matrix stiffness and architecture, growth factor presentation and concentration have been implicated in modulating stem cell differentiation, maturation, and ultimately function. Therefore, it is desirable to have independent control over both the biochemical and mechanical cues presented to stem cells to analyze their relative and combined effects on stem cell function. Accordingly, we have developed a range of materials systems to study stem cell function. This presentation will discuss our progress in developing: 1) self-organizing human cardiac microchambers mediated by geometric confinement; and, 2) *in vitro* disease specific tissue models (e.g., 'organs on a chip') to be used for high content drug screening and patient specific medicine. Examples of how biointerface science is important in these applications will be highlighted. For example, in the former we used PEG-patterned polystyrene substrates to geometrically confine human pluripotent stem cell colonies and spatially present mechanical stress. Upon chemical modulation of the Wnt/ $\beta$ -catenin pathway, biochemical and biophysical cues synergistically induced self-organizing lineage specification and creation of a beating human cardiac micro-chamber confined by the pattern geometry. In the second theme, we employed microfabrication technologies to form cardiac and liver micro-tissues from patient-specific human induced pluripotent stem cells (hiPSC), to be used for high content drug screening and patient specific medicine. Ideally, the use of human disease specific tissues organized into a single integrated physiological system could have an enormous impact on the early screening of candidate drugs.

11:40am **BI-WeM12 Characterization of Tethered Phospholipid Bilayers by the Electrochemical Impedance Spectroscopy**, *Gintaras Valincius, M. Mickevicius, T. Penkauskas*, Vilnius University, Lithuania

We discuss the characterization of tethered phospholipid bilayer membranes (tBLMs) utilizing the electrochemical impedance spectroscopy (EIS). An emphasis is put on applications of tBLMs in protein (peptide)/phospholipid membrane interaction studies. Such interactions modulate the dielectric properties and affect the integrity of phospholipid bilayer. Because of highly asymmetric structure tBLMs exhibit a unique EI response, which cannot be modeled by simple equivalent circuits consisting of capacitors and resistors. We discuss the special functions that describe the characteristic features of the EI spectra. Those analytical functions obtained by solving problem of voltage-current distribution at the interface take into account the structural and dielectric properties of tBLMs. Also, our analysis of the EIS provides the theoretical background for the utility of tBLMs as bioanalytical sensors for the membrane damaging agents, such as pore-forming toxins. We demonstrate that the magnitude and frequency of the negative of the impedance phase minimum, as well as the magnitude of impedance are the parameters indicative of the extent of the membrane damage, and may be used to estimate the defect density in bilayers, as well as the activity of the membrane damaging proteins and peptides. The precision of such estimates is highly dependent on the knowledge of the electric properties of the submembrane electrolyte reservoir separating phospholipid bilayer and solid surface. We present an algorithm, which allows to make estimates of the submembrane specific resistance. Clustering of the defects affects EI response in a unique way, which may be used for the qualitative analysis of the protein membrane interactions.

## Energy Harvesting & Storage

### Room: Lehua - Session EH-WeM

## Characterization of Materials for Energy Applications I

### Moderator: Mayo Villagran

8:00am **EH-WeM1 Hindering Effect of Surface Point-Defects for Photoreactivity on TiO<sub>2</sub>(110)**, *Igor Lyubinetzky*, Pacific Northwest National Laboratory

**Hindering Effect of Surface Point-Defects for Photoreactivity on TiO<sub>2</sub>(110)**

I. Lyubinetzky\*

EMSL and Institute for Integrated Catalysis, Pacific Northwest National Laboratory.

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While surface point-defects are expected to act as charge trapping and/or recombination centers in photoinduced processes, their direct impact of surface defects on photoreactivity is not well explored. We present the first observation of a suppressing effect of oxygen vacancy ( $V_O$ ) defects on photoreactivity of TiO<sub>2</sub>(110). Direct scanning tunneling microscopy imaging reveal a pronounced site-selectivity in the hole-mediated photooxidation of trimethyl acetate (TMA) on TiO<sub>2</sub>(110) upon ultra-violet light irradiation, wherein the reaction readily occurs at regular Ti sites but is completely inhibited at  $V_O$  defects. Utilizing electron energy loss spectroscopy and density functional theory, we show that the lack of reactivity of TMA groups adsorbed at  $V_O$ 's cannot be attributed to either a less active adsorption conformation or electron transfer from the  $V_O$  defect. Instead, we propose that the excess unpaired electrons associated with the  $V_O$  promptly recombine with photoexcited holes approaching the surface, effectively 'screening' TMA species at  $V_O$  site. We also show that this screening effect is spatially short-ranged, being predominantly localized at the  $V_O$ , and only mildly affecting TMA's at adjacent Ti sites. The direct impact of O vacancies on TMA photoreactivity over TiO<sub>2</sub>(110) is expected to have similar implications for other hole-mediated (e.g., photooxidation) reactions in which adsorption at or near electronic point-defects is possible. Furthermore, the localized influence of these defects on hole-mediated chemistry offers opportunities for additional study of site-selective photocatalysis on TiO<sub>2</sub>.

\* In collaboration with Z.-T. Wang and M.A. Henderson, PNNL and N.A. Deskins, Worcester Polytechnic Institute. We acknowledge support from the US DOE BES, Division of Chemical Sciences, Geosciences & Biosciences. A portion of this research was funded by the Chemical Imaging Initiative LDRD at PNNL.

8:20am **EH-WeM2 Atomic Structure and Intrinsic Electronic States of the In<sub>2</sub>O<sub>3</sub>(111) surface**, *Holger Eisele Eisele, R. Zielinski, A. Lenz*, Technische Universität Berlin, Germany, *Z. Galazka*, Leibniz Institute for Crystal Growth, Germany, *M. Dähne*, Technische Universität Berlin, Germany

Indium oxide as transparent semiconductor is one of the most promising materials for contact layers in photovoltaic applications. Nevertheless, due to the delicate fabrication process for single crystals only a few intrinsic properties are known about In<sub>2</sub>O<sub>3</sub>, yet. Especially the storage under air conditions may influence the surface properties. Hence it is hard to decide, which properties are intrinsic and which ones are influenced by physisorbed and/or chemisorbed atoms and molecules from the ambient air.

In this contribution for the first time we studied high quality single crystals at their freshly UHV-cleaved (111) surfaces by scanning tunneling microscopy (STM) and spectroscopy (STS). From these investigations we achieve knowledge about the atomic configuration at the surface. This configuration fits well with recent density functional theory calculations, and indicate a local charge enhancement within the surface unit cell. Furthermore, STS reveals intrinsic electronic surface states within the fundamental band gap. The Fermi level is also energetically located within the fundamental bulk band gap, which leads to the assumption that previously reported electron accumulation at this surface is not an intrinsic property, but related to extrinsic effects, such as e.g., non-stoichiometric material reorganization. After oxidation of the In<sub>2</sub>O<sub>3</sub>(111) surfaces outside the UHV their structural as well as their electronic properties look quite different: astonishingly both show much more metallic behaviour as the freshly cleaved ones kept under UHV-conditions. The processes leading to such an behaviour are still under discussions, but the data fits much better to previous observations.

8:40am **EH-WeM3 Laser-Excited Scanning Tunneling Spectroscopy of Materials for Solar Cell Application**, Verena Portz, M. Schnedler, R.E. Dumin-Borkowski, P. Ebert, Forschungszentrum Jülich GmbH, Germany

Materials for solar cell and optoelectronic applications are critically affected by defects. The defects can give rise to deep gap states, which can lead to non-radiative carrier recombination centers. These are detrimental to both the electron-light and light-electron conversion efficiencies in optoelectronic and solar cell devices, respectively. In order to understand the physical processes involved at the atomic scale, the materials used in the device structures need to be investigated under illumination with atomic resolution.

Therefore, we investigated the prototype group III-V semiconductor GaAs as a model system by light-excited scanning tunneling microscopy and spectroscopy. We used GaAs(110) cleavage surfaces, which are free of intrinsic surface states in the band gap, and hence the surface potential is governed by the underlying bulk doping. The effect of the laser irradiation on the scanning tunneling spectra was determined on the clean defect-free surface, at dopant sites, and close to defects, using a newly developed measurement methodology, whose advantages will be discussed. The atomically-resolved spectra show distinct changes of the local potential at the different sites, which can be related to the local distribution of the illumination-induced carrier concentration. In order to analyze the spectra in detail, we developed a simulation program, which allows us for the first time to calculate quantitatively the effect of laser irradiation on the tunnel current. The physical models used for the simulation will be discussed. Fits of the simulated spectra to the measured ones allow the determination of the local redistribution of light-excited carriers and the identification of atomic scale carrier recombination centers

9:00am **EH-WeM4 TEM Observation of Nano Porous Gold in Reaction Environment**, Takeshi Fujita, Tohoku University, Japan  
**INVITED**

Nanoporous gold (NPG) produced by dealloying possesses a self-organized, self-supporting three-dimensional (3D) nano-architecture, which gains increased attentions as a multifunctional material for a wide range of applications. Similar to small gold nanoparticles, NPG has been demonstrated to be catalytically active for a number of important chemical/electrochemical reactions, but at a much larger characteristic size (>20 nm) for both gold ligaments and nanopores. While many factors have been suggested to explain the nano-size chemical effect of gold nanoparticles, such as quantum size effects, charge transfer between gold nanoparticles and oxide supporters, and enhanced concentration of low-coordination atoms, on the other hand the self-supported NPG indicates that the unique morphological characteristics alone is responsible for the catalytic activity of NPG.

We characterized the microstructure of NPG using spherical-aberration-corrected transmission electron microscopy (Cs-corrected TEM). The atomic structure of the internal surfaces of NPG, responsible for the catalytic activity, was imaged by scanning transmission electron microscopy (STEM) using a high-angle annual dark-field (HAADF) detector. The arrangement of near-surface atoms was also measured accurately by Cs-corrected high-resolution TEM (HRTEM), which provides phase-contrast images with high displacement sensitivity. On the basis of extensive HRTEM and STEM characterization, the high catalytic performance of NPG was suggested to originate from surface strains and a high concentration of low-coordination atoms stabilized by the complex geometry of bicontinuous nanoporosity of NPG. In addition to the static observation in inert vacuum environment, we also characterized the surface atomic structure evolution during CO oxidation in a reactive atmosphere using a newly dedicated environmental HRTEM [1].

Our key observation also provided the first direct atomic observations of the coarsening process of the porous catalyst, which shows completely different mechanisms of catalytic degeneration when compared to conventional nanoparticulate catalysts. More importantly, the atomic observation provides compelling evidence that planar defects such as twins can effectively prevent structure coarsening, suggesting a new strategy for developing chemically active and structurally sound catalysts. The effect of planar defects on catalysis has been highlighted recently and our observation offers the first direct experimental evidence of this important phenomenon [2].

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9:40am **EH-WeM6 Characterizing Automotive Fuel Cell Materials by Soft X-Ray Scanning Transmission X-Ray Microscopy (STXM)**, Adam Hitchcock, V. Lee, McMaster University, Canada, V. Berejnov, D. Susac, J. Stumper, AFCC, Canada

Low temperature, hydrogen-fueled, proton exchange membrane fuel cell (PEM-FC) based engines are being developed rapidly for near-term implementation in mass production, personal automobiles. Materials and process research aiming to further optimize these systems is focused on understanding and controlling various degradation processes (carbon corrosion, Pt migration, cold start), and reducing cost by reducing or eliminating Pt in the electro-catalyst, especially for the oxygen reduction reaction (ORR). We are using soft X-ray scanning transmission X-ray microscopy (STXM) at the S 2p, C 1s, O 1s and F 1s edges to study a variety of issues related to optimization of PEM-FC materials for automotive applications. STXM provides spectroscopic identification and quantitative mapping of chemical components with 30 nm spatial resolution in both 2D projection and 3D spectro-tomography. Themes of our studies include: mapping ionomer in cathodes of beginning-of-life and end-of-life membrane electrode assemblies [1,2, 3]; investigating Pt-in-membrane [4] and carbon corrosion degradation [3]; studies of alternate electrode technologies (3M nanostructured thin films [5], ink-jet print [6]); and measuring water distributions *in situ* [7]. The O 1s spectra of the 3 phases of water differ from those of membrane electrode assemblies (MEA) constituents allowing direct *in-situ* visualization of water uptake and quantitative mapping of gas and liquid/sorbed water. A newly developed environmental cell for *in situ* studies with controlled humidity and temperature will be described and its current performance will be outlined.

Research funded by AFCC and NSERC. Measurements were made at the Canadian Light Source (supported by NSERC, NRC, CIHR, and the University of Saskatchewan) and at the Advanced Light Source (supported by the Division of Basic Energy Sciences of U.S. DoE).

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10:20am **EH-WeM8 New Insights into Energy-Related Materials from Advanced Electron Microscopy Methods**, Gianluigi Botton, McMaster University, Canada  
**INVITED**

Electron Microscopy and electron energy loss spectroscopy are invaluable techniques to study the detailed structure and the chemical state of materials at unprecedented spatial resolution. In today's modern electron microscopes, it is possible to tackle problems requiring the highest energy resolution, down to 60meV, and highest spatial resolution, down to the angstrom level, so that atomic resolved spectroscopy with high spectroscopic sensitivity and resolution can be obtained. This leads to the potential of covering excitation phenomena from the mid-infrared, soft-X-rays and even hard-X-ray regime.

In this presentation, various examples of applications of electron microscopy will be given based on a modern electron microscope. After an overview of the imaging conditions used to detect core-shell ordering changes in PtFe, PtRu, PtAu alloy nanoparticles [1,2] graphene and single atoms on doped graphene [3] used for fuel cell catalysts, using a combination of high-angle annular dark-field STEM imaging, EELS elemental mapping and simulations, we will discuss the application of atomic-resolved EELS mapping in to study complex oxide and oxide support materials used to promote strong metal support interaction [4]. Here we demonstrate how electron energy loss spectroscopy can be used to probe the valence change of the oxide following the interaction with the catalyst. This powerful technique can also be used to study of the structure and substitutional effects from single atom dopants in phosphors [5] and metallic alloys.

Additional examples will highlight the application of microscopy technique to the analysis of perovskite structures. These examples demonstrate that compositional and chemical state (valence and coordination) information can be obtained down to the Ångström level on surfaces [6].

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11:00am **EH-WeM10 The Use of Massive Ar Clusters for the Sub-Surface Characterization of Organic and Inorganic Materials**, *David Surman*, Kratos Analytical Inc., *J. Counsell, S. Hutton, H. Brannon*, Kratos Analytical Ltd., UK

Over the last several years massive Argon gas cluster ion sources as accessories for sputter depth profiling of organic materials have increased in popularity. These sources utilize Argon cluster ions formed via adiabatic isentropic expansion of Argon gas into a vacuum followed by subsequent electron impact ionization and cluster size selection. In ideal cases the aforementioned massive cluster ions efficiently sputter the surface of organic materials revealing undamaged subsurface structure for analysis. More recently, developments in the technology have expanded the use of these sources to allow for the sputtering of inorganic materials.

Advanced software controlled ion sources and flexible sample handing equipment allow a wide range of experimental conditions to be routinely employed during sputter depth profiling with these massive Argon clusters. In this study we have investigated a variety of parameters such as incident ion energy and cluster size distribution on the effectiveness of the sputtering process and the degree of chemical damage that is induced using X-ray Photoelectron Spectroscopy (XPS) as the monitor. A range of both organic and inorganic materials have been analysed. It has been observed that for most organic materials large cluster sizes with a medium beam energy (typically less than 10keV) are very effective for sputtering with no observable chemical damage. This is in contrast to sputtering of inorganic materials where typically high beam energies (greater than 10keV) and small cluster sizes are required for effective sputtering. The identification of a minimum partition energy for sputtering will be discussed. In addition, it will be demonstrated that, although preferential Oxygen sputtering can be observed on many oxides resulting in the formation of reduced chemical states, this effect is substantially reduced when compared to the use of monoatomic Ar ions.

11:20am **EH-WeM11 Recent Applications and Results in Near Ambient Pressure XPS - In-situ Cell Designs for Liquid Environments**, *Thomas Schulmeyer, A.T. Thissen*, SPECS Surface Nano Analysis, Inc.

Modern devices are often only functional in environments far away from ultrahigh vacuum, which is still considered the standard operating condition for all Surface Science techniques. Due to miniaturization down to the nanoscale, surfaces are increasingly important for device performance. In order to contribute to advanced material analysis in future Photoelectron spectroscopy, Scanning Probe Microscopies and related techniques must be performed in generic or near generic device environments. Such an environment would mean high, elevated or near ambient pressures of defined working gas mixtures, liquid media, potentials or magnetic fields; extremely low or high temperatures might also be necessary. Of course, all standard Surface Science Techniques did not work under these extreme environments previously. This work summarizes and presents existing solutions for present and future development routes to new instruments, and displays how material analysis methods are functional under these working conditions. The opportunities and limitations will be discussed from the perspective of suppliers of scientific instruments. And finally, application examples and results from existing In situ methods will be demonstrated. These methods include: high pressure treatment cells, complete High Pressure or Near Ambient Pressure Photoelectron Spectroscopy or Scanning Probe Microscopy Systems (NAP-PES or NAP-SPM), liquid and electrochemical cells, Liquid sample "manipulators", and concepts and status of equipment working in the highest or lowest temperatures, high magnetic fields and static or dynamic potentials.

11:40am **EH-WeM12 Dynamic H<sub>2</sub>O/GaP (111) Interfacial Chemistry Monitored by Near-Ambient Pressure XPS in Real Time**, *Xueqiang Zhang, S. Ptasinska*, University of Notre Dame

A photoelectrochemical (PEC) solar cell for water splitting can convert solar energy into chemical energy and store it in the form of hydrogen, a molecule regarded as a promising candidate for sustainable and clean fuels [1]. PEC solar cells using phosphide-based III-V semiconductors are known to have higher efficiency than other materials. They are, however, usually limited by issues such as photocorrosion or decreased electron extraction efficiency due to formation of interfacial oxide species, which becomes

especially critical when operating electrodes (typically, semiconductors) are exposed to aqueous electrolytes [2]. Therefore, It is desirable to understand the process of water interactions with semiconductors and possible oxidation and reduction mechanisms at the H<sub>2</sub>O/semiconductor interface, especially under near realistic conditions.

In the present study, water dissociative adsorption on a GaP (111) surface was investigated using near ambient pressure X-ray photoelectron spectroscopy (NAP XPS) at various pressures and temperatures. The interfacial chemistry was tracked by recording high resolution photoemission spectra of Ga 2p<sub>3/2</sub>, O 1s and P 2p. In the pressure-dependent study (room temperature, ~300 K), enhanced surface Ga hydroxylation and oxidation were observed with an increase of water vapor pressure, which was also mirrored by the photoemission spectra of O 1s. In the temperature-dependent study, surface Ga hydroxylation and oxidation were further enhanced at temperatures below 673 K. While a large-scale conversion of surface O-Ga-OH species into Ga hydroxide, along with surface P oxidation, was observed at a temperature of 773 K. The formation of Ga and P oxide/hydroxide networks with a schematic formula of G<sub>a</sub>P<sub>b</sub>O<sub>c</sub>(OH)<sub>d</sub> (a, b, c and d represent a ratio of different elements and groups) is suggested. Our results can be compared with recent theoretical findings [3, 4] and lead to a better understanding of water splitting mechanisms and photo-corrosion on semiconductor surfaces.

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## Nanomaterials

**Room: Hau - Session NM-WeM**

### Nano Composites

**Moderator:** David Williams, The University of Auckland, New Zealand

8:20am **NM-WeM2 Microwave Absorption Properties of Core Double-Shell FeNi@BN@BaTiO<sub>3</sub> Nanocapsules**, *Shi G.M.*, Shenyang University of Technology, China

#### Abstract

Recently, with the rapid advancement of wireless communication, the microwave absorbing materials are becoming increasingly important for applications in some special fields such as silent rooms, radar systems and military applications. Among the candidates for EM wave absorbers, magnetic nanocapsules, i.e. magnetic nanoparticles coated with an insulator shell including graphite, oxidation etc., are now becoming a study focus of researchers. The reason is that this type of EM wave absorbers not only possess a high saturation magnetization and Snoek's limit at high frequencies, but also decrease eddy current phenomenon induced by electromagnetic wave.

The determining key factor of microwave absorption performance of the absorbers is EM impedance matching of the absorbers. Multilayer structures are a good way to increase EM impedance matching. However, the relative permittivity due to the interface polarization in the heterogeneous composites is rarely focused on. BaTiO<sub>3</sub> with excellent dielectric/ferroelectric properties has been studied for its EM wave absorption properties, and FeNi nanoparticles with large saturation magnetization are prominent magnetic microwave absorbers. Hence, in this study, core double-shell FeNi@BN@BaTiO<sub>3</sub> nanocapsules were synthesized by a two-step [app:addword:synthesis] method, consisting of an arc- evaporating a FeNi-B amorphous alloy target in a mixture atmosphere of Ar and N<sub>2</sub> and a subsequent chemical liquid deposition process. Microwave absorption properties of core double-shell FeNi@BN@BaTiO<sub>3</sub> nanocapsules were investigated in the 1–18 GHz frequency range. High resolution transmission electron microscopy studies the core double-shell type nanocomposite with FeNi nanoparticles as the core, while BN and BaTiO<sub>3</sub> are the inside and the outside shells, respectively. Enhanced relative permittivity made the core double-shell FeNi @BN @BaTiO<sub>3</sub>,

nanocapsules with better electromagnetic impedance matching than that of a FeNi@BN and BaTiO<sub>3</sub> mixture. Reflection loss (RL) values of FeNi@BN@BaTiO<sub>3</sub> paraffin composite are far greater than those of the FeNi@BN-paraffin composite at the absorbent thickness from 1.1 to 6 mm. An optimal Reflection loss of -40.3 dB was reached at 10.9 GHz with 1.5 mm thickness, and the broadest absorption bandwidth of 5.9 GHz (RL < -10dB) is from 8.7 to 14.6GHz frequency range. The microwave absorptive mechanisms of BN@BaTiO<sub>3</sub> coated FeNi nanocapsule absorbent were discussed.

8:40am **NM-WeM3 Nanocomposite Coatings – Playing with Nanostructures to Achieve New Properties**, Joerg Patscheider, Empa, Switzerland **INVITED**

Thin film technologies allow the preparation of materials that are compositionally modulated down to the nanometer scale. When the grain size of crystalline materials approaches the ten nanometer range, the properties known from their large-scale counterparts often change substantially. Such changes affect electronic and optical properties as well as the mechanical behavior of nanoscaled thin films. Examples include hard materials with built-in functionalities such as coloration, designed frictional properties through a variety of mechanisms as well as hardness-enhancement in wear-resistant coatings. Nanocomposite coatings, which consist of nanocrystalline nitrides or carbides can provide combinations of advantageous properties such as enhanced hardness and low friction for the case of TiC/a-C:H, high hardness and optical transparency in Al-Si-N thin films or designed thermal conductivity with oxynitride coatings for wear protection on cutting tools. Various examples of nanostructured thin film systems will be presented and the underlying principles for the successful operation of such thin film materials will be discussed.

9:20am **NM-WeM5 High Thermal Conductivity with Electrically Insulating Ceramic/polymer and Ceramic/Ceramic Nanocomposite Films Using Ceramic Nanosheets**, C.H. Kim, S. Nahm, Korea University, Republic of Korea, **HyoTae Kim**, Korea Institute of Ceramic Engineering and Technology, Republic of Korea

High thermal conductivity films with electrically insulating properties have a great potential for the effective heat transfer as substrate and thermal interface materials in high density and high power electronic packages. There have been lots of studies to achieve high thermal conductivity composites using high thermal conductivity fillers such as alumina, aluminum nitride, boron nitride, CNT and graphene, recently. Among them, boron nitride (BN) and aluminum nitride (AlN) ceramics are promising candidates for high thermal conductivity with electrically insulating filler materials. This work presents an enhanced heat transfer properties of ceramic/polymer and ceramic/ceramic nanocomposite films using BN/AlN nanosheets (nanoflake) and polymer resins. BN nanosheet was prepared by a chemical exfoliation using organic media and subsequent ultrasonic treatment. High thermal conductivity over 5W/mK in transverse and 10W/mK in in-plane direction of cast films were achieved for BN nanosheet/polymer nanocomposites that were prepared under 250°C. Also, thermal conductivity over 5W/mK were achieved for BN/AlN nanosheets/glass ceramic composites which can be sintered under 900°C. Further improvement of thermal conductivity up to 15W/mK was achieved by applying high thermal conductivity polymers and adequate alignment of nano size ceramic sheets and high density packing through multimodal powders and two stage film forming process including first cast, resin infiltration and pressured-roll cast at elevated temperatures.

9:40am **NM-WeM6 Magnetoluminescent Nanoparticles For Detection And Treatment Of Cancer By Thermal Ablation**, Nuyeli Izaguirre, Centro de Investigación Científica y de Educación Superior de Ensenada, Mexico, **A. Hirata**, Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México, Mexico

In recent years has increased the interest for developing multifunctional materials which can be used for diagnosis and therapies for major diseases such as cancer. The purpose of this work is the synthesis and characterization of luminescent/magnetic nanoparticles (LMNPs) made of magnetite (Fe<sub>3</sub>O<sub>4</sub>) and their simultaneous combination with europium doped lanthanum oxide (La<sub>2</sub>O<sub>3</sub>:Eu), terbium doped lanthanum oxide (La<sub>2</sub>O<sub>3</sub>:Tb) or thulium doped lanthanum oxide (La<sub>2</sub>O<sub>3</sub>:Tm) for possible applications as contrast and thermal ablation agents in cancer treatment.

The method used to obtain the LMNPs is spray pyrolysis due it allows the synthesis of nanoparticles with narrow size distribution, adjustable size, high crystallinity and good stoichiometry. Luminescent nanoparticles were prepared with different concentration of dopant material and were post annealed at different temperatures in order to find the best luminescent response. Once obtained the luminescent materials with the highest luminescence, the synthesis of magnetoluminescent materials was followed. This second step was done for different concentration of luminescent and

magnetic nanomaterials in order to obtain the best multifunctional properties material. The determination of the best material was made by characterizing the nanoparticles with different techniques such as spectrophotometry, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and measurement of magnetic properties using a vibrating-sample magnetometer (VSM) and a magnetic induction device.

Partial support from CONACyT (Grant 100555) and DGAPA-UNAM (Grant IN-109913) and technical work provided by E. Aparicio, F. Ruiz and I. Gradilla is gratefully acknowledged.

10:40am **NM-WeM9 Nanoparticles-Reinforced Aluminum Matrix Composite Materials Fabricated by Powder Technology**, Seungjin Kim, K. Kim, J. Cho, Pukyong National University, Republic of Korea, S. Cho, Korea Institute of Materials Science, Republic of Korea, **M. Leparoux**, Empa, Switzerland, **H. Kwon**, Pukyong National University, Republic of Korea

Nanosized silicon carbide (nSiC) particles were used as a solid mixing agent in order to homogeneously well dispersion of the carbon nanotubes (CNT) in the aluminum (Al) powders by a high energy ball milling process. The CNT-nSiC-Al composite powder was prepared depending on different milling times of 10, 30, 60, 180, and 360 min. The nSiC particles were well infiltrated into the CNT agglomerations and induced physical separation of the CNTs. Another expected advantage of nanoparticle mixing agents is that no necessary to remove the mixing agent after bulk fabrication, because they are also can be offered fine-particle-strengthening effect. The powder particle size and morphology showed differently depending on the process times. A lot of flaky morphology of the Al particles was observed until 60 min milled one. However, relatively spherical shapes of the Al powder particles were observed over 180 min milled conditions. It is estimated that morphology of the Al powder particles which is highly affected to final materials properties can be controlled by controlling milling times. The composite powders have been sintered by spark plasma sintering (SPS) process. The SPSed composite materials were characterized based on microstructure, hardness, crystallite, and defect rate of the CNT in the composites. The SPSed flaky-composite powders showed lower relative density (around 98%) than the SPSed spherical-composite powder which was fully densified. However, the Vickers hardness of the SPSed spherical-composite powders were showed almost three times higher values than the SPSed flaky-composite powders. It means that the morphology of powder particles is significantly affected to the hardness of composite materials. However, we believe that the nanoparticle mixing agent could be used for CNT-reinforced composite materials system.

11:20am **NM-WeM11 Surface Modification with Polyhedral Oligomeric Silsesquioxanes Silanols**, Luis Cabrales, F. Valencia, K. Calderon, I. Hinojosa, California State University Bakersfield

Hydrophobicity, water repellency, is a desirable surface property for materials in many industries. Water repellent surfaces are used to prevent deleterious effects of water such as; corrosion and degradation, on various materials. There are several methods which can be used to modify the properties of surfaces. Some of these techniques include sol-gel method, plasma, chemical vapor deposition, atomic layer deposition, and also traditional wet chemistry methods. Some novel materials for surface modification are Polyhedral oligomeric silsesquioxanes (POSS) silanols. These materials possess some of the surface modification characteristics of other silicon-based materials. In this project, Polyhedral Oligomeric Silsesquioxanes (POSS) were used to treat hydrophilic materials such as cotton and glass. Two POSS silanols, TriSilanolIsooctyl POSS and TrisilanolPhenyl POSS, were deposited by immersion methods on glass and polymeric surfaces. Several concentrations and curing temperatures were evaluated. Contact angle measurements of water and other liquids were used to calculate the surface properties and wettability. Dynamic capture mode was used to calculate the hysteresis of advancing and receding contact angles. The hysteresis provided information regarding the wettability properties of the obtained surfaces. Statistical Analysis was performed on the contact angle data collected from the glass, cotton, and PVA samples. The analysis of the PVA films coated with TrisilanolIsooctyl POSS demonstrated an effect of the curing temperature in the water repellency. Whereas the PVA coating with the TrisilanolPhenyl POSS had a lower variability in the contact angle as the curing temperature was increased. The cotton samples coated with POSS where compared with contact angles measured at 10 seconds and 60 seconds after placing the droplet. The results for 0.1% TrisilanolPhenyl POSS cotton samples proved that only water repellency is achieved at higher curing temperatures. The results of 4% TrisilanolPhenyl POSS cotton samples showed a higher repellency even at lower curing temperatures at 10 seconds. The results of the contact angles at 60 seconds demonstrated that as the curing temperature is increased, the coating prevents the absorption of water. The results demonstrated that POSS can impart hydrophobic properties to these materials even at low

concentrations. The unique properties of POSS silanols for surface modification are also discussed.

11:40am **NM-WeM12 Application of Ultrananocrystalline Diamond/Hydrogenated Amorphous Carbon Composite Films to Photodiodes**, *Tsuyoshi Yoshitake, Y. Katamune, T. Hanada, S. Takeichi*, Kyushu University, Japan, *S. Ohmagari*, National Institute of Advanced Industrial Science and Technology

Ultrananocrystalline diamond (UNCD)/hydrogenated amorphous carbon (a-C:H) composite (UNCD/a-C:H) films are aggregates consisting of ultrananocrystalline diamond (UNCD) grains of less than 10 nm in diameter and an a-C:H matrix [1]. In our previous study, we have realized the film growth without the pretreatment of substrates using diamond powder by pulsed laser deposition (PLD) and coaxial arc plasma deposition (CAPD), and experimentally proved the formation of p-type and n-type conduction accompanied by enhanced electrical conductivities by the doping of boron and nitrogen, respectively [2,3].

In this work, heterojunction diodes comprising B-doped UNCD/a-C:H films and n-type Si substrates were fabricated by PLD and CAPD and they were evaluated as photodetectors. The B-doped UNCD/a-C:H showed obvious photoconduction in the UV and visible ranges. Heterojunction diodes exhibited a typical rectifying action. Photocurrent was evidently observed, and the external quantum efficiency was estimated to be more than 70% for UV monochromatic light under negative biases.

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## Thin Films

### Room: Makai - Session TF-WeM

## Thin Film Synthesis and Characterization II

Moderator: Naho Itagaki, Kyushu University, Japan

8:00am **TF-WeM1 Novel Methods for Fitting the Fe 2p and Sn 3d XPS Data from Metallic and Oxidized Surfaces**, *M. Bravo-Sanchez*, CINVESTAV-Unidad Queretaro, Mexico, *Jorge A. Huerta-Ruelas*, CICATA-Queretaro, Mexico

Fe and Sn oxides are present in many products and industrial processes. Surface analysis with techniques such as X-ray photoelectron spectroscopy (XPS) plays a crucial role in understanding their properties. Most of the core level spectra from metallic and oxidized Fe and Sn surfaces show very large background signals, highly asymmetrical line-shapes, and a series of shake-up satellites that overlaps with the higher binding-energy branch of the peak doublets. For these reason, a proper fit of these spectra has been elusive. This has prevented the quantification, through the analysis of XPS data, of the composition of oxidized surfaces and of the thickness of thin oxide layers. In this work we jointly employed the SVSC background [1] and the double Lorentzian line-shape [2] to closely model the Fe 2p and Sn 3d spectra. With this approach it was possible to resolve previously unreported shake-up satellites and to quantify the thickness and composition of thin oxide films. The validity of the method is strongly suggested from the reproduction of the thickness assessed with transmission electron microscopy. The expected compositions are also reproduced. Examples of oxide films ranging from 2 to 5 nm will be discussed in full. [1] A. Herrera-Gomez, M. Bravo-Sanchez, O. Ceballos-Sanchez, and M.O. Vazquez-Lepe. Journal of Electron Spectroscopy and Related Phenomena (in press) DOI 10.1002/sia.5453. [2] A. Herrera-Gomez. "A double Lorentzian shape for asymmetric photoelectron peaks." Internal Report. Cinvestav-Queretaro.(2011). <http://www.qro.cinvestav.mx/~aherrera/reportesInternos/doubleLorentzian.pdf>

8:20am **TF-WeM2 Microstructure Control in Transition-Metal Nitride Alloy Films via Hybrid HIPIMS/Magnetron Co-sputtering using Selective Metal-Ion Irradiation**, *Greczynski, Lu, Jensen*, Linköping University, Sweden, *Ivan Petrov, J. Greene*, Linköping University, Sweden, University of Illinois at Urbana-Champaign, *Kölker, Bolz, Schiffers, Lemmer*, CemeCon AG, Germany, *L. Hultman*, Linköping University, Sweden **INVITED**

It was realized early on in the HIPIMS literature<sup>1</sup> that there exist a time separation between the Ar and metal-ion dominated fluxes at the substrate which opens the possibility for selection one of the components for ion-assisted by using a pulsed bias voltage with suitable synchronization. Here, we explore systematically this avenue by using pseudobinary TiN-based model systems TiMeN (i.e. TiAlN, TiSiN, and TiTaN) to carry out

experiments in a hybrid configuration with one target powered by HIPIMS, the other operated in DCMS<sup>2,3</sup> mode and probe the effects of (i) metal versus rare-gas ion irradiation as well as (ii) the type of metal ion used (Ti vs Me). We employ a metastable NaCl-structure Ti<sub>0.39</sub>Al<sub>0.61</sub>N as a model system to demonstrate that switching from Ar<sup>+</sup> to Al<sup>+</sup>-dominated bombardment eliminates phase separation, minimizes renucleation during growth, reduces the high concentration of residual point defects, and thus results in dense, single-phase, stress-free films.<sup>4</sup> For metastable alloys, TiAlN and TiSiN, mechanical properties are shown to be determined by the average metal-ion momentum transfer per deposited atom ( $p_d$ ).<sup>5</sup> Irradiation with lighter metal-ion ( $M_e = \text{Al}^+$  or  $\text{Si}^+$  during Me-HIPIMS/Ti-DCMS) procures fully-dense single-phase cubic Ti<sub>1-x</sub>(Me)<sub>x</sub>N films. In contrast, with higher-mass film constituents such as Ti, ( $p_d$ ). Easily exceeds the threshold necessary for phase segregation which results in precipitation of second w-AlN or Si<sub>3</sub>N<sub>4</sub> phases. With the TiTaN system we show that synchronized pulsed ion bombardment in the hybrid system with the heavy-metal ions (Ta) permits to grow dense, hard, smooth, and stress-free thin films at lowered substrate temperature, with no external heating.<sup>6</sup> Overall, we demonstrate that using synchronous bias to select the metal-rich portion of the ion flux opens new dimension for ion-assisted growth in which momentum can be tuned by selection of the metal ion in the hybrid/cosputtering configuration and stresses can be eliminated/reduced since the metal ion is a component of the film.

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9:00am **TF-WeM4 Mechanical and Electrical Properties of ZrB<sub>2</sub> Thin Films**, *Lina Tengdelius*, Department of Physics, Chemistry, and Biology (IFM), Linköping University, Sweden, *E. Broitman, F. Eriksson*, Department of Physics, Chemistry, and Biology (IFM), Linköping University, *M. Samuelsson*, Impact Coatings AB, Linköping, *J. Lu, J. Birch*, Department of Physics, Chemistry, and Biology (IFM), Linköping University, *T. Nyberg*, Department of Solid State Electronics, Uppsala University, *H. Högborg*, Department of Physics, Chemistry, and Biology (IFM), Linköping University

Zirconium diboride (ZrB<sub>2</sub>) exhibits a number of favorable properties including high melting point, high hardness, and low resistivity [1,2]. In addition, the compound is chemically inert and shows good wear and corrosion resistance, even at elevated temperatures. These properties make ZrB<sub>2</sub> thin films interesting for applications in demanding environments.

In order to enable reliable evaluation of the mechanical and electrical properties of this material, the films should exhibit well defined properties, including being stoichiometric, show high crystalline ordering, and being free of contaminants. Moreover, the substrate material must be appropriately chosen for the measurements of the functional properties.

The aim of the current study is to investigate and determine the electrical and mechanical properties of ZrB<sub>2</sub> thin films. In order to do so, well defined ZrB<sub>2</sub> thin films, were deposited using direct current magnetron sputtering (DCMS) from a compound source, on Al<sub>2</sub>O<sub>3</sub>(0001) substrates enabling evaluation of said properties.

It was found that epitaxial growth of ZrB<sub>2</sub> films, up to a thickness of 1.2 μm, is possible by DCMS of a ZrB<sub>2</sub> compound target on Al<sub>2</sub>O<sub>3</sub>(0001) substrates, and at a temperature of 900 °C. The obtained ZrB<sub>2</sub> thin films were characterized with regards to mechanical and electrical properties, and the results showed that the films exhibited resistivity values of ~125-200 μΩ cm, and notably high hardness values of up to 50 Gpa, as well as high elastic recovery.

## References

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9:20am **TF-WeM5 Effect of Vacuum Annealing on the Thin Films Of Copper Oxide prepared by Reactive DC Magnetron Sputtering.** Dhanya S. Murali, M.K. Jain, A. Subrahmanyam, Indian Institute of Technology Madras, India

Cu<sub>2</sub>O is an interesting p-type semiconductor; it has high optical absorption coefficient in the visible region and reasonably good electrical properties. It finds application in p-n junction based devices such as solar cells and high mobility p-type thin film transistors<sup>1,4</sup>. Among p-type oxides, cuprous oxide (Cu<sub>2</sub>O) in single crystal form<sup>1</sup> is known to have the highest hole mobility  $\sim 100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  at room temperature (300 K). Lee *et al.*<sup>3</sup> reported a Hall mobility of  $62 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for Cu<sub>2</sub>O thin films at room temperature. Sohn *et al.* performed vacuum annealing of copper oxide (CuO) thin films on Si substrate in order to obtain Cu<sub>2</sub>O thin film which possesses Hall mobility of  $47.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and good optical properties<sup>4</sup>.

In the present communication, we report the effect of vacuum annealing (at 623K and 700 K) on polycrystalline copper oxide thin films deposited (at room temperature 300 K) on a borosilicate glass substrate employing reactive DC magnetron sputtering. Argon and oxygen are the sputter and reactive gases respectively. Pure (99.9%) copper is the target. Deposition pressure is  $3.5 \times 10^{-3}$  mbar and the target power density is  $1.4 \text{ Wcm}^{-2}$ . The films were characterized by X-ray diffraction, Hall effect (with temperature variation in the range 20 K to 300 K) and Raman spectroscopy (excitation wavelength 532 nm and in the temperature range 77 K to 700 K). Optical band gap is evaluated using UV-Vis spectrometer (400 – 1100 nm). The “as prepared” films show CuO phase. At an annealing temperature of 623K (in vacuum at  $5 \times 10^{-6}$  mbar), transition to a mixed phase of CuO and Cu<sub>2</sub>O is observed. Further annealing at 700 K, CuO transforms completely to a cubic Cu<sub>2</sub>O phase. Sohn *et al.*<sup>4</sup> reported similar transition at 773 K (CuO prepared on Si substrate by RF sputtering). The optical direct band gap is observed at 2.06-2.51 eV. The reduction of phase CuO to Cu<sub>2</sub>O is observed to enhance the optical transmittance in the visible region<sup>4</sup>. The Hall mobility measurements showed that the vacuum annealed Cu<sub>2</sub>O thin films have high Hall mobility ( $51 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) at 300 K room temperature. High temperature (300 K to 700 K) Raman studies were carried out to confirm the phase by keeping the CuO sample on a hot stage in argon atmosphere, the phase change is observed at 723 K.

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9:40am **TF-WeM6 A Study to Reduce Deviations of Sensitivities to Constant CO Gas of Pt Doped SnO<sub>2</sub> Thin Film Based Micro Gas Sensor.** Jun-gu Kang, Sungyunkwan University, Korea, Republic of Korea, J.-S. Park, Korea Electronics Technology Institute (KETI), Republic of Korea, H. Lee, Sungyunkwan University, Korea, Republic of Korea  
Gas sensors based on metal oxide semiconductors have been used for detecting low level toxic and explosive gas for a long time, since metal oxide semiconductors enable to make gas sensors operate at low power consumption as well as supply with low price. Recently, researchers have studied nanostructured metal oxide semiconductors to improve sensitivity by enlarging the surface area that react gas directly. However, such gas sensors based on nanomaterials suffer from a large deviation of sensitivities among gas sensors. In the present work, we employed a SnO<sub>2</sub> thin film, with a well-defined surface area and thus a small deviation in sensitivity, and, in addition, doped it with a noble metal to improve stability. For the fabrication of the micro platform, which consists of a micro heater and sensing electrode on SiN<sub>x</sub> membrane, we started with a Si substrate(100) by deposition of a low stress 2 $\mu\text{m}$ -thick SiN<sub>x</sub> film using a low pressure chemical vapor deposition process. After deposition of a tantalum layer, serving as an adhesion layer, a Pt film was deposited as a heating element. The heater layer of Pt on Ta was patterned and etched using a dry etching process with an advanced oxide-etching equipment. An 1 $\mu\text{m}$ -thick insulating layer was produced on the patterned heater layer. A sensing electrode layer of Pt was sputtered and then patterned using a dry etching process. A SnO<sub>2</sub> thin film, as sensing material, was deposited with RF sputtering on the sensing electrode of a micro platform. And then, Pt doping was done by Pt thin film sputtering, and heat treatment to form Pt islands on SnO<sub>2</sub> thin film. After finishing the front side process of the wafer, we patterned the back-side of the wafer and etched it in a KOH solution to release the SiN<sub>x</sub> film as a membrane. In this presentation, sensing properties of fabricated gas sensors to indoor pollutant gases such as CO, HCHO and toluene will be presented. We will also show the possibility to reduce deviations of sensitivities to the constant CO gas concentration among thin film based micro gas sensors.

[Acknowledgement] This work was supported by the "Project (10043800) of the Technology Development Program of S/W Convergence Component" by MOTIE and KEIT in Korea. The authors appreciate government for research funding.

10:20am **TF-WeM8 Barium Oxide Glass Targets for Thin Film Dielectric Material.** C. Stutz, Air Force Research Laboratory, G. Kozlowski, University of Dayton Research Institute, S. Smith, University of Dayton Research Institute, J. Goldstein, Air Force Research Laboratory, G. Landis, University of Dayton Research Institute, C. Hollbrook, John Jones, Air Force Research Laboratory

Barium-rich, alkali free glasses are expected to be useful for high voltage capacitors due to the high energy storage capacity of Barium, the high resistivity of alkali-free glasses, and the possibility of forming a smooth, glassy surface to minimize the surface electric field intensity. To better understand the structure-property relationships in these glasses, we have synthesized 17 samples of eight different compositions ranging from 22% to 48% mol percent BaO, with a constant ratio of SiO<sub>2</sub> to B<sub>2</sub>O<sub>3</sub>. These samples were studied with Raman and showed a narrow intermediate range (29-32% BaO) that was independent of BaO content between the stressed-rigid elastic phase (24-29% BaO) and the flexible elastic phase (32-48% BaO). The samples were fabricated into 2.5 cm diameter targets for a pulsed laser deposition (PLD) thin film process. They were nominally clear and made from a melt that was poured into a mold. However the targets would break up when exposed to the 248 nm one joule laser and the deposition onto the substrate was negligible. The targets were also annealed at 50 degrees below the glass transition temperature, but this did not help. A new target process was developed that was more involved and instead of pouring the melt into a form it was poured into de-ionized water to be quenched then ground using a mortar and pestle. After grinding the glass was pressed into a pellet and sintered for densification. The new targets were not transparent. Due to the new process the glass targets were able to withstand the 248 nm one joule laser. Also good coverage of the substrate was obtained during PLD growth. We will discuss the characterization of the thin films based on results from atomic force microscopy, x-ray, and Raman spectra. Also impedance spectroscopy will be presented.

10:40am **TF-WeM9 Near Infrared Photodiodes Comprising Iron Disilicides Prepared by Sputtering.** T. Yoshitake, Kyushu University, Japan, M. Shaban, Aswan University, Egypt, N. Promros, King Mongkut's Institute of Technology Ladkrabang, Thailand, Motoki Takahara, T.M. Mostafa, Kyushu University, Japan, R. Baba, Kysushu University, Japan  
Semiconducting iron disilicide ( $\beta\text{-FeSi}_2$ ) is a new candidate applicable to near-infrared photoelectronic devices [1-3], because it possesses features such as a direct optical band gap of 0.85 eV above an indirect gap (0.76 eV) and a large absorption coefficient, which is  $10^5 \text{ cm}^{-1}$  at 1.0 eV[4]. Since  $\beta\text{-FeSi}_2$  can be epitaxially grown on Si, a heterojunction diode comprising a  $\beta\text{-FeSi}_2$  film and singlecrystalline Si substrate is a device that can be briefly formed by employing vapor deposition. For near-infrared light detection in the Si/b-FeSi<sub>2</sub> heterojunction diodes, near-infrared light transmitted through the front-side Si substrate can be absorbed in the depletion region of the back-side  $\beta\text{-FeSi}_2$  film.

In our previous works, we have progresses researches on p-type Si/n-type  $\beta\text{-FeSi}_2$  heterojunction diodes, totally from the epitaxially growth of  $\beta\text{-FeSi}_2$  film on Si(111) by sputtering [5] to the evaluation of p-type Si/n-type  $\beta\text{-FeSi}_2$  heterojunctions as photodetectors [6,7]. It was confirmed that  $\beta\text{-FeSi}_2$  in the heterojunction evidently contributes to the photodetection of near-infrared light from the photoresponse spectrum. In addition, the heterojunction clearly exhibited current due to photogenerated carriers for 1.33  $\mu\text{m}$  light in the *I-V* curves in comparison with that in the dark. The detectivity at temperatures lower than 100 K reach approximately  $2 \times 10^{11} \text{ cmHz}^{1/2}/\text{W}$ , which is comparable with that of existing near infrared photodiodes comprising PbS and InAs at the same temperature. However, the external quantum efficiency is less than 10 % [6,7].

In this presentation, the progress thus far of our research and recent problems that we are facing and should be solved for the next step will be introduced. A serious problem for the heterojunctions is that a barrier due to a band offset appears in the valence band and it prevents from the flow of photogenerated carriers from the n-type  $\beta\text{-FeSi}_2$  layer to the p-type Si layer. The opposite combination, namely n-type Si/p-type  $\beta\text{-FeSi}_2$ , is structurally ideal because of it has no barriers due to the band offset. In order to form p-type  $\beta\text{-FeSi}_2$ , the residual carrier density should be reduced for controlling the conduction type. Carbon doping, which might be effective for a reduction in the carrier density, will be introduced.

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- [2] Y. Maeda et al. SPIE Proc. 3419 (1998) 341916.
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11:00am **TF-WeM10 Epitaxial Growth of Ag/MgO(001) and Ag/Si(111) by Pulsed Laser Deposition for Use as an Alternative to Single Crystal Metallic Substrates.** *Jeff Terry, D. Velazquez*, Illinois Institute of Technology

Single crystal metal substrates are often used as platforms for growth. Epitaxial films are potentially cheaper starting points for chemical synthesis single crystal substrates. We report on the epitaxial growth of thin silver films in the crystallographic orientations (001) and (111) using pulsed laser deposition (PLD). The films were deposited on MgO(001) and Si(111) substrates to a thickness of 40 nm at 150 °C and 170 °C, respectively. For the first 2-4 nm, growth was three-dimensional at which point a gradual transition to two-dimensional growth occurred, as monitored by reflection high-energy electron diffraction (RHEED). Scanning tunneling microscopy (STM) was used to show that the surface roughness was less than 5 Å in 100×100 nm<sup>2</sup> for either orientation. Photoelectron spectroscopy (PES) was used to probe the chemical state of the films. The positions of the Ag 3d<sub>5/2</sub> and Auger MNN peaks were used to calculate the Auger parameter to be 726.3 eV, which corresponds to metallic Ag. These films may be inexpensive replacements for single crystal Ag substrates in certain applications.

11:20am **TF-WeM11 Enhancement of Uniformity and Whiteness of Electrogalvanized Steel Sheet by Deposition of a Transition Metal Thin-Film between Deposited Zinc and Iron Substrate.** *Wonhwi Lee*, POSCO, Republic of Korea

Electrogalvanized steel sheets are widely used in automobiles, building interior decorations and home appliances because of its excellent surface uniformity and formability. Among the wide areas of its applications, barely post-treated electrogalvanized steel sheets used in home appliances are processed no further treatments but to form essential resin coating layers for the functions of anti-fingerprinting or Chromate-free. In this case, it is a key quality to have uniformity and good whiteness of its surface.

However, the electrogalvanized zinc layer with partially oriented and enlarged grains is normally produced due to the epitaxial growth along the iron substrate. The oriented zinc grains on the surface lead to the dispersion of reflecting light that results in lowering whiteness.

In addition, iron oxide scales or oil stains remained on the substrate even after the all pre-treatments of rinsing, degreasing and pickling processes may induce poor uniformity of the galvanized surface.

To solve these problems which are derived from the iron substrate, some manufacturers have created a nickel nano-layer on a substrate. The deposition of the nickel layer on a substrate has brought a galvanized surface not only the uniformity but also the better whiteness. This is because the nickel layer significantly enhances the quality of deposited zinc since the condition of substrate is no longer transferable. Recently, however, its high cost as a raw material and harmful fumes during welding processes have arisen as critical problems to solve.

In this article, we suggest to deposit a thin film of a single or as an alloy of transition metals between the deposited zinc and the iron substrate. The thin layers were made by electrodeposition method and several transition metals were selected for the coating materials. These coating materials were electrodeposited with the coating weights in the range of 10 to 50mg/m<sup>2</sup>. The results show that the better whiteness and uniformity of the galvanized zinc can be achieved by the thin layer which minimizes the influences from the substrate and interrupts coarsening of zinc grains as well. Furthermore, it is a remarkable finding that the zinc grains are randomly oriented on the surface with much smaller sizes.

11:40am **TF-WeM12 Effect of Organic Substrate Materials on Electrical and Mechanical Properties of Cr Thin Film Prepared by DC Magnetron Sputtering.** *H. Park, D. Kim, I. Park, K. Bae*, Pusan National University, *Young-Rae Cho*, Pusan National University, Republic of Korea

Sputtering is one of the most popular physical vapor deposition methods due to their versatility and reproducibility. Effect of organic substrate materials on electrical and mechanical properties of chrome (Cr) thin films was investigated. For the application of wearable or flexible electronic devices, the materials for substrate were selected from flexible organic materials such as leather, cloth (melton), paper and plant. The Cr films were deposited on the several different substrates by DC magnetron sputtering. The thickness of Cr films was varied from several tens to 500 nm. For the explanation of the electrical and mechanical properties, a sheet resistance and fatigue properties in cyclic stress of the samples were characterized. When we deposited Cr film over 400 nm in thickness, the sheet resistance of Cr film on smooth substrates (leather, A4 paper, melton) showed small

values. However, the sheet resistance of Cr film on rough substrates (toilet paper, wool) showed very large values. Furthermore, we will try to prepare more wide range of organic substrates such as rubber and plant. Finally, the relationships between their physical properties of samples and the change of substrate shape will be discussed in detail.



## Energy Harvesting & Storage Room: Mauka - Session EH-WeP

### Energy Harvesting & Storage Poster Session

**EH-WeP1 Lifetime Prediction of Encapsulated Organic Photovoltaic Modules in Accelerated Conditions, SungHyun Kim, N. Kim,** Korea Electronics Technology Institute (KETI), Republic of Korea

Organic photovoltaic (OPV) modules consisting of ITO/ZnO/photoactive layer/PEDOT:PSS/Ag inverted structure were fabricated using slot-die coating method and encapsulated by a barrier film deposited on polyethylene terephthalate (PET). Effective water vapor transmission rate was measured in both the transient and steady-state regimes of PET with a barrier layer. Acceleration tests were conducted under 65°C and 85% relative humidity to investigate the degradation of OPV modules. Total amount of water vapor into OPV module was calculated and correlated with the degradation rate of it. The lifetime of encapsulated OPV module under ambient condition is calculated and will be presented in the conference.

**EH-WeP2 Effect of Surface Roughness on the Contact Resistance between the Gas Diffusion Layer and Bipolar Plate in a Polymer Electrolyte Membrane Fuel Cell, Changhee Choe, J.J. Lee,** Seoul National University, Korea, Republic of Korea

In a polymer electrolyte membrane fuel cell (PEMFC), one of the most important factors affecting the performance is ohmic loss arising from the contact resistance at the interface of the gas diffusion layer (GDL) and bipolar plate (BP). As a method to reduce the contact resistance between the bipolar plates and gas diffusion layer, the contact area of the bipolar plates were increased by inducing roughness on the surface. The environment of the highly porous GDL being pressed by an external compaction pressure was simulated, and the contact area between the GDL and bipolar plates was calculated. The calculated contact resistance using the contact area was compared with the experimental contact resistance results of the bipolar plates polished with various grades of abrasive paper. As the average surface roughness increased, the contact resistance values decreased, which is in good agreement with the results of this study. In a single cell test, the efficiency of the cell increases when the rough bipolar plate is used.

**EH-WeP3 Fully flexible and Transparent Piezoelectric Touch Sensor is based on ZnO nanowires with BaTiO<sub>3</sub>, MoolKyul Kang, J.H. Park, K.I. Lee,** Korea Electronics Technology Institute (KETI), Republic of Korea, *B.K. Ju,* Korea University, Republic of Korea, *C.S. Lee,* Korea Electronics Technology Institute (KETI), Republic of Korea

ZnO nanowires (NWs) can be grown by chemical approach at low temperature (<100 °C) on any substrate and any shape substrate. A relatively small force is required to induce the mechanical agitation, so that it can be fabricated sensitive devices.[1] But piezoelectric device based on ZnO NWs, which can not improve the piezoelectric properties of a single material due to a low piezoelectric d constant of ZnO NWs (d≈12pC/N).

In this paper, we demonstrated fully flexible and transparent piezoelectric touch sensor based on ZnO NWs, and composed that touch sensor with BaTiO<sub>3</sub> of Perovskite structure for improving piezoelectric properties. In order to maintain the flexibility of sensing spot, the BaTiO<sub>3</sub> (10 wt%) are dispersed in flexibility-improved SiO<sub>2</sub> capping solution and coated on ZnO NWs surface as a capping layer by spray coating method. Also, By replacing Indium tin oxide (ITO) electrodes with transparent flexible CNT-Ag nanowires electrode, the flexibility of the entire structure was enhanced. ITO is commonly used as transparent electrodes. However due to its high cost and limited supply of indium, the fragility and lack of flexibility of ITO layer, its alternative are being sought. It is expected that conductive films using carbon nanotubes and Ag NWs could be a prospective replacement of ITOs.

The ZnO NWs based sensor generated the output voltage of ~ 50 mV. The sensor with BaTiO<sub>3</sub> generates a higher output voltage (~1.2 V) than a ZnO NWs based sensor. We confirmed that the output voltage of sensor with ZnO NWs and BaTiO<sub>3</sub> was dramatically increased. We measured the resistance of capping layer and CNT-Ag NWs electrode during the periodic bending. When bent and flexed over 1,000 cycles, the films did not show significant degradation in sheet resistance compared to Ag thin film and ITO film on the same PET substrate. The bending test results conducted to confirm the mechanical stability of capping layer and CNT-Ag NWs as a electrode. The measurement results suggest that the our Piezoelectric touch sensors are suitable for flexible device such as flexible touch sensor, wearable and rollable touch panel.

[1] Zhong Lin Wang, "Piezopotential gated nanowire devices: Piezotronics and piezo phototronics", *Nano Today*, 5, 2010, pp.540~552

**EH-WeP4 Analysis of Steam Reforming Reaction by Vibrationally-Excited Methane Based on First-Principle Molecular Dynamics Simulation, Naoki Yokoyama, Y. Higuchi, N. Ozawa, H. Yugami, M. Kubo,** Tohoku University, Japan

For an environmentally-friendly energy system, hydrogen is expected as a resource to replace fossil fuels. Recently, steam methane reforming (SMR) is mainly used for hydrogen production. However, the promotion and the cost reduction of hydrogen production in SMR is strongly desired for stable supply of hydrogen because SMR requires a large amount of heat. To increase hydrogen production, Maegami et al. proposed the vibrationally-excited method, in which infrared light vibrationally excites a C-H bond of a CH<sub>4</sub> molecule [1]. While hydrogen production is promoted by the vibrational excitation of a CH<sub>4</sub> molecule, the detailed analysis at atomic scale is necessary for higher efficient hydrogen production. Thus, by using the first-principles molecular dynamics (FPMD) simulation method, we examined the effect of vibrational excitation of the C-H bond on chemical reaction dynamics for hydrogen generation from CH<sub>4</sub> and H<sub>2</sub>O.

To reveal the chemical reaction dynamics, we simulated collision process of a H<sub>2</sub>O molecule with a CH<sub>4</sub> molecule in the vibrationally-excited state by using our development FPMD code "Violet" [2]. The vibrationally-excited state was reproduced by extending a C-H bond. After the collision, a dissociation of C-H bond was observed. Moreover, the H atom of the dissociated C-H bond reacted with a H atom of the H<sub>2</sub>O molecule, and H<sub>2</sub> and CH<sub>3</sub>OH were generated. Next, to examine the effect of vibrational excitation, we simulated collision processes with the collision angle from -60° to 60° and collision energy from 9 eV to 20 eV in the ground state and the vibrationally-excited state. In the ground state, hydrogen molecules were generated in the range of collision angle from -50° to -10° and collision energy from 17 eV to 20 eV. On the other hand, in the vibrationally-excited state, hydrogen molecules were generated in the range of collision angle from -60° to 0° and collision energy from 14 eV to 20 eV. Therefore, in the vibrationally-excited state, H<sub>2</sub> molecules were generated in a wider range of collision angle and lower collision energy than those in the ground state. This simulation result suggests that the H<sub>2</sub> generation was promoted by vibrational excitation, which is consistent with the experiment [1]. We also examined the later process after the H<sub>2</sub> and CH<sub>3</sub>OH were generated. Accordingly, CH<sub>2</sub>(OH)<sub>2</sub>, HCHO, HCOOH, and CO were observed as intermediate products. Consequently, we indicated the chemical reaction dynamics of H<sub>2</sub> generation from H<sub>2</sub>O and vibrationally-excited CH<sub>4</sub> in gas phase.

[1] Y. Maegami, F. Iguchi, and H. Yugami, *Appl. Phys. Lett.*, **97**, 231908 (2010).

[2] T. Shimazaki and M. Kubo, *Chem. Phys. Lett.*, **503**, 316 (2011).

**EH-WeP7 The Integration of XPS and Ar-Gas Cluster Ion Sputtering to Study the Corrosion of Stainless Steel Surfaces, D. Surman,** Kratos Analytical Inc., *Helen Brannon, J. Counsell, S. Hutton,* Kratos Analytical Ltd., UK, *J. Morrison,* University of Birmingham, UK, *C. Blomfield,* Kratos Analytical Ltd., *A. Roberts,* Kratos Analytical Ltd., UK

Stainless steels are vital construction materials in all areas of industry, combining excellent corrosion resistance with good mechanical properties. For these reasons, stainless steels are used extensively in power stations of all varieties – of particular interest is the use of stainless steel in Pressurised Water Reactor (PWR) type nuclear power plants, such as the Sizewell B power station, Suffolk, UK.

The corrosion of steel in contact with hot, pressurised water in a PWR is a common problem. This side reaction is undesirable due to the reduced heat transfer efficiency caused by the deposited oxide layers.

Stainless steel's corrosion resistance is derived from the formation of a passivation layer at the surface of the material. Under atmospheric conditions this is thought to be a vanishingly thin layer of Chromia (Cr<sub>2</sub>O<sub>3</sub>), however, under conditions found in the coolant cycles of a PWR, it is thought that the passivation layer grown forms a double layer – the inner layer consisting of corrosion resistant, non-stoichiometric Chromite (FeCr<sub>2</sub>O<sub>4</sub>), while the outer layer consists of non-stoichiometric Nickel Ferrite (NiFe<sub>2</sub>O<sub>4</sub>). The thickness of this film is believed to vary with the steel surface finish, and the Environment Degradation Group at the University of Birmingham has recently begun a programme to study the dependence of corrosion rate and passivation layer thickness on surface finish, system chemistry and temperature.

The samples were ground to a 120 and 1200 grit finish using silicon carbide paper to produce samples with significantly difference roughness levels

(approximate  $R_a$  values of 1050 and 110 nm, respectively), before being inserted into a flowing rig, where they were exposed to deoxygenated water at pH 10 and 300°C at a pressure of 10 MPa. Sets of samples were removed from the rig every 250 hours, up to 1000 hours total exposure time.

X-ray photoelectron spectroscopy (XPS) was used to determine the type of corrosion chemistry that occurs. It was combined with a high energy, medium sized argon gas cluster source, which is shown to be advantageous compared to a conventional monatomic argon when depth profiling such layered structures, causing reduced structural and chemical damage from the ion beam sputtering process. Data acquisition at small analysis areas gives well resolved spectra, revealing the multi-layered oxide structures produced from the corrosion process. [1] Depth profiling of the Passive Layer on Stainless Steel using Photoelectron Spectroscopy, Wendy Fredriksson, Uppsala University [2] Applied Surface Science, 257, (2011), 2717–2730 [3] The Radiochemistry of Nuclear Power Plants with Light Water Reactors, By Kark-Heinz Neeb

**EH-WeP9 Current Enhancement in Hybrid Solar cells prepared with Quantum Dots and PFN**, *D. Esparza, J. Oliva UC, T. Lopez, I. Zarazua, Elder De la Rosa*, Centro de Investigaciones en Optica A.C., Mexico

This work presents a hybrid solar cell made with quantum dots and poly [(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN), which is commonly used as electron transport layer in organic solar cells. Those cells were fabricated by Successive Ionic Layer Adsorption and Reaction (SILAR) method and spin coating. The configuration used in this work was: TiO<sub>2</sub>/PbS/PFN/CdS/ZnS. The presence of PFN produced an increase of 33% in the short circuit current ( $J_{sc}$ ) respect to the sample of reference: TiO<sub>2</sub>/PbS/CdS/ZnS. Such increase in current caused an increment of the cell efficiency from 2.6% to 3.6%. PTB7 was also used as donor in our hybrid solar cells instead of quantum dots, when the PFN is added in this system, the current increased 60% respect to the cell of reference and the efficiency increased from 1.1% to 3.0%.

**EH-WeP11 On the Role of Plasma System for CO<sub>2</sub> Dissociation**, *H.Y. Chang*, Korea Advanced Institute of Science and Technology (KAIST), South Korea

The CO<sub>2</sub> capture and storage technology (CCS technology) needs immediate action, but does not have complete solutions yet due to the efficient and economical CO<sub>2</sub> conversion problems. In this presentation, the governing fundamental quantities will be identified to obtain the maximum energy efficiency and capacity for CO<sub>2</sub> dissociation. Several CO<sub>2</sub> conversion ideas will be introduced, describing the advantages and disadvantages of each conversion techniques. The plasma reactor has been known as one of the most promising candidate for CO<sub>2</sub> dissociation. However, the problems on how to achieve high efficiency, stable discharge at atmospheric pressure, and reliability at high power density should be solved. The ICP( Inductively coupled plasma ) source will be introduced along with other sources such as microwave, DBD( Dielectric barrier discharge), and DC for the efficient CO<sub>2</sub> dissociation. In this presentation, the technical issues for the mass production of CO<sub>2</sub> conversion will also be discussed.

**EH-WeP15 Positive Temperature Coefficient of CdS/Cu(In,Ga)(S,Se)2 Solar Cell**, *Sangmok Kim, C.-W. Jeon*, Yeungnam University, Republic of Korea

In the recent years, Cu(In, Ga)Se<sub>2</sub> (CIGS)-based thin-film solar cells with efficiency of readily over 20% have been reported by several groups, therefore, it is strongly expected to replace the crystalline silicon solar cell rapidly. Unlike crystalline silicon cell of a homo-junction, CIGS thin-film solar cell consists of hetero-junction between absorbing layer and CdS buffer layer. In CBD (Chemical Bath Deposition)-CdS, which is commonly used for a high efficiency CIGS solar cell, the kind and concentration of source materials and bath temperature is known to affect the characteristics of the CIGS/solar cell as well as CdS film properties. In general, the efficiency of solar cell decreases with increasing ambient temperature due to the reduction of band gap energy of absorber layer and higher reverse saturation current at an elevated temperature. In other words, temperature coefficient (TC) of a solar cell is normally negative. [1] While this tendency is observed in the CIGS/CdS solar cells, according to this study, it was confirmed that the behavior of TC depends on the synthesis conditions of the CdS. In this study, we prepared several solar cells of ZnO/CdS/CIGS/Mo/glass with different CdS deposition conditions by changing [Cd] and [S] in the solution over the range of [Cd]=15~135mM, [S]=12.5~50mM. And the variation of TC's were monitored by measuring IVT (Current-Voltage-Temperature) in the temperature range of 10~50°C. Some of solar cells with high [Cd] of low [S] were found to have positive TC's. In these devices, while Voc decreased as expected with increasing temperature, fill factor increased on the contrary. The enhancement of fill factor stemmed from the lower series resistance at higher operating

temperature. The thermal characteristics of the solar cells depending on the [S]/[Cd] composition ratio in the solution will be discussed with the results of IV, CV, QE measurements. Acknowledgement This research was financially supported by the Ministry of Knowledge Economy(MKE), Korea Institute for Advancement of Technology(KIAT) and Dae-Gyeong Leading Industry Office through the Leading Industry Development for Economic Region. References [1] A.Virtuani, D. Pavanello, and G. Friesen, 25th European Photovoltaic Solar Energy Conference and Exhibition/5th World Conference on Photovoltaic Energy Conversion. 2010, p6-10

## Nanomaterials

### Room: Mauka - Session NM-WeP

#### Nanomaterials Poster Session

**NM-WeP1 Facile Preparation of (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> Particles with High Fluorescence Quantum Yield**, *Shun Kitazawa, K. Sato*, Tokyo Denki University, Japan, *N. Fukata*, National Institute for Materials Science, Japan, *K. Hirakuri*, Tokyo Denki University, Japan

Fluorescence materials are used for a broad range of industry and biomedical technology applications involving electroluminescent displays and fluorescent contrast dye of bioimaging. However, they are confronting some serious problems, such as complicated preparation techniques and low production yield. Therefore, it is necessary to develop new synthesis approaches for realization of facile preparation and large-scale production of fluorescence materials. We have prepared ammonium hexafluorosilicate ((NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub>) particles as one of the fluorescence materials using a chemical route with good productivity. These (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> particles possess excellent advantages such as high-efficiency fluorescence and long-term photostability compared to the other silicon (Si)-based fluorescence materials. In this presentation, we propose a new way to fabricate (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> particles by simplified procedures based on a chemical approach. The features of our synthesis technologies are to adopt the simplified synthesis system in which only Si powders and chemicals consisting of nitric hydrofluoric acid solution were hermetically sealed in polymeric container without any vacuum systems. The (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> particles with mean diameter of approximately 700 nm were densely deposited on the Si substrate by using this novel synthesis system. The crystalline structures and the chemical compositions of (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> particles were confirmed by X-ray diffraction (XRD) patterns and Fourier transform infrared (FTIR) spectroscopy. The XRD patterns were consistent with the sharp diffraction peaks derived from the cubic phase of crystalline (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> with space group of Fm3m(225). For the FTIR characterization, the absorption peaks related to the SiF<sub>6</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup> ions in addition to N-H mode were also observed. These results demonstrate that the (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> particles are not only maintained high crystallinity but also composed of ammonium and silicon fluoride as major ingredients. Such (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> particles exhibited bright reddish orange fluorescence with a peak wavelength at 630 nm under the irradiation of xenon lamp equipped with optical bandpass filter of 365 nm. The main advantages of (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> particles are to attain the high fluorescence quantum yield of 34 %. Additionally, the fluorescence intensity was maintained about 80% of the initial maximum intensity even after aging beyond six months. Therefore, our suggested synthesis technologies can provide a new chemical route for the fabrication of high-brightness and stable fluorescence particles.

**NM-WeP2 The Flashover and Hydrophobicity Recovery Characteristics of RTV Silicone Rubber Nanocomposites**, *K.J. Lim, JiSung Park, J.H. Kwon*, Chungbuk National University Korea, Republic of Korea

Many researches about silicone rubbers which are applied to materials of outdoor insulators and bushings have been conducted. Recently, As nano technologies have been developed, nano fillers are added to electrical materials to improve mechanical and electrical performances. In this paper, Room Temperature Vulcanizing(RTV) silicone rubber nanocomposites was studied about electrical performances and hydrophobicity recovery under the AC electrical stress and contamination. Silica and ATH was added as nano fillers, and specimens was contaminated by a dipping method. Flashover voltage and contact angle was measured. As a result, Nano filler improved electrical performances, and not reduced the hydrophobicity recovery.

**NM-WeP3 N-containing ZnO Rods with Tunable Concentration Synthesized by Hydrothermal Method, Taiki Ihara, K. Katsumata, Tokyo Institute of Technology, Japan, T. Watanabe, Meiji University, Japan, K. Okada, N. Matsushita, Tokyo Institute of Technology, Japan**

Recent research has shown that N-doping into TiO<sub>2</sub>, Ta<sub>2</sub>O<sub>5</sub>, or LaTaO<sub>4</sub> is effective for narrowing the band-gap and attaining the visible-light photocatalysis. N-doped metal oxide powder is commonly synthesized by elevating metal oxide specimens temperature over 500°C with flowing ammonia gas or nitrogen. In this study, we succeeded in synthesizing N-containing ZnO rods by hydrothermal process using ammine-hydroxo zinc complex solution at 100°C.

10 ml of 2.5 M NaOH (aq) was added in drops to 15 ml of 0.5 M Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O aqueous solution over stirring vigorously. The resulting hydroxide slurry was centrifuged and the supernatant was removed. The hydrated precipitate was dissolved in 50 ml of 6.6 M NH<sub>3</sub> (aq) to form a stock solution. 30 ml of the solution was transferred into a 35 ml Teflon-lined stainless steel autoclave, followed by heating in an oven at 100°C for 6-24 h. After the reaction, the precipitates were separated by centrifugation, and then washed with water.

The diffraction peaks in XRD patterns for synthesized sample was good agreement with those of the hexagonal wurtzite structure of ZnO (JCPDS card 36-1451). The morphology of the ZnO particles were hexagonal rods and the size was about 20 μm in long axis and about 1 μm in diameter. UV-vis spectra for the sample prepared for different reaction time revealed that the absorption band was shifted to visible region as increasing the reaction time. In the raman spectra, typical Ramanactive modes for ZnO (E<sub>2</sub>, A<sub>1</sub>(TO), A<sub>1</sub>(LO), E<sub>1</sub>(TO), and E<sub>1</sub>(LO)) were clearly observed for all samples. In addition to the above, new peak was observed at 582 cm<sup>-1</sup> on N-containing ZnO rod which is attributed to the E<sub>2</sub>(Zn-N) mode. N concentration calculated from XPS data was increased as increasing the reaction time. XPS spectrum of N 1s for the sample prepared at 100°C for 6 h showed the asymmetric broad peak indicating that more than one chemical states of N were present. The binding energy at ~399.0 eV was attributed to the surface species of NH<sub>3</sub> or amines. The another peak at ~397.0 eV was ascribed to N atom in Zn-N bond indicating that N was incorporated in ZnO rods.

**NM-WeP4 Synthesis of TiO<sub>2</sub> Monolith Structure Modified Nanotubes, Ken-ichi Katsumata, Tokyo Institute of Technology, Japan, M. Yamamoto, Tokyo Institute of Technology, N. Matsushita, K. Okada, Tokyo Institute of Technology, Japan**

TiO<sub>2</sub> is actively studied as photocatalyst with environmental applications effected on photocatalytic performance by adjusting many factors in the structure. Recently, TiO<sub>2</sub> monolith with unique three-dimensional structure has been reported. This is expected to various applications because the pore size and volume are able to control by the synthesis condition. The material, generally used as an adsorbent, extended the applications with visual light-sensitive. In this research, TiO<sub>2</sub> monolith was synthesized with various heating temperatures, and its photocatalytic activity was investigated under visible light.

Porous TiO<sub>2</sub> monolith was synthesized by sol-gel method. HCl, the aqueous solution of Polyethylen glycol (10000) in water and N-methyl formamide are added to Titanium propoxide stirring under ice-cooled condition. The gel is aged at 60°C for 24 h and heat-treated at 200°C for 2 h in stainless-steel autoclave with a Teflon inner liner. The wet gel plate thus obtained is washed by 1-propanol for 12 h, slowly drying for 1 week at room temperature and calcinated at 600, 700, 800 and 900°C for 5 h. Each of temperature rising rates is 1.0 °C/min. Each sample is immersed in the CuCl<sub>2</sub> (molar ratios of Cu/TiO<sub>2</sub> = 1.0 × 10<sup>-3</sup>) aqueous solution at 90°C for 3 h. After washing by water and drying at 80°C, they are measured photocatalytic activity.

The samples heated at 600, 700, and 800°C had monolith structure, and the pore size and primary particle size depend on calcination temperature. However, the sample heated at 900°C did not maintain monolith structure. From the results of XRD patterns and Raman spectra, anatase was main phase at less than 700°C while rutile started to be observed at more than 700°C. It is expected that Cu(II)-grafted rutile monolith samples exhibit excellent photocatalytic activity under visiblelight. In addition, it was succeeded that rutile nanotubes were formed on the surface of the monolith structures by solvothermal treatment. The monolith with nanotubes had very high specific surface area compared to the monolith without nanotubes. In detail, I will report the activity on the day.

**NM-WeP5 Surfactant-Free Solution Phase Synthesis of CuO Nanostructures with Controlled Dimensions, BG Ganga, P. Santhosh, Indian Institute of Technology Madras, India**

CuO is a versatile p-type transition metal oxide semiconductor with a narrow band gap in the region 1.2-1.8 eV [1]. It is a naturally abundant, nontoxic and stable material and is commonly used as a component material

in a wide range of applications such as gas sensing, catalysis and energy storage and conversion [2-4]. Three dimensional ellipsoidal shaped CuO nanostructures and two dimensional nanosheets have been successfully synthesized using surfactant free simple solution phase method. Synthesis of CuO nanostructures was followed by structural, morphological characterization using X-ray diffraction, Scanning Electron Microscopy and Transmission Electron Microscopy. We have demonstrated that morphology and dimensionality of nanostructures can be controlled by changing the initial reactant concentrations. It is observed that ordered aggregation and growth of smaller CuO subunits generates an ellipsoidal shaped morphology at lower reactant concentration, while at higher reactant concentration, sheet like structures are generated. Self-assembled structures provide an opportunity to investigate the formation mechanism and aggregation based growth of nano subunits as fundamental building blocks. This bottom-up method offers facile synthesis of nanostructures of controlled morphology and functionality. We have also observed a change in morphology as the nanostructures were thermally annealed. A morphological transformation from rod-like to plate-like structure was observed as the flake-like nanostructures were annealed at 400°C and 600°C respectively. The formation mechanism that plays behind the generation of different CuO nanostructures is explored. Optical properties are investigated using UV-Vis spectroscopy and Raman spectroscopy. We found that morphology of the nanostructure strongly reflect on the optical properties as band gap widening and the change in the position and width of Raman modes.

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**NM-WeP16 Nanocrystalline Diamond Powder Fabricated using Coaxial Arc Plasma Equipped with Chromium-Blended Graphite Targets, Aki Tominaga, H. Naragino, Kyushu University, Japan, D. Deguchi, Kyushu Institute of Technology, Japan, K. Takeda, Fukuoka Institute of Technology, Japan, T. Yoshitake, Kyushu University, Japan**

Nano-sized diamond, such as nanocrystalline diamond (NCD), ultrananocrystalline diamond (UNCD), and diamondoids, is a new nanocarbon. Since it was reported that diamond exhibits strong photoluminescence due to nitrogen-vacancy center and generates defect-induced magnetization, the application of nanodiamonds to drug delivery has received much attention. In order to induce the novel functionalities in diamond, doping should be carried out precisely.

Nano-sized diamond powder has ever been fabricated by detonation, and the doping of foreign elements to the powder has been made mainly by ion implantation. In-situ doping during the formation should enable us to incorporate foreign element atoms into nano-sized diamond, effectively and simply. In this work, we employed a coaxial arc plasma gun for the formation of UNCD powder and demonstrated the in-situ doping of chromium during the formation. A coaxial arc plasma gun (ULVAC APG-1000) equipped with a chromium-blended graphite target was operated in vacuum and hydrogen atmospheres. The head of the gun was pointed at a quartz plate. The distance between the plate and gun head was 15 mm. Quartz plate's temperatures are 550 °C. Films that quickly and automatically exfoliated from the plate were gathered, and they were smashed into powder. The XRD pattern of 10 at% Cr doped powdered diamond nanoparticles, measured with 12 keV X-ray at beamline 15 of the SAGA-LS, exhibited obvious peaks due to diamond-111 and 220. The electron diffraction also exhibited the similar results. Chromium K-edge XAFS spectra were measured at beamline 6 of the SAGA-LS (Kyushu University Beamline). The magnetic properties were measured by a vibrating sample magnetometer and superconducting quantum interference device. The details will be reported in the conference presentation.

This work was partially supported by JSPS KAKENHI Grant Number 26790019, Kazuchika Okura Foundation, and JGC-S scholarship foundation. The experiment using synchrotron radiation were performed at the beamline BL15 of the SAGA Light Source with the approval of the Kyushu Synchrotron Light Research Center (Proposal No. 1303019A). XAFS measurements were performed at Kyushu University Beamline (SAGA-LS/BL06).

**NM-WeP18 Effect of Heat Treatment on the Damping Capacity and Texture of Magnesium Alloy**, *Jongyoung Lee*, College of Engineering, Pukyong National University, Republic of Korea, *H. Kwon*, Pukyong National University, Republic of Korea, *J. Choi*, College of Engineering, Pukyong National University, Republic of Korea, *K. Kim*, Pukyong National University, Republic of Korea

Much attention has been paid on Magnesium alloys in electronics and automobiles industrial parts, due to lightweight and other excellent properties, such as low density, high specific strength, and good castability. However, due to the limited number of slip systems associated with their hexagonal close-packed crystal structure, both magnesium and its alloys show poor room-temperature formability. It is well-known that crystallographic texture plays an important role in both plastic deformation and macroscopic anisotropy of magnesium alloys. Therefore, many authors have been studied to understand the texture control of magnesium alloys, focusing on improvement of the room temperature formability in Magnesium alloy. However, despite having many excellent properties in magnesium alloys, the study for various properties of magnesium alloys have not been clarified enough.

It was well-known that magnesium alloys have a good damping capacity compared to the other alloys. Also, the damping properties of metals are generally recognized to be dependent on microstructural factors such as grain size and texture. However, there are very few studies on the relationship between the damping ability and texture of Mg alloys. Therefore, in this study, the AZ31 magnesium alloy which was carried out by heat treatment was experimentally investigated about the relationship between the texture and damping capacity.

A 60 mm × 60 mm × 40 mm rectangular plate was cut out by machining an ingot of AZ31 magnesium alloy (Mg-3Al-1Zn in mass%), and rolling was carried out at 673 K to a rolling reduction of 30%. Then, heat treatment was carried out at temperatures in the range of 573–723 K for durations in the range of 30–180 min. The samples were immediately quenched in oil after heat treatment to prevent any change in the microstructure. Specimens for damping capacity measurements were machined from the rolled specimen, to have a length of 120 mm, width of 20 mm, and thickness of 1 mm. The damping capacity was measured with a flexural internal friction measurement machine at room temperature. Texture was evaluated on the compression planes by the Schulz reflection method using nickel-filtered Cu K $\alpha$  radiation. Electron backscatter diffraction measurements were conducted to observe the spatial distribution of various orientations. It was found that the damping capacity increases with both increasing heat-treatment temperature and time, due to grain growth and also, the pole densities of texture increase with increasing the internal friction.

**NM-WeP20 Total Analysis of Silica Nanotube Surface by using TOF-SIMS**, *Jong Sung Jin, Kim, Kim, Jeong, Kahn*, Korea Basic Science Institute, Korea, *Lee, Jin*, Korea Institute of Industrial Technology, Korea

Recently, many researchers have been interested in the self-assembled 3D supramolecular structures to synthesis of helical silica nanotubes. We have been studied the solvent-effects on the synthesizing of helical silica nanotubes via polycondensation of tetraethoxysilane (TEOS) on self-assembled structures that were composed 1,2-diphenylethylenediamine based neutral (G1) and cationic (G1N) gelators.[1] In this study, we analyzed helical silica nanotubes and derivatized chiral stationary phases by using TOF-SIMS. We discussed products of each steps for the derivatized organic compound on the silica surface in order to confirm the reactions.

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**NM-WeP21 Photodetector and Pressure Sensor Based on Field-Effect Transistor with the Nanohybrid Channel of ZnO Nanorods and Graphene**, *Dang Vinh Quang, T.Q. Trung, D.-I. Kim, L.T. Duy, B.-Y. Kim, B.-U. Hwang, D.-W. Lee, N.-E. Lee*, Sungkyunkwan University, Korea

Field-effect transistors (FETs) with a nano-hybrid channel of chemical-vapor-deposited graphene (CVD Gr) and vertically aligned ZnO nanostructures are successfully fabricated and operated at low voltage. By the combination of highly conductive Gr and the high UV absorption of ZnO, ultraviolet (UV) photodetectors are investigated under illumination at various incident photon intensities and wavelengths. The change in the transfer characteristics of hybrid-channel FETs under UV light illumination allows to detect both photovoltage and photocurrent. The shift of the Dirac point ( $V_{Dirac}$ ) observed during UV exposure led to a clearer explanation of the response mechanism and carrier transport properties of Gr, and this phenomenon permits the calculation of electron concentration per UV power density transferred from ZnO nanorods (NRs) and ZnO nanoparticles (NPs) to Gr, which is  $9 \times 10^{10}$  and  $4 \times 10^{10}$  per mW, respectively. The time-dependent behaviours of hybrid-channel FETs exhibit high UV responsivity (RI) and high photoconductive gain (G). The maximum values of RI and G infer from the fitted curves of RI and G versus UV intensity are  $3 \times 10^5$  A

$W^{-1}$  and  $10^6$ , respectively. More interestingly, due to the piezoelectric property of ZnO, a piezoelectric-coupled hybrid channel GFET can be used as a pressure-sensing device with high responsiveness and a fast response time. The shifts of  $V_{Dirac}$  under mechanical pressurization are analysed to explain clearer the charge transferred mechanism with electron transfer of  $4 \times 10^8$  cm $^{-2}$  kPa $^{-1}$  from the CVD Gr to ZnO NRs. Therefore, hybridization of semiconductor 1D nanomaterials with Gr channel in FET structures resulting in high performance and low power consumption opens up new opportunities for future optoelectronic devices.

Suggested topic: Nanomaterials (NM1-Nano Devices)

**NM-WeP22 Defect Induced Visible Light Photocatalytic Activity of SnO<sub>2</sub> Nanoparticles**, *Sajid A. Ansari, M.M. Khan, M.O. Ansari, Cho*, Yeungnam University, South Korea

We report the defect-induced band gap narrowing of pure SnO<sub>2</sub> nanoparticles (p-SnO<sub>2</sub>) using an electrochemically active biofilm. The proposed approach is biogenic, simple and green. The systematic characterization results of the modified SnO<sub>2</sub> nanoparticles (m-SnO<sub>2</sub>) revealed EAB-mediated defects in p-SnO<sub>2</sub>. m-SnO<sub>2</sub> nanoparticles in visible light showed the enhanced photocatalytic degradation of p-nitrophenol and methylene blue compared to p-SnO<sub>2</sub> nanoparticles. Photoelectrochemical studies, such as electrochemical impedance spectroscopy and linear scan voltammetry, also revealed a significant increase in the visible light response of m-SnO<sub>2</sub> compared to p-SnO<sub>2</sub> nanoparticles. The enhanced activities of m-SnO<sub>2</sub> in visible light was attributed to the high separation efficiency of the photoinduced electron-hole pairs due to surface defects created by EAB, resulting in band gap narrowing of the m-SnO<sub>2</sub> nanoparticles.

## Thin Films

### Room: Mauka - Session TF-WeP

## Thin Films Poster Session

**TF-WeP1 Inductively Coupled Ar-Based Plasma Etching of Palladium for Low Damage in Underlying GaN Semiconductor**, *Yong-Yeon Kim, J.K. Kim, J.M. Lee*, Sunchon National University, Republic of Korea

The etch characteristics of Pd for the fabrication of blue laser and light emitting diodes were investigated by using inductively coupled Ar-based plasma for low damage in underlayer. Up to date, the etch characteristics of Pd was not fully understood, because the suitable gas to form a volatile etch-product was not known due to the chemical inertness of Pd. Furthermore, the control of gas mixture for the low damage in underlying GaN semiconductor is more preferable in order to fabricate high quality optical devices. Therefore, it is important to selection of gas mixture in plasma. Furthermore, it was found that the photoresist was eroded when the ICP source power was increased above 100 W, when the Ar plasma were used as active etchant.

When the 50 sccm of Ar was used as etchant gas, the highest etch rate of 60 nm/min was achieved at source and table power of 50 W and 200 W, respectively. The etched sidewall was observed to be most anisotropic, where the angle was about 88 degree. When the additional gas, such as Cl<sub>2</sub> and CHF<sub>3</sub>, was added in the Ar plasma, different effect on the etch characteristics were observed, especially for the sidewall angle. On the other hand, when the Ar gas was used, the carrier concentration of the underlying GaN was decreased by two orders of magnitude due to the etch-damage. However, the addition of Cl<sub>2</sub> and CHF<sub>3</sub> by 20 %, respectively, the carrier concentration of the etched GaN surface was increased to the value of as-grown sample, maybe due to suppression of the etch-damage. In this presentation, more detailed results about etch-characteristics of Pd will be reported.

**TF-WeP2 Effect of Copper Layer Thickness on the Thermal Performance of LED Ceramic Package Substrate**, *HyunMin Cho, S. Jang, S. Ha*, KETI, Republic of Korea

LED (Light Emitting Diode) has been one of the promising technology for the energy saving. Now, conventional lamps such as incandescent and fluorescent lamps are rapidly being replaced by LED lamps. By the progress of LED technologies, the efficiency and reliability of LED devices have been dramatically increased compared to decade ago. Also, the power of LED lightings have been increased. To maintain LED performance, it is very important to manage heat from the LED chip. To deal with high power LED chip over 3 W or COB (Chip on Board) type arrayed LED chips over 10 W, ceramic substrate such as aluminum nitride has been adopted instead of plastic or aluminum oxide substrate because of its high thermal conductivity in the range of 170–250 W/m.K. For the metal circuit pattern on the substrate, mainly copper is used for the high thermal and electrical

conduction. We investigated the effect of metal layer thickness on the thermal performance of high power LED package. First we simulated the junction temperature of LED package according to copper layer thickness. The decrease of LED junction temperature was occurred with the increase of metal layer thickness. But, the effect was reduced with higher thickness. We also manufactured LED packages with various copper layer thicknesses and tested thermal performance by thermal transient measurement and compared with the simulation data. With this results, we could optimize the copper layer thickness of the LED package substrate.

**TF-WeP3 Characteristics of Al, Ag, and Cu Metal Mesh Prepared by Photolithography for Touch Screen Panels, M.J. Kim, Pungkeun Song, S.H. Cho,** Pusan National University, Republic of Korea  
Pusan National University, Republic of Korea

**TF-WeP4 Improved Initial Growth Behavior of Atomic Layer Deposited SrTiO<sub>3</sub> Films with [Sr(demamp)(tmhd)]<sub>2</sub> as Sr-precursor, Woongkyu Lee, W. Jeon, Y.W. Yoo, C.H. An, M.J. Chung,** Seoul National University, Republic of Korea, T.-M. Chung, B.K. Park, S.M. George, C.G. Kim, Korea Research Institute of Chemical Technology, C.S. Hwang, Seoul National University, Republic of Korea

Strontium titanate (SrTiO<sub>3</sub>, STO) has been attracting a great deal of attention as the capacitor dielectric material for DRAM with design rule < 20 nm due to its much higher dielectric constant ( $k > 100$ ) compared with those of presently adopted dielectrics based on ZrO<sub>2</sub> ( $k \sim 30 - 40$ ). Because of the severe three-dimensional geometry of DRAM capacitors, atomic layer deposition (ALD), which provides the ultimate step coverage, is indispensable. The conformality of film is generally induced by self-limited growth mechanism of the ALD. However, in previous studies, non-ideal excess growth was observed during the early stage of STO deposition on Ru electrode, the most promising electrode material. The excessive growth was more dominant for the incorporation of Sr into the film compared with Ti. This was mainly attributed to the reduction of in-situ oxidized Ru substrate during the O<sub>3</sub> pulses in the previous ALD steps.<sup>[1,2]</sup> Such adverse effect was further aggravated by the high growth temperature (370 °C), which was adopted for the in-situ crystallization of the STO film. Also, the weak chemical bonding between the cyclopentadienyl(Cp)-based ligands and Sr ions in the conventional Cp-based Sr-precursor induced such problem.

In this study, therefore, [Sr(demamp)(tmhd)]<sub>2</sub>, developed by Korea Research Institute of Chemical Technology,<sup>[3]</sup> which is supposed to have a chemical properties in medium of the Cp-based Sr-precursor and tmhd-based homoleptic Sr-precursor, was adopted as the new Sr-precursor and attempted ALD process of STO film. A high density (250 g/m<sup>3</sup>) O<sub>3</sub> was employed as the oxygen source for SrO deposition and sputtered Ru was used as the substrate with its temperature of 370 °C. Ti(Me<sub>3</sub>Cp)(O Me)<sub>3</sub> was employed as the Ti-precursor which is also reacted with O<sub>3</sub>. With this novel heteroleptic Sr-precursor, good ALD-specific saturation growth behaviors were observed with respect to the precursor injection, Ar purge, O<sub>3</sub> injection, and Ar purge step times. Most importantly, the unwanted overgrowth of Sr element in initial stage of film growth decreased substantially, and the linear growth behavior of both Sr and Ti were achieved. Meanwhile, the growth rate was decreased to 0.50 Å/cycle, which was lower than the previous case with Cp-based Sr-precursor (1.23 Å/cycle) but assisted to have a denser as-deposited film. With more ideal-like ALD process, the deposited film showed excellent film properties including high purity, high crystallinity, high electrical properties, and excellent step coverage.

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**TF-WeP5 Nanoscale Wrinkle Structures on Polydimethylsiloxane using Ion-Beam Bombardment, JuHwan Lee, H.-G. Park, H.-C. Jeong, Y.H. Jung, D.-S. Seo,** Yonsei University, Republic of Korea

Research on topological wrinkle structures at the nano- or micrometer scale is continuously growing because of the development of robust techniques for controlled patterning of polymer and the emergence of novel applications that benefit from the wrinkle structures. The wrinkle structures can be applied to various systems such as stretchable electronics, microlens arrays, microelectromechanical devices, tunable surface adhesion, friction and robotics. To produce a wrinkle structure on this scale, photolithographic, printing, embossing or writing techniques have traditionally been used. However, these methods have relatively high costs and limited throughput when producing customized features. Therefore, alternative spontaneous wrinkle structure fabrication methods have attracted considerable attention in recent decades. These methods, including plasma activation, UV/ozone treatment, laser excitation, and ion-beam (IB) treatment, use surface reformation on the polymer layer, which minimizes

the combination of the bending energy of the outer layer and the stretching energy of the inner layer. Among the various alternative methods, IB bombardment has excellent penetrability with high-energy Ar<sup>+</sup> ions, which leads to stable and reliable wrinkle structure fabrication. Recently, we have shown that irradiation of Ar<sup>+</sup> ions on the surface of a polydimethylsiloxane (PDMS) substrate results in the formation of a stiff skin on the substrate, which has a chemical composition resembling amorphous silica. Since the stiff skin deformation is constrained by the PDMS substrate, the skin experiences in-plane compressive strain upon ion beam irradiation and buckles to accommodate the induced mismatch strain between the skin and the polymeric substrate.

Here, we demonstrated the formation of a wrinkle structure on the surface of PDMS through IB bombardment. We fabricated various sizes of wrinkle structures as a function of IB irradiation time and confirmed the formation of these structures using a variety of AFM analyses.

**TF-WeP6 Molecular Arrangements and Electronic States of Well-Defined K-Doped Coronene and Picene Monolayers, Masahiro Yano, M. Endo, R. Shimizu, Y. Hasegawa, Y. Yamada, M. Sasaki,** University of Tsukuba, Japan

In this paper, we demonstrate that K-doped coronene and picene monolayers form well-defined structures and they are model systems suitable to clarify the mechanism of electronic and structural modifications of aromatic hydrocarbon crystals due to alkali doping. It can be a basis to control the electronic properties of organic materials by foreign metal-doping.

Modification of the electronic properties of organic materials by doping with foreign metals is one of the key technologies used in next-generation organic electronics. In general, microscopic structural information is essential for understanding the underlying mechanisms. However quite few number of investigations have addressed the microscopic structural features with respect to doping, mainly due to difficulties in the measurement of inhomogeneous samples. Therefore, basic investigation into the microscopic structural nature of metal-doped organic systems utilizing well-defined models is necessary.

In the present study, we have investigated molecular-scale structure and electronic state of K-doped coronene and picene monolayer. For the substrate, we employ inert surfaces, such as Au(111) and highly oriented pyrolytic graphite (HOPG), to minimize the effect of the substrate on the reaction between K and molecules.

After the coronene and picene monolayers were prepared on Au(111) or HOPG using vacuum deposition, K was deposited on the monolayer from alkali dispensers.

The structures were observed by means of scanning tunneling microscope (STM). STM images show significant structural changes of coronene and picene monolayers upon K deposition. Both the K-doped monolayers exhibit well-defined herringbone-like molecular arrangement. In this phase, while the surface reconstruction of Au(111) is still visible, individual K atoms are not observed. We speculate that K atoms intercalate between molecular planes and directly interact with the molecules.

The electronic states were investigated by means of photoemission spectroscopy on a HOPG substrate. In both the monolayers, with increasing doping, a new state appears more clearly just below the Fermi level. The formation of this state is very sensitive to the molecular arrangement [1].

Moreover, it should be noted that a very similar photoemission spectrum has been reported in K-doped thick picene film on HOPG [1]. This similarity ensures the perspective that the well-defined K-doped monolayer can be a model for the doped aromatic hydrocarbons crystals.

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**TF-WeP7 Failure Behaviors of Stretchable Electrodes Based on Metal Nanostructure Percolation Networks, Guh-Hwan Lim, H. Sim, B. Lim,** Sungkyunkwan University, Korea, Republic of Korea

Metallic nanostructures such as nanowires and nanosheets are promising candidates for the fabrication of highly conductive electrodes, but the practical application of metal nanostructure-based electrodes in stretchable electronics is often limited by significant performance degradation associated with poor mechanical stability of a nanowire or nanosheet percolation network against repeated deformation. We studied failure behaviors of stretchable electrodes made of Ag nanowires or Au nanosheets deposited on various elastomeric substrates such as PDMS and Ecoflex during stretching cycles, and suggested a way of improving stretchability and stability of these metal nanostructure-based stretchable electrodes.

**TF-WeP8 Properties of Photo-Induced Hybrid Channel Thin-Film Transistors Via Solution Process, YoonHo Jung, H.-G. Park, H.-C. Jeong, D.-S. Seo, Yonsei University, Republic of Korea**

Oxide thin-film transistors (TFTs) have been actively studied to this day and suggest the promising technique with carbon nanotube, nanowire, nanoparticle, or small molecules. Oxide TFTs are made of metals that have sufficiently large ns orbitals to overlap with each other. Thus, they can transport charge carriers without being sensitive to the crystalline structure. An advantage of these devices is that they can be conductive even when the material is in an amorphous phase. With this technique, solution processing is a useful method for generating amorphous oxide TFTs. In addition to its low manufacturing cost, easy deposition, and simple procedure, this method is important because of its outstanding synthesis capacity. With this method, each material can be simply mixed, and uniform films can be formed to achieve multi-component systems. Thus, this property is essential for making oxide films that consist of more than two materials.

Among a variety of solution-processed oxide TFTs, InGaZnO TFTs are the most widely used materials. In InGaZnO TFTs, Ga suppresses carriers and suppression of carriers is achieved by increasing the number of oxygen vacancies. Oxidization of the material is highly related to an electronegativity and a lower electronegativity increases the tendency to be oxidized. In this study, we chose yttrium because the electronegativity of Y is 1.2 which is much lower than that for Ga. Therefore, more oxidization occurs in the channel lattice, which leads to additional suppressing oxygen vacancies.

Azobenzene is a small organic molecule that has been frequently used for organic TFTs. Furthermore, the photo-induced isomerization of azobenzene is an interesting property. In each phase, which is trans- or cis-phase, the molecular structure is different. Normally, the molecule remains in the trans-phase because of higher stability. When exposed to an appropriate light source, azobenzene changes into the cis-phase.

Herein, we investigated solution-processed amorphous InYZnO with azobenzene channel TFTs. The effects on the electrical and structural characteristics of TFT channels due to the photo-induced isomerization of azobenzene were analyzed using a field effect-scanning electron microscope (FE-SEM), X-ray photoelectron spectroscopy (XPS), and electric characteristic analysis.

**TF-WeP9 Uniform Alignment of Liquid Crystal Molecules on Solution-Based Oxide Films, Hae-Chang Jeong, H.-G. Park, D.-S. Seo, Yonsei University, Republic of Korea**

Liquid crystal displays (LCD) are useful and important device because it is closely related in our daily life, such as mobile display, portable devices, TV and so on. The uniform LC orientation on the alignment film is very important to obtain high quality display. The conventional method, rubbing on the polyimide layer, has some drawback such as generation of debris and accumulation of electrostatic charge. To resolve the shortcomings of LC alignment, alternatives have been investigated for a long time but it is difficult to apply to a commercial purpose. We investigate the solution process using tin-oxide as an alignment layer. In this process we can obtain alignment layer of self-alignment properties. LC molecules are well aligned in higher annealing temperature process along to the filling direction. Because fully oxidized films keep strong van der Waals force between LC molecules and solution-based oxide films. At higher annealing temperature, a tin oxide alignment layer has uniform and increasing nano-crystalline. The average transmittance of oxide alignment layer at higher annealing temperature has 81.21%. This transparency is similar to those of conventional LC alignment materials. The electro-optical properties of solution-based oxide films can be obtained by electrically controlled birefringence (ECB). At higher annealing temperature, the threshold voltage is 1.408V and this result is better performance to conventional method and material. Because process of solution-based oxide films allows for uniform alignment as well as high performance property, it is very simple and useful method.

**TF-WeP10 Fabrication of SiC based AFM Cantilever for NSOM Application, S.-H. Nam, K.-H. Hwang, J.H. Yu, Jinsu Lee, J.-H. Boo, Sungkyunkwan University, Republic of Korea**

Silicon carbide thin films were deposited on Si(100) substrates by metal-organic chemical vapor deposition(MOCVD) in high vacuum condition at  $2.0 \times 10^{-7}$  Torr using 1,3-disilabutane as a single source precursor which contains silicon and carbide in 1:1 ratio at various temperature in the range of 700 ~ 1000 °C. The XPS result shows that the SiC thin film grown at 950 °C which have carbon rich for silicon and carbon at 1:1.2 ratio. XRD result shows that the SiC thin film grown at 900 °C which appeared at  $2\theta = 41.6^\circ$  for SiC (200) reflection at a large intensity and a single shape diffraction peak. SEM images result show that the SiC thin film grown at 900 °C which has influence on the small grain size and single crystallinity. AFM images result show that the SiC thin film has smooth surface at RMS = 20nm. In

this paper, we fabricated the small aperture for the better performance such as less noise, higher resonant frequencies and fast imaging. We will apply that silicon carbide thin film has smooth surface on NSOM application.

**TF-WeP11 Reliability and Life Time Flexible OLED Device Fabricated on ITO/Ag NW/ITO Thin Film on PES Substrate, WooJin Yeon, Y.T. Oh, K.H. Kim, E.S. Kim, DongChan. Shin, Chosun University, Republic of Korea**

We demonstrate OLED device on ITO/Ag NW/ITO thin film on PES substrate and investigate degradation of life time. Transparent conducting layers are fabricated in three type of ITO, ITO/Ag thin film (TF)/ITO, and ITO/Ag nano wire (NW)/ITO. The total thickness of TCO layers is set to be 150 nm. Single ITO thin film shows the highest transparency of 97%, ITO/Ag NW/ITO 90%, and ITO/Ag TF/ITO is the lowest of 81%. Sheet resistance of ITO/Ag NW/ITO is reduced to be 12.74  $\Omega/\square$  compared to single ITO TF of 32.42  $\Omega/\square$ . Figure of merit of Ag nano wire inserted TCO shows the best value. According to bending test, Single ITO thin film layer shows abrupt failure on just one time bending, resistance of ITO/Ag TF/ITO increases 130% at 60 times bending, but ITO/Ag NW/ITO shows only 26% increase. Double layered simple OLED device of NPB and Alq<sub>3</sub> is fabricated and resultant device properties will be discussed.

**Acknowledgment:**Followings are results of a study on the "Leaders in Industry-university Cooperation" Project, supported by the Ministry of Education, Science & Technology (MEST) and the National Research Foundation of Korea (NRF), and this work was supported by the Human Resources Development program (No. 20114010100090) of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Trade, Industry and Energy. This research was also supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (NRF-2013R1A1A4A01008233).

**TF-WeP12 A Study of the Mechanical Properties of Trench Type Cu/Mo Thin Films for Flexible Copper Interconnect, JongHyun Seo, Korea Aerospace University, Republic of Korea, H.-S. Kim, Korea Aerospace University, H.H. Choe, J.-H. Jeon, J.H. Yoon, Korea Aerospace University, Republic of Korea**

In this work, the adhesion properties sputtered molybdenum (Mo) thin films as a copper (Cu) diffusion barrier layer on polymer substrates were examined using micro-scratch tests. We fabricated trench type copper interconnect rather than typical metal inlaying type.

There was made a comparison of the mechanical properties between a new trench copper layer and a traditional metal inlay type copper interconnect by means of photolithography technique followed by wet patterning. The metal / polymer interface were examined by using the auger electron spectroscopy. Cu/Mo trench typed films have 50% higher values of adhesion forces than that of Cu/Mo inlay type. A physical modeling is proposed, on average volume stress analysis to explain an improvement in the mechanical stability of the buried Cu interconnects in the flexible substrate.

**TF-WeP14 Computational Simulation Study on Structure Change of Si-DLC Films, Takeshi Tsuruda, H. Murabayashi, Y. Wang, Y. Kobayashi, T. Kuwahara, S. Bai, Y. Higuchi, N. Ozawa, K. Adachi, Tohoku University, Japan, J.M. Martin, Ecole Centrale de Lyon, France, M. Kubo, Tohoku University, Japan**

Diamond-like carbon (DLC) consisting of sp<sup>2</sup> carbon (Csp<sup>2</sup>) and sp<sup>3</sup> carbon (Csp<sup>3</sup>) has low friction property. Therefore, DLC is used as solid lubricant in the sliding parts of machinery to decrease energy loss by friction. It was suggested that the low friction property of DLC is caused by formation of a graphene layer on the surface [1]. Moreover, Si-doped DLC (Si-DLC) films show excellent tribological property because of formation of Csp<sup>2</sup> on the surface [2]. Therefore, transformation from Csp<sup>3</sup> to Csp<sup>2</sup> on the DLC surface is important for the low friction. For further decrease in the friction of the DLC films, we need to clarify the mechanism of the transformation from Csp<sup>3</sup> to Csp<sup>2</sup> at atomic scale. In this study, to elucidate the transition mechanism from Csp<sup>3</sup> to Csp<sup>2</sup> on the DLC films by Si-doping, we develop our tight-binding quantum molecular dynamics simulator [3].

First, to reproduce van der Waals interaction and transformation for Csp<sup>2</sup> and Csp<sup>3</sup>, we add Lennard-Jones and trigonometric functional potential to our simulator. Next, to confirm the accuracy of our developed simulator, we perform compression simulation of a-graphite layers under a pressure. Here, the bottom layer is fixed and load pressure is applied to the top layer. From 1 to 15 GPa, the structure change is not observed for 50 ps. At a pressure of 16 GPa, Csp<sup>3</sup>-Csp<sup>3</sup> bonds continuously increase when graphite layers become close. Then, the six-membered rings of diamond structure are generated from graphite layers. This indicates the transformation from Csp<sup>2</sup> to Csp<sup>3</sup>. In the experiment, the structure change from graphene to diamond

takes place at 17 GPa [4]. Thus, the simulation result is in good agreement with the experimental result. Thus, our developed program succeeds to reveal the transformation from  $Csp^3$  to  $Csp^2$ .

Next, to investigate how Si-doping influences on the surface structure of the DLC films, we perform relaxation calculation for Si-doped diamond(111) surface with 3.225 % Si content. At 48.9 ps, the chemical bond between the C atom bound with the doped Si atom and C atom of the lower layer is dissociated. Furthermore, we observe generation of the  $Csp^2$  atoms after the dissociation. This indicates that the Si-doping induces the transformation from  $Csp^3$  to  $Csp^2$  and generation of graphene-like structure on the surface. Thus, we propose that Si-DLC films show low friction because Si-doping generates  $Csp^2$  on the surface of the DLC films.

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**TF-WeP15 Tight-Binding Quantum Chemical Molecular Dynamics Simulation on Chemical Reaction of Molybdenum Dithiocarbamate on DLC surface**, *Hiroki Murabayashi, T. Tsuruda, Y. Wang, Y. Kobayashi, S. Bai, Y. Higuchi, N. Ozawa, K. Adachi*, Tohoku University, Japan, *J.M. Martin*, Ecole Centrale de Lyon, France, *M. Kubo*, Tohoku University, Japan

In recent years, diamond-like carbon (DLC) is expected as a solid lubricant material for engines because of its excellent friction properties such as low friction and high wear resistance. DLC films are lubricated with oil in the engine. Furthermore, molybdenum dithiocarbamate (MoDTC) is used as friction modifier in oil. DLC coating with oil and MoDTC solution showed a low friction coefficient [1]. Moreover, the low friction of the DLC films with MoDTC was enhanced by a chemical reaction during friction, since the friction coefficient gradually decreased with increasing friction time. Understanding of the low friction mechanism of DLC with MoDTC is strongly required to decrease in the friction of the DLC films. Then, our purpose is to reveal the chemical reactions between the MoDTC and DLC films by our tight-binding quantum chemical molecular dynamics code [2].

To investigate chemical reaction between MoDTC and DLC film during friction, we perform the friction simulation of MoDTC sandwiched by the DLC surfaces. At first, we compress linkage isomer of MoDTC (LI-MoTC) by the DLC surfaces. Here, we use LI-MoDTC because it is isomerized in oil phase [3]. We apply a pressure of 1 GPa to the upper DLC film. After the compression, the C atom of the DLC surface binds with the S atom of LI-MoDTC and the C-S bond is generated between the DLC surface and LI-MoDTC. Next, to perform the friction simulation of DLC films with LI-MoDTC, we apply a pressure of 1 GPa to the DLC film and forcibly slide it with 100 m/s. The S-Mo bond in the adsorbed LI-MoDTC is elongated from 2.52 Å to 3.76 Å and the S-Mo bond is dissociated during the sliding. To reveal chemical reaction during the S-Mo bond dissociation in detail, we investigate electron transfer between LI-MoDTC and the DLC surface during the compression. The charge of S atom of LI-MoDTC changes from +0.45 to +0.82 before and after the generation of C-S bond. This indicates that electrons transfer from the sulfur atom of LI-MoDTC to the DLC films. We think that S-Mo bond is weakened due to the electron transfer between LI-MoDTC and DLC film. Thus, we suggest that the electron transfer from LI-MoDTC to DLC films during the LI-MoDTC adsorption on the DLC surface weakens the S-Mo bond and the mechanical force dissociates the weakened S-Mo bond during the friction.

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**TF-WeP20 Lifetime Calculation of Encapsulated Organic Device Under Specific Weather Conditions**, *Namsu Kim*, Korea Electronics Technology Institute (KETI), Republic of Korea, *D. Kim*, Korea Electronics Technology Institute (KETI), *K. Hwang*, University of California at San Diego, *S. Graham*, Georgia Institute of Technology, *S. Kim*, Korea Electronics Technology Institute (KETI)

One of primary technical obstacles toward commercialization in organic device is the achievement of reliable long lifetimes. The low work function materials and transparent conductive oxides used to form electrical contacts to the active layers are generally reactive and susceptible to water vapor and oxygen. Thus, developing thin-film encapsulation technologies protecting organic electronic devices from water vapor and oxygen is critical. In addition, variable environment of photovoltaic modules makes it difficult in predicting lifetime of them.

In this study, the lifetime of encapsulated organic device under specific weather condition was predicted based on total amount of permeated water

permeated through barrier layers. Previous study presented the relation between the overall barrier performance and the shelf lifetime of encapsulated organic solar cells experimentally. Based on previous study, the total permeated water vapor through identical barrier layer under continuously varying environment can be calculated and compared to experimental data. For analytical calculation, diffusion and solubility coefficients were experimentally determined using quartz crystal microbalance as well as water vapor permeation instrument.

**TF-WeP22 Spin Valve Junctions Based on  $Fe_3Si/FeSi_2/Fe_3Si$  Trilayered Films**, *Tsuyoshi Yoshitake*, Kyushu University, Japan, *K. Sakai*, Kurume National College of Technology, Japan, *Y. Asai*, *K. Ishibashi*, *Y. Noda*, Kyushu University, Japan, *K. Takeda*, Fukuoka Institute of Technology

Since the discovery of GMR and TMR effects, spin-dependent carrier transport has received attention from physical and engineering viewpoints. Whereas GMR and TMR films generally employ nonmagnetic metal and insulator spacers, respectively, we have studied  $Fe_3Si/FeSi_2$  artificial lattices, in which  $FeSi_2$  is semiconducting and its employment as spacers is specific to our research. The combination of  $Fe_3Si$  and  $FeSi_2$  has the following merits: (i) a magnetoresistance effect in the CPP structures is easily detectable since the electrical conductivity of  $FeSi_2$  spacer layers is distinctively larger than that of  $Fe_3Si$  layers; (ii) a spin injection efficiency might be higher than that in TMR films; (iii) the epitaxial growth of  $Fe_3Si$  layers on Si(111) substrates is successively kept up to the top  $Fe_3Si$  layer across  $FeSi_2$  spacer layers, which is beneficial to the coherent transportation of spin-polarized electrons; (iv)  $Fe_3Si$  is feasible for a practical use since it has a high Curie temperature of 840 K and a large saturation magnetization, which is half of that of Fe.

A spin valve is one of the most important principle for spin-dependent carrier transport, and the formation of parallel or antiparallel alignments of ferromagnetic layer magnetizations should be realized and controlled in devices with spin valves. Previously, we have prepared  $Fe_3Si/FeSi_2$  artificial films, wherein interlayer coupling was induced between  $Fe_3Si$  layers across  $FeSi_2$  spacers and the formation of parallel and antiparallel alignments of ferromagnetic layer magnetizations was induced owing to the interlayer coupling [1,2]. The parallel or antiparallel alignments of layer magnetizations can be realized in multilayered films comprising ferromagnetic layers with different coercive forces, and it needs not the precise control of the spacer thickness. In this work,  $Fe_3Si/FeSi_2/Fe_3Si$  trilayered films were prepared and the magnetic properties as spin valves were investigated.

An  $Fe_3Si(7000 \text{ \AA})/FeSi_2(7.5 \text{ \AA})/Fe_3Si(1000 \text{ \AA})$  artificial film was fabricated by facing-targets direct current sputtering with using a mask method. The magnetization curve was measured using a VSM. The shape of the magnetization curve clearly exhibited the formation of parallel and antiparallel alignments with the magnetic field. This should originate from a difference in the coercive force between the top and bottom  $FeSi_2$  layers. The electrical properties accompanied by the change in the magnetization alignment will be presented at the conference.

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**TF-WeP23 Application of Double-Lorentzian Line-Shape in XPS Analysis of Metallic Zn and ZnO Thin Films**, *Gabriela Molar-Velazquez*, *G. Gomez-Sosa*, *A. Herrera-Gomez*, CINVESTAV-Unidad Queretaro, Mexico

There are several line-shapes widely employed in XPS spectra analysis, such as Gaussian, Lorentzian, Voigt, Doniach-Sunjic, among others. In the case of transition metals, the high asymmetry present in the main core levels peaks might lead to misinterpretation as considering artificial peaks during fitting. Some of this problems could be avoided by employing the double-Lorentzian line-shape. In this study, analysis of XPS spectra of Zn and ZnO films (including the early oxidation stages at room temperature) were performed using double-Lorentzian line-shape. The chemical composition of ZnO samples were calculated and different peaks for the metallic Zn 2p, Zn 3p, Zn 3s and Zn 3d core levels were identified.

**TF-WeP25 Double-Lorentzian Line Shape in XPS Analysis of Metallic Nickel, Chromium, Cobalt and Their Oxide Films**, *Gustavo Gomez-Sosa*, *J.A. Torres-Ochoa*, *M. Bravo-Sanchez*, *J.H. Mata-Salazar*, *D. Cabrera-German*, *J. Ibarra-Nuno*, *A. Herrera-Gomez*, CINVESTAV-Unidad Queretaro, Mexico

The current methods for quantitative analysis of X-ray photoelectron spectroscopy (XPS) data are clearly insufficient for closely reproducing the high asymmetry and strong background signal of the core level peaks of transition metals and their oxides. Using the double-Lorentzian asymmetric line-shape [1] and the active background approach [2], it is possible to obtain close fits to these core levels. The samples were prepared by metal

sublimation on Si (100) wafers. The asymmetry factor found from the analysis was 1.83 for Ni 2p, 2.84 for Cr 2p and 2.9 for Co 2p. Previously unreported shake-up satellites were identified at 0.45, 1.1 and 1.9 eV away from the main peak in the metallic films of the Cr 2p, Co 2p and Ni 2p core levels, respectively. The evolution of the oxidation of metals was also studied by exposing metallic films to UHP oxygen in a range from 4 L to 400 GL. Further oxidation was obtained using a tubular oven with UHP oxygen with positive pressure. The final thickness of oxide films ranged from 2 to 3 nm. The composition was calculated employing the MultiLayer Model. The close agreement with the expected values (1:1 for nickel oxide, NiO; 2:3 for chromium oxide, Cr<sub>2</sub>O<sub>3</sub>; and 1:1 for cobalt oxide, CoO) validates the peak areas obtained with the double-Lorentzian line-shape.

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**TF-WeP26 Improved Adhesion of Diamond-Like Carbon Films by r.f. Plasma CVD Process with Cylindrical Electrode, Keisuke Shiba,** Tokyo Denki University, Japan, *Y. Ohgoe*, Tokyo Denki University, *M. Hiratsuka*, Nanotec Corporation, *K. Ozeki*, Ibaraki University, *K. Hirakuri*, *K. Sato*, Tokyo Denki University, Japan

Diamond like carbon (DLC) film has been widely used because of its good properties such as good biocompatibility, anti-corrosion, high hardness, and high wear resistance. Therefore, DLC film has been applied to practical uses in medical and industrial fields. However, lack of film adhesion onto metallic materials has limited DLC coating applications. In order to improve adhesion strength of DLC film onto a substrate, intermediate layer such as Si layer has been introduced between the DLC layer and the substrate.

In this study, DLC films were deposited on stainless steel substrate by using r.f. plasma chemical vapor deposition (r.f. plasma CVD) without intermediate layer. To improve adhesion of DLC film onto metallic materials, the cylindrical electrode around a sample was installed on the cathode side electrode (Fig. 1, 2). Cylindrical electrode was selected for the height of 5, 10, and 20 mm, respectively. DLC film was deposited under the following condition ( CH<sub>4</sub> gas pressure: 10 Pa, r.f. electrical power: 200 W, film thickness: 200 nm).

The adhesion of the DLC films was measured by using a scratch test. The characteristics of the DLC films were investigated using Raman spectroscopy, X-ray photoelectron spectroscopy (XPS).

In the scratch test, the critical load of the film with 10mm-cylinder height showed 8.5 N, as compared with the film without the cylinder (4.6 N) (Fig. 3). Additionally, the Raman spectrum of the film on the stainless steel substrate showed peaks at approximately 1550 cm<sup>-1</sup> and 1350 cm<sup>-1</sup>, referred to the G-band and D-band, respectively.

These results showed that the films were a typical DLC film and the DLC film was completely deposited with strong adhesion between the films and substrates by using only r.f. plasma CVD technique. This technique affects to DLC film adhesion property onto metallic materials under r.f. plasma CVD process.

**TF-WeP28 Inductively Coupled Plasma Reactive Ion Etching of CoFeB Thin Films Using a CH<sub>3</sub>COOH/Ar Gas Mixture, Adrian Garay,** S.M. Hwang, J.H. Choi, C.W. Chung, Inha University, Korea

Magnetic random access memory (MRAM) holds the promise of replacing traditional memory devices such as DRAM, SRAM and flash memory. The MRAM device compared to its counterparts (DRAM, SRAM, flash memory, etc.), offers higher density, faster access time, unlimited read/write endurance and non-volatility. MRAM devices are mainly composed of a magnetic tunnel junction (MTJ) stack and CMOS.

In order to achieve high storage densities in MRAM devices, the pattern transfer in magnetic layers that comprise the MTJ stacks is a critical step. In the early stage of research, a wide range of etching gases such as HBr, Cl<sub>2</sub> etc has been employed for the ICPRIE of CoFeB thin films. In general, when using halogen gases, the etch rates are extremely high; but the sidewall redeposition and corrosion problems are common. Recently, an effort to improve the etching characteristics of magnetic layers, while at the same time reducing post-etching treatment, non-corrosive etching gases

such as CO/NH<sub>3</sub>, CH<sub>3</sub>OH, CH<sub>4</sub> have been researched. The use of this etching gases mixed with Ar gas had to prove to yield a redeposition-free anisotropic etch profile despite the low etch rates compared to halogen gas mixtures.

In this paper the inductively coupled plasma etching characteristics of TiN hard masked CoFeB thin films was studied by using a CH<sub>3</sub>COOH/Ar gas mixture. A CH<sub>3</sub>COOH solution was introduced into the chamber using a specially designed feeding system. The etch rates were obtained using a surface profilometer (Tencor P-1) and etch profiles were observed by using a field emission scanning electron microscopy (FESEM-HITACHI 4300SE). The surface chemistry and etch mechanism were analyzed by using optical emission spectroscopy (OES-Ocean Optics Maya 2000 Pro) and X-ray photoelectron spectroscopy (XPS).

**TF-WeP29 Electronic Transmission of Two, Three and Four Magneto-Electrostatic Barriers on Graphene: An Approach to Diode, Transistor and Thyristor., R.A. Reyes Villagrana, Jesús Madrigal Melchor, J.R. Suárez López, I. Rodríguez Vargas,** Universidad Autónoma de Zacatecas, México

In 1904, J.A. Fleming patented the first thermionic diode. Then in 1947, J. Barden, W. H. Brattain, and W. B. Shockley invented the bipolar transistor. Later in 1958, J. S. Kilby and R. Noyce developed the first integrated circuit. Since then it has researched, developed and implemented analog electronics. Both the diode and bipolar transistor structures have pn and pnp or npn respectively. However, there is another device having a pnpn structure, known as the *thyristor*. This device has different applications, but its main function is to control high power systems. This paper presents a study on the transport properties of Dirac electrons through a structure of two, three and four magneto-electrostatic barriers on a sheet of graphene, an approach to the structures of a diode, transistor and thyristor is presented. The calculation of pn, pnp, and pnpn structures was conducted using the transfer matrix method and the formalism of linear Landauer-Büttiker scheme. The results show that at normal incidence, with increasing two, three and four barriers increases the number of oscillations in the transmission bands. Furthermore, increasing the value of the thickness ratio of the barrier / well width, the transmission bands are shifted toward the blue and decrease transmission windows. Increasing the electrostatic potential decreases the size of the transmission bands. The effect of the magnetic field causes the transmission spectra increase the width of the central maximum band, and reduces the width of the bands of transmission side. Also, the increase of the magnetic field produces peaks in the transmission bands that arise in this type of structure, number of peaks in the transmission bands, corresponding to the number of wells in the structure. The conductance shows oscillations, which has an explanation by the bound states. Exists interest from the authors continue to explore further the benefits presented graphene in the development of new devices.

**TF-WeP32 Influence of Deposition Conditions on the Structural and Optical Properties of nc-Si/SiO<sub>2</sub> Films in SiO<sub>2</sub> Matrix using HW-CVD, Ateet Dutt, Matsumoto,** Centro de Investigación y de Estudios Avanzados del IPN, Mexico, *Santana-Rodríguez*, Universidad Nacional Autónoma de México, Mexico, *Santoyo Salazar*, *Godavarthi*, Centro de Investigación y de Estudios Avanzados del IPN, Mexico

We have find the influence of deposition time and chamber pressure on the morphology and optical properties of the nanocrystalline silicon (nc-Si) and related composite particles embedded in the amorphous silicon oxide (a-SiO<sub>2</sub>) matrix using hot wire chemical vapor deposition (HW-CVD). Catalyst material Tungsten (W) was employed for the decomposition of source gases in the reaction chamber. Differences in the crystalline nature of the film deposited on crystalline-Silicon and glass substrates have been explained before also as a function of filament temperature [1]. In this studies using X-Ray diffraction (XRD) and Raman spectroscopy phase differences has been explained with respect to time of deposition and deposition pressure. XRD results demonstrate the presence of crystalline particles related to silicon composites in the amorphous matrix. Fourier transform infrared spectroscopy has been used to study the various surface species present in the film. The as-deposited samples grown at low substrate temperature of about 200°C, has shown photoluminescence spectra in almost all of the visible range (white emission). Photoluminescence has been found to be in correlation with the size of nc-Si particles and/or the defects present in the thin film. This low temperature deposited material could open gateways in future for further device fabrication based on the Si thin film technology.

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**TF-WeP34 Chemically Enhanced Raman Scattering of Rhodamine 6 G Molecule Adhere to Graphene, MoS<sub>2</sub> and WSe<sub>2</sub>: Efficiency Variation determined by Pressure and Charge Transfer.** *Hyunmin Kim*, Daegu Gyeongbuk Institute of Science and Technology, Korea, *Y. Lee*, Sungkyunkwan University, Korea, *S.M. Jeong*, Daegu Gyeongbuk Institute of Science and Technology, Korea, *J.H. Cho*, Sungkyunkwan University, Korea, *J.-H. Ahn*, Yonsei University, Korea

Recently, graphene enhanced Raman scattering (GERS) is very popular as a method to extract chemical information from dye molecules due to its excellent quenching effect on otherwise superfluous fluorescent backgrounds. Here, we introduce a new method to enhance Raman signals of a graphene-rhodamine 6G (R6G)-graphene sandwich structure by creating a magnet-induced static pressure to maximize the chemical contact of the R6G molecules with graphene. The increase in pressure in the graphene-R6G-graphene sandwich geometry plays a crucial role in enhancing the Raman signal by approximately up to 30 times in comparison to that acquired from a R6G/graphene layered film. In addition, we found that the pressure-induced enhancement effects in the planar vibrational motion of the R6G (1200–1500 cm<sup>-1</sup>) were more recognizable than the low wavenumber region and were almost comparable to the surface-enhanced Raman scattering signals observed from the spontaneously formed “folded” pseudo  $\pi$ -bonded graphene-R6G-graphene sandwich structures. The enhancement effect diminished with an increase in the number of graphene layers (on the bottom side), clearly discernible upon imaging the graphene/glass sandwiched structures placed on top of exfoliated multilayered graphene coated with R6G. We also studied the surface enhanced Raman scattering of R6G using 2-dimensional hexagonal honeycomb layers such as MoS<sub>2</sub>, WSe<sub>2</sub> systems to compare with graphene. Thick (~10 nm) physisorbed adsorptions of R6G onto MoS<sub>2</sub> and WSe<sub>2</sub> nanosheets were made with soaking ~ 100 M level of aqueous R6G solution, allowing us to implement a photocurrent measurement and subsequently correlate it with Raman spectroscopy. The fluorescence quenching factor of R6G molecules coated on MoS<sub>2</sub> and WSe<sub>2</sub> systems was measured by approximately 100 times higher than that of solution-state R6G molecules. All results were quantitatively correlated with the amount of charge transfers obtained from phototransistor measurement, strongly suggesting that the Raman enhancement factor of molecules coated to hexagonal atomic layered systems can be predicted by photocurrent measurements. We also investigated the thickness dependence of MoS<sub>2</sub> and WSe<sub>2</sub> layers on the enhanced Raman signals of adsorbed R6G, showing that the enhancement effect of MoS<sub>2</sub> systems was maximized in the single layered nanosheets, demonstrating almost a linear-scale tailoring of Raman signals with the increase of the numbers of layers, while that of WSe<sub>2</sub> still remained substantial until the double layered nanosheets followed by a drastic decrease above them.

**TF-WeP36 Negative Thermal Expansion of Polystyrene Ultrathin Films Supported on Si Substrates revealed by X-Ray Reflectivity: Quench Rate Dependence.** *Kazuki Nishimori*, *S. Nakahara*, *K. Sekiya*, Kwansai Gakuin University, Japan, *Y. Chunming*, Shanghai Institute of Applied Physics, China, *I. Takahashi*, Kwansai Gakuin University, Japan

Understanding of ultrathin functional polymers is important for various fields of nanotechnology. However, physical property of polymeric thin films with thicknesses comparable to the size of molecules is significantly different from that of bulk due to the confinement effect and heterogeneity peculiar to thin films sandwiched between air and solid substrate. As one of the deepest and most interesting unsolved problems, origin of negative thermal expansion (NTE) often observed in ultrathin glassy polymer films has attracted considerable attention. In the present study, we find key factors for the emergence of NTE with polystyrene (PS) ultrathin films quenched from the rubbery state with different cooling rates. Samples are mono-dispersive atactic PS with molecular weight  $M_w = 955,000$  and glass transition temperature of 375 K. Thin films around 6 nm thick were formed by spin-coating technique on Si (100) substrates. Prior to the rapid cooling, thin PS films were annealed at 405 K for 12 hours in a low vacuum. From 405 K, the films were cooled to the liquid nitrogen temperature with different cooling rates and heated to room temperature in vacuum. Thermal expansivity was evaluated with X-ray reflectivity (XR) measured isothermally from room temperature to 405 K, which affords us precise temperature dependence of thickness, average electron density and root mean square of surface roughness. Relaxation in glassy state is also obtained through temporal variation in thickness at a certain temperature that can be monitored by XR. A strong correlation between cooling-rate-dependent-NTE and relaxation behavior at room temperature is revealed in this study.

**TF-WeP37 Large-Scale Laser Scribing of Complex Motifs.** *Goran Rasic*, North Carolina Central University

Micro- and nanolithography techniques are a key factor in pushing the limits of science and technology. This is especially true in the

semiconductor industry which has made remarkable progress over the last 20 years. With the technology focus moving to progressively smaller scale, numerous lithography methods of manufacturing complex micro- and nanostructures (such as photo, nanoimprint, e-beam, soft and focused ion beam) have been developed. However, most of these techniques have limitations in the form of material choices, speed, cost and/or pattern shape/size. Clearly a fast, low-cost and versatile method of producing high quality surface nanostructures is needed. Here, an approach that offers low-cost, fast manufacturing of complex patterns over large scale is presented. By utilizing existing and well known technology such as the optical disc drive and combining it with tools used in photolithography a novel manufacturing technique is made available. The method proposed can be used to directly scribe the desired pattern on the light sensitive material or create a master to be used for transferring a pattern to the appropriate material. In all cases the procedure is similar. First, the desired motif is drawn on a computer using any drawing program. Second, a label enabled media such as lightscribe or labelflash DVD is coated with the material to be inscribed (e.g. photoresist to create a master). The disc is then inserted in the appropriate labeling disc drive and the pre-drawn image is engraved in material/photoresist. If necessary the disc can be treated post-scribing to create the structures; e.g. develop the photoresist. Finally, the surface of the material is engraved with the predetermined pattern. The method described here represents an affordable, fast and versatile way of manufacturing complex micro- and nanostructures without some of the design, throughput and material limitations faced by costlier techniques, making state of the art research more affordable and accessible.

**TF-WeP38 Probing Ni(111)-graphene interface using Raman spectroscopy.** *Guanjun Cheng*, *I. Calizo*, *A.R. Hight-Walker*, National Institute of Standards and Technology

Theoretical simulations have shown that due to the hybridization of Ni d-electrons with the  $\pi$ -orbitals of graphene, graphene phonon dispersion is significantly altered and there is no Raman signal from graphene on Ni(111) due to the suppression of the Kohn anomaly (Nano Lett, 2010, 10, 4335-4340). In this work, we deposit Ni thin film by thermal evaporation onto mechanically exfoliated graphene, few-layer graphene (FLG), and graphite, and probe the Ni-graphene interface using Raman spectroscopy. When the sample is annealed in forming gas, Ni(111) thin film is produced on graphene, FLG, and graphite. We observe the disappearance of Raman signals from graphene underneath Ni(111) using a low power excitation laser and the re-appearance of Raman signals from graphene with a higher power excitation laser. This work provide direct experimental evidence for the strong interactions between Ni(111) and graphene.

**TF-WeP40 High Temperature Self-Lubricant Coatings with Release of a Lubricious Agent for Machining Applications.** *F. Fernandes*, University of Coimbra, Portugal, *T. Polcar*, University of Southampton, UK, *Albano Cavaleiro*, University of Coimbra, Portugal

Binary TiN and ternary (TiX)N hard coatings, with X = Cr, Al, Si, Cr, etc, are well established in commercial tribological applications due to their high oxidation resistance and high hardness. Such coatings have been used to protect the surface of milling and machining tools; however, their friction coefficient revealed to be fairly high, at high temperature. This is a key point during machining of low thermal conductivity materials such as Ti-alloys. Liquid lubricants and oils have been used to reduce the friction and temperature between the sliding contacts; however, they frequently volatilize at high temperature, leading frequently to the failure of the cutting tools and, consequently, to increasing machine down times. To face these problems, solid lubricant coatings have been developed in the last decades to reduce the friction coefficient. The approach has been combining the intrinsic properties of binary and ternary coatings with elements that give lubricious properties, as it is the case of V. Such element forms thin reaction films of V-O on the surface of coatings with interesting properties at high temperature. Thus, the main goal of this work was to study the effect of V content on the oxidation and tribological properties of TiSi(V)N coatings deposited by DC reactive magnetron sputtering. Comparison of these results with those achieved for TiN, and TiSiN coatings prepared as references is also provided. The oxidation resistance of films was characterized by thermo gravimetric analysis and the tribological properties evaluated in pin-on-disc wear equipment, using as counterparts Al<sub>2</sub>O<sub>3</sub> and HSS balls. V additions increased the oxidation rate and decreased the friction coefficient and volume loss of coatings. SEM and Raman analysis showed that V<sub>2</sub>O<sub>5</sub> phase is the responsible for this tribological performance. TiSiN displayed the lowest wear resistance among all the tested coatings.

# Wednesday Afternoon, December 10, 2014

## Energy Harvesting & Storage

Room: Lehua - Session EH-WeE

### Characterization of Materials for Energy Applications II

Moderator: Jim McQuillan, University of Otago, New Zealand

6:20pm **EH-WeE3 Nano Structured Thin Films for Hydrogen Permeation Barrier**, *Motonori Tamura*, The University of Electro-Communications, Japan

A considerable increase in scientific exploration concerning hydrogen production and storage has occurred within the last ten years. Numerous technologies including blast furnace production, biomass production, high temperature electrolysis, thermochemical cycles, advanced gaseous storage tanks, chemical hydrides, and advanced metal hydrides are being developed to provide competitive alternatives to fossil fuel energy technologies. One issue for successful commercial implementation of these technologies is the ability of structural materials for process vessels and piping, storage containers, and engineered components to resist embrittlement from hydrogen.

Hydrogen embrittlement, hydrogen induced cracking, and hydrogen corrosion cracking have long been studied for a wide variety of materials and operating conditions. Major structural component materials for hydrogen service applications are austenitic stainless steels such as Type 304, 316L, etc. These austenitic stainless steels have been previously shown to have a mild susceptibility to hydrogen embrittlement. However, this susceptibility can vary with changing environmental conditions. And as such these materials are often coated with permeation barriers to minimize the potential impact from hydrogen exposure. Some permeation barrier materials such as Al or Al<sub>2</sub>O<sub>3</sub> have been evaluated. These materials have shown permeation reductions that range from 10 to 10000 times. This variation is due to several factors such as inherent permeation resistance and microstructure or nanostructure of thin films. Previous study showed that fine-grained dense films obtained by physical vapor deposition performed low hydrogen permeability. In this study, effect of nanostructure of thin films on hydrogen permeation is evaluated.

The hydrogen permeation behavior of thin films coated Type 316L stainless steel was investigated. Thin films of TiN, TiC, Al<sub>2</sub>O<sub>3</sub> were deposited by ion plating. Coated samples were examined using optical microscopy and scanning electron microscopy (SEM). The coating chemistry was determined using Energy Electron Probe Micro Analysis (EPMA) and the crystallography was analyzed by X-ray diffraction (XRD). Hydrogen permeation test of samples, 35 mm diameter and 0.1 mm thick, was conducted at 773K. The fine-grained and (111) oriented TiN film whose grain size was under 100 nm reduced hydrogen permeation by three orders of magnitude compared to untreated stainless steel. Grain interface was thought to be effective hydrogen trap sites.

6:40pm **EH-WeE4 Laser Processing and Photoacoustic Characterization of Nanomaterials and Thin Films**, *Mayo Villagrán-Muniz*, *CSA. Sánchez-Aké*, *F.T. Tenopala*, *M.A.V.A. Valverde-Alva*, *A.C. Canales*, *J.M.DL. Martínez-De León*, *B. de la Mora*, *C.G.S. García-Segundo*, Universidad Nacional Autónoma de México, *T.G.F. García-Fernández*, Universidad Autónoma de la Ciudad de México, México, *F.A.C.M. Alvarez-DelCastillo-Manzanos*, Universidad Nacional Autónoma de México **INVITED**

The synthesis of metallic nanoparticles (NPs) either covered or embedded in transparent dielectric thin films has recently received great attention for its possible applications as plasmonic structures. There are several methods to synthesize and incorporate metal NPs such as chemical synthesis, photoreduction, thermal and laser annealing<sup>[1]</sup>. The annealing methods have the advantage of being free of chemical wastes. The formation of NPs by thermal annealing of thin films inside ovens is the result of the minimization of surface energy, and thus the disaggregation of the film into particles. For the case of laser annealing, nanoparticles of few tens of nm are produced irradiating metal thin films with nanosecond laser pulses<sup>[2]</sup>. The physical mechanisms behind the annealing of metallic thin films have been widely studied<sup>[3]</sup>. These studies mainly focus on the resulting final nanostructure as a function of the involved experimental parameters, without studying the evolution of the process in time; notwithstanding the formation of NPs is a time-dependent process. For example, the shape and size of the NPs depends on the number of pulses in the case of laser annealing<sup>[4]</sup>. For the case of thermal annealing, the NPs size strongly depends on the interval of time in which the sample is inside the oven<sup>[5]</sup>. In this work we study the formation of gold NPs by thermal and laser

annealing of thin films. Simultaneously we use pulsed- photoacoustic and laser scattering techniques to analyze in situ the synthesis of NPs during the annealing process. The influence of the initial film thickness on the size and size distribution of the resulting NPs was studied. The cumulative effect of the laser pulses and the temperature and annealing time were also analyzed. The changes in the photoacoustic signal and in the scattered intensity of the laser were compared with the SEM images of the samples. The current results suggest that both techniques are suitable for real time monitoring of the changes produced by the annealing. [1] M.J. Beliatis, S.J. Henley, S. Han, K. Gandhi, A.A.D.T. Adikaari, E. Stratakis, E. Kymakis, S.R.P. Silva, Phys. Chem. Chem. Phys., 15, 8237, 2013. [2] S. Imamovaa, N. Nedyalkov, A. Dikovska, P. Atanasov, M. Sawczak, R. Jendrzewski, G. Sliwinski, M. Obara, Appl. Surf. Sci., 257, 1075-1079, 2010. [3] C.V. Thompson, Annu. Rev. Mater. Res., 42, 399-434, 2012. [4] H. Krishna, N. Shirato, C. Favazza, R. Kalyanaraman, J. Mater. Res., 26(2), 154-169, 2011. [5] C. Worsch, M. Kracker, W. Wisniewski, C. Russel, Thin solid films 520, 4941-4946, 2012.

7:40pm **EH-WeE7 Mapping the Propagation of Excitons through Organic and Inorganic Light Harvesting Nano Composites**, *Alexander Weber-Bargioni*, *S.Y. Leblebici*, *J. Lee*, *M. Melli*, *W. Bao*, *K. Munechika*, *S. Barja*, *S. Aloni*, Lawrence Berkeley Lab, USA, *F. Intonti*, European Laboratory for Non Linear Spectroscopy, *D.F. Ogletree*, Lawrence Berkeley Lab, USA

Here we present unprecedented insight into the local exciton transport through organic and inorganic semiconducting nano building block assemblies using state of the art near field optics, hyperspectral mapping, and Field Effect Transistors to control the exciton transport electronically.

Controlling individual excitons and their deliberate movement through a material will provide the access to a new parameter space for the development of next generation light harvesting materials. Nano materials have in principle the potential to realize this vision due to their tuneability. However, the lack of spatial resolution has so far prevented the insight needed to control the transport of optically excited electronic states at their native length scale.

To study the local exciton transport we use optical antennae to locally excite our sample optically and map spatially independent the energy flow by detecting either the local photo luminescence or the local photo current. We use this approach to study exciton transport through three model systems: Inorganic nano wires, 2-D assemblies of inorganic nano crystals, and through organic PV materials.

In InP nanowire system we demonstrate that the transport is mediated by locally enhanced exciton recombination velocity due to charge puddles on nanowire surfaces. CdSe Quantum Dot assemblies are another excellent absorber material system for light harvesting purposes. We determined exciton transport length through well ordered 2-D films of CdSe Nano Crystals of 80 nm and 120 nm for the 1-D case, mediated by Foerster Resonance Energy Transfer (FRET). To develop a better understanding of FRET between quantum dots (which is still not really understood) we used a graphene Field Effect Transistor to study FRET between individual quantum dots and graphene. In this device we can systematically tune with high precision the distance between graphene and quantum dot and the electronic structure of the exciton adsorber (graphene), while building the currently smallest light switch in the world.

Exciton diffusion is also a key hurdle for the systematic development of Organic Photo Voltaic. We used our techniques to directly measure the exciton diffusion length in polymer (P3HT) and small molecule (rubrene) organic photo voltaic materials and show a crystallinity dependent exciton diffusion length that correlates to the OPV device power conversion efficiency. Furthermore we have evidence that local electric field gradient can modify the exciton diffusion length in organic semiconductors, where the exciton binding energy is large (1 eV) and the transport is mainly mediated by tunneling processes.

8:00pm **EH-WeE8 Probing Exciton Diffusion in Thin Film Organic Photovoltaics with Femtosecond Stimulated Raman Spectroscopy**, *P. Hoffman*, *Y. Leblebici*, *A. Mathies*, University of California Berkeley, *Adam Schwartzberg*, Lawrence Berkeley Lab, USA

The nature of the organic photovoltaic (OPV) bulk heterojunction interface, and how charge carriers diffuse through the individual components of this system, is of critical importance to understanding how these devices function, and how they can best be optimized. Using femtosecond stimulated Raman spectroscopy (FSRS), we have observed that in the MDMO-PPV/PCBM system there is a 150 fs time window during which excitons may propagate to the interfacial donor/acceptor region, despite the fact that the excitons persist for as much as 170 ps, greatly limiting the

mobility of exciton mobility and device performance. In addition, we have found that the charge transfer region where carriers efficiently pass from donor to acceptor is approximately one monolayer wide, significantly narrower than was previously believed. This understanding is possible through the examination of electron density and chemical modifications in the molecular species which we observe using the FSRS technique in thin film samples for the first time.

**8:20pm EH-We9 Correlating Local Morphology and Local Opto-Electronic Properties of Hybrid Organic-Inorganic Perovskite Solar Cell Materials, Sibel Leblebici, Y. Li, F.M. Toma, M. Melli, I. Shlesinger, I.D. Sharp, A. Weber-Bargioni, Lawrence Berkeley Lab, USA**

We demonstrate an in-depth characterization of local opto-electronic properties in hybrid organic-inorganic perovskite materials for solar cells using complementary scanning probe techniques.

Perovskite solar cells have the potential to combine high efficiency and low-cost fabrication compared to other third-generation solar technologies; Since 2009, power conversion efficiency of perovskite solar cells has rapidly increased from 3.8% to almost 20%. However, one of the main challenges to systematically increase power conversion efficiency and to develop cost efficient fabrication techniques is the lack of understanding of the exact operating mechanism in perovskite solar cells. In particular, the relationship between morphology, chemical composition, and optoelectronic processes and their impact on overall performance in these materials is hardly understood.

We have studied two promising solution processed hybrid organic-inorganic perovskite materials,  $\text{CH}_3\text{NH}_3\text{PbI}_3$  and  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ , using scanning probe techniques to determine local photocurrent generation, topography, and the local electronic structure. Depending on composition and fabrication approach, we observed substantial differences in local morphology, crystallinity, photocurrent generation, and photoluminescence. Specifically, we have measured a significant heterogeneity in the local photocurrent generation that does not correlate with topography but rather with the local electronic structure.

**8:40pm EH-WeE10 Oxide Heterojunction Electrodes for Sunlight Conversion and Storage, S. Kim, Hyunwoong Park, Kyungpook National University, Korea**

$\text{TiO}_2$  and  $\text{WO}_3$  heterojunction electrodes are studied for their bifunctionality on harvesting light and storing energy. Both semiconductors are fabricated either 'single' (mixed) electrodes or two different electrodes galvanically coupled in a mixed electrolyte of 0.1 M sodium formate and 0.1 M sodium chloride. Irradiation of AM 1.5-light shifts the open circuit potentials (OCPs) of the mixed and coupled electrodes from around  $-0.1V_{\text{SCE}}$  (dark OCPs) to a potential range between  $-0.8$  and  $-0.5V_{\text{SCE}}$ , which slowly return to their respective dark OCPs over a period of around 14 hours. Such discharging periods are significantly influenced by the irradiation (photocharging) time and weight or area ratios of  $\text{TiO}_2$  and  $\text{WO}_3$ . When the  $\text{TiO}_2$  and  $\text{WO}_3$  mixed electrodes are galvanically coupled to stainless steel electrodes for application to anticorrosion, the mixed potentials of the couple are maintained at ca.  $-0.4 V_{\text{SCE}}$  over 10 hours even after light off. The measured galvanic currents verify that the photogenerated electrons of  $\text{TiO}_2$  flow to  $\text{WO}_3$  (charging) and even overflow to the steel (cathodic protection) during the irradiation, while the stored electrons at  $\text{WO}_3$  flow to the galvanically coupled steel electrodes directly or through the  $\text{TiO}_2$  upon light off. This research was financially supported by the Basic Science Research Program (NRF-2012R1A2A2A01004517) and Frame-work of International Cooperation Program (NRF-2013K2A1A2052901).

## Thin Films

**Room: Makai - Session TF-WeE**

### Thin Film Synthesis and Characterization III

**Moderator:** HugoR. Navarro Contreras, Coordinación para la Innovación y la Aplicación de la Ciencia y la Tecnología (CIACyT-UASLP)

**5:40pm TF-WeE1 Static and Dynamic Magnetic Properties in FeCoN Thin Films Deposited Under Various Deposition Powers, Yuping Wu, National university of singapore, Z.H. Yang, National university of Singapore, F.S. Ma, B.Y. Zong, National University of Singapore**

In this work, we deposited FeCoN thin films by reactive magnetron sputtering. The applied deposition power was changed from 150 W to 1000 W. The dynamic magnetic properties were measured with the shorted microstrip transmission-line perturbation method, which was developed in

our lab. The damping coefficient was estimated by analyzing the measured permeability spectra based on Landau-Lifshitz-Gilbert (LLG) equation. Both the static magnetic properties and the damping coefficient in the magnetization dynamics can be conveniently and effectively tuned by varying the sputtering deposition power, which results in controllable and modified dynamic magnetic properties. The physical origin of the influences is related to the changed deposition rate, which is a critical factor determining the microstructure of films.

**6:00pm TF-WeE2 Substrate Heating during Reactive Magnetron Sputtering, Julio Cruz, J. Restrepo, S. Muhl, IIM-UNAM, Mexico**

Substrate heating by the plasma during magnetron sputtering is known to occur, however, there have been very few detailed studies of this process which involves a combination of bombardment by ions, excited and neutral species and UV radiation incident on the substrate. We have studied the heating of the substrate during DC magnetron sputtering of a 4" titanium target as a function of the experimental conditions; plasma power, Ar gas pressure, floating, grounded and biased substrates. We have also studied the substrate heating during reactive sputtering mode by using a gas mixture of argon with nitrogen. On the other hand, it is known that the crystalline orientation of titanium nitride depends on the sputtering conditions. Here we report the effect of the plasma substrate heating, as a consequence of the plasma conditions, on the morphology and the crystalline structure of titanium nitride. The properties of the films were analyzed using SEM and X-ray Diffraction and the film thickness was measured using a stylus profilometer. The measurements of the non-reactive sputtering showed that the substrate temperature could reach temperatures higher than 200°C with a plasma power of 200W and showed a non uniform temperature distribution over the substrate, with the highest temperature in front at the racetrack and the lowest temperatures in front of the edge of the target. Finally by using a Fluke Ti300 camera we show the temperature change in the substrate with time for both reactive and non-reactive processes.

**6:20pm TF-WeE3 The Hollow Cathode Discharges; How They Have Been used to Produce Thin Films and the Novel Toroidal Planar Hollow Cathode System, Stephen Muhl, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Mexico, A. Perez, Universidad Nacional Autónoma de México, Mexico, A. Tenorio, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Mexico, E. Camps, Instituto Nacional de Investigaciones Nucleares, Mexico**

In 1916 F. Paschen first report the hollow cathode discharge he demonstrated that the system was capable of producing a high electron flux with relatively low ion and neutral temperatures. Approximately 40 years later Lidsky showed that hollow cathode arc discharges were one of the best plasmas sources available at that time. The term "hollow cathode discharges" has been used in reference to almost any discharge in a cathode with a cavity-like geometry, such that the plasma was enclosed by the walls which are at the cathode potential. Just as trapping of electrons in a magnetron cathode by the magnetic field results in an increase in the plasma density, in the hollow cathode the geometry of the cathode also produces a high plasma density. In general, three types of discharge can be established in a hollow cathode; at low power and / or at relatively low gas pressures the plasma is a "conventional" discharge characterized by low currents and medium to high voltages (a Discharge in a Hollow Cathode or D-HC). However, even this simple plasma has a higher density than a normal planar parallel electrode system because the hollow geometry reduces the loss of electrons. If the combination of gas pressure, applied power and hollow cathode diameter is correct, the negative glow of the plasma almost completely occupies the interior volume of the cathode. Under this condition the plasma current can, for the same voltage, be 100 to 1000 times the values for the "simple" D-HC discharge and the plasma density is very large (this is the Hollow Cathode Discharge or HCD). If the temperature of cathode can increase so that Thermal-Field electron emission becomes an important additional source of electrons the discharge can change into a dispersed arc (this is the Hollow Cathode Arc or HCA). The accepted explanation for the HCD phenomenon involves the existence of high energy "pendulum" electrons reflected from sheath to sheath on either side of the inside of the cathode; the long trajectory of these electron is thought to produce an increased number of secondary electrons, which produces the high plasma density and plasma current. We will discuss some of the problems associated with the well-accepted model and we will propose a new explanation which has some important implications.

Finally, we will describe how hollow cathodes can be used to deposit thin films and nanostructured coatings, including the use of our novel toroidal planar hollow cathode to produce bismuth thin films, nanoparticles and bismuth/a-C:H nanocomposites.

6:40pm **TF-WeE4 Depth Profiling Organic Thin Films with Argon Cluster Beam**, *Jean-Jacques Pireaux, Nittler, Noël, Houssiau*, University of Namur, Belgium

Many modern devices are based on multilayers of different materials, combined to reach a specific application. Monoatomic ion beam depth profiling did – and still do – immensely contribute to the learning of such multilayered structures containing metallic and oxide films; but one couldn't study (in ToF-SIMS, AES or XPS) an organic/other material interface, or an organic multilayered structure because of the damages induced by the ion beam. For the profiling of organic layers, the development and commercial availability of sputtering sources based on poly-atomic ions (SF<sub>6</sub>, C<sub>60</sub>, coronene) came as a significant and promising evolution; the still more recent Argon cluster-ion source appears now as a revolution for a true quantitative depth analysis of organic films. Numerous applications of gas cluster ion beams have been presented at international conferences; publications study the influence of cluster size, of cluster energy on sputter rates on series of different polymers, and on depth resolution in sputter depth profiles [1]. The present work aims to study by XPS the sputter yield, and the depth resolution in samples consisting of multilayered amino-acid films while profiling with different Ar cluster ions (Thermo Fisher Scientific Escalab 250Xi spectrometer, MAGSIS source). The materials were chosen for their ease to be reproducibly deposited by sequential thermal evaporation in high vacuum under quartz-crystal balance monitoring; the method revealed successful for the study of delta layers in dual beam Cs+/Bi<sup>3+</sup> profiling in ToF-SIMS [2]. Phenylalanine (Phe) and tyrosine (Tyr) were used for this study. Although both amino acids differ only by an OH- group, their characteristic chemical fingerprints could be differentiated throughout the whole depth profile. Both materials surprisingly present a very different sputter yield: the erosion yield of Phe is larger (almost twice the value, depending on the Ar cluster size and energy) than for Tyr – a trend that is completely reversed in ToF-SIMS using Cs+[2,3]; this strongly suggests different sputtering mechanisms, that will be reviewed during the presentation. Depth resolution at the interface between two layers is found to be better when sputtering from the high sputter yield material to the low one. It is worth to note in addition that, as suggested by Laser scanning confocal microscopy, the gas cluster ion beam profiling does not increase significantly the sample surface roughness.

[1] P.J. Cumpson et al, J.V.S.T. A31 (2013)020605 ; SIA 45 (2013)601

[2] C. Noël, University of Namur, Master Thesis, 2013

[3] C. Noël, L. Houssiau. SIMS Europe 2014 Conf., Münster.

7:00pm **TF-WeE5 Adaptive Functional Surfaces: Ni-Ti-(Cu) Shape Memory Thin Films**, *M. Callisti*, University of Southampton, *Tomas Polcar*, University of Southampton, UK

Shape memory alloys could be effectively used as thin films acting either as active/passive actuators or superelastic interlayers. In this study a series of NiTiCu coatings with increasing Cu was fabricated by magnetron sputtering with a thickness of 2 μm. In order to obtain superelastic properties, the films were isothermally annealed for 1 hour at 500 °C in a high vacuum environment. Subsequently the superelastic layers were coated by magnetron sputtering with a functional tribological coating (DLC-W and self-lubricant WSC film).

The chemical composition of every single layer was measured by Energy-dispersive X-ray spectroscopy (EDS), while the structure was evaluated by grazing-incidence X-ray diffraction (GIXRD) and transmission electron microscopy (TEM). The mechanical properties of the single layers as well as those of the bilayers were measured by nanoindentation. Finally, the tribological behaviour of the bilayers and of the single layers were characterised by pin-on-disc.

We will demonstrate that superelastic interlayer could significantly increase coating adhesion. Pure NiTi interlayers underwent progressive irreversible martensitic transformation during the sliding and lost superelasticity; on the other hand, transformation of NiTiCu film was fully reversible. We will show that we can control compressive and shear stress in functional coating during sliding by selection of an optimum superelastic interlayer.

7:40pm **TF-WeE7 Metal Oxide thin Films for Medical Applications**, *Sandra Rodil, A. Almaguer-Flores*, Universidad Nacional Autónoma de México, *P. Silva-Bermudez*, Instituto Nacional de Rehabilitación **INVITED** Nowadays, it is generally accepted that surfaces are critically important to nearly all aspects of biomedical technology since most of the biological reactions occur at the interfaces. In vitro studies have demonstrated that the surface properties are directly related to important biological events, such as protein adsorption, bacterial attachment and cell growth. In the case of medical implants, during the last years the research has evolved from the improvement of bulk properties and design of the implants to the development of a variety of bio-functional surface modifications, such as surface topography at the nanoscale, adhesion of growth factors or coating

deposition. There is an extensive research to find methods of designing tailored surfaces, which might act as stimuli to guide specific cell responses according to the specific medical application.

This presentation explores one of the many surfaces modifications that have been proposed; plasma deposited coatings. The talk is then divided into two parts. Firstly, a short review about the specific needs to improve odontological implants. Secondly, the results of the physical, chemical and biological characterization of metal oxide thin films (TiO<sub>2</sub>, ZrO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub> and Ta<sub>2</sub>O<sub>5</sub>) deposited by magnetron sputtering are presented. The factors considered of biological relevance in order to understand the surface interaction and that will be presented include: a) protein adsorption on the metal oxides studied by Ellipsometric Spectroscopy, Atomic Force Microscopy and X-ray photoelectron Spectroscopy, b) Corrosion behaviour of the oxides immersed in simulated biological solutions, c) Bacterial attachment and d) Cell adhesion, proliferation and differentiation.

8:20pm **TF-WeE9 Synthesis and Characterization of TiO<sub>2</sub> and Bi<sub>2</sub>O<sub>3</sub> Thin Films for Photocatalytic Applications**, *JuanCarlos Medina, M. Bizarro*, IIM-UNAM, Mexico, *M. Giorcelli, A. Tagliaferro*, Politecnico di Torino, Italy, *P. Silva-Bermudez*, Instituto Nacional de Rehabilitación, Mexico, *S.E. Rodil*, IIM-UNAM, Mexico

The magnetron sputtering technique was used to obtain bismuth oxide (Bi<sub>2</sub>O<sub>3</sub>) and titania (TiO<sub>2</sub>) thin films. The films were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray Photoelectron Spectroscopy (XPS) and contact angle measurements. The results indicated that the Bi<sub>2</sub>O<sub>3</sub> thin films presented the cubic delta phase and the TiO<sub>2</sub> thin films showed a combination of rutile-anatase. The photocatalytic activity for both films was evaluated testing the degradation of methyl orange dye (C<sub>14</sub>H<sub>4</sub>N<sub>3</sub>SO<sub>3</sub>Na) under ultraviolet light and a solution of pH 3.5. The dye degradation and the kinetic of the reaction were estimated using the variation of the corresponding absorption band as a function of the irradiation time. The results pointed out that the photocatalytic activity was always larger for Bi<sub>2</sub>O<sub>3</sub> films than for TiO<sub>2</sub> films. Moreover the activity was also larger for Bi<sub>2</sub>O<sub>3</sub> in comparison to equivalent mass-amounts of TiO<sub>2</sub> powders (P25) under the same experimental conditions. However XPS tests showed that after a degradation cycle bismuth oxide transforms to Bismuth Oxochloride (BiOCl) due to the interaction with Cl ions from the HCl solution used to decrease the pH, and as a consequence the photocatalytic effect was reduced. After calculating and comparing the reaction kinetic constants for both oxide films, it is concluded that under UV light, the Bi<sub>2</sub>O<sub>3</sub> reaction rate is three-fold larger than TiO<sub>2</sub> reaction rate constant. These results suggest that the Bi<sub>2</sub>O<sub>3</sub> films are a new promising photocatalytic material for water treatment application. Moreover, studies of photoinduced changes in the wettability demonstrated a similar behavior between Bi<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> thin films.

8:40pm **TF-WeE10 Preparation of Ce-doped Hafnium Oxide Thin Films by Sol-Gel Method**, *Luis Garcia-Cerda, A. Puente*, Research Center on Applied Chemistry, Mexico, *S. Galvez-Barboza, L.A. Gonzalez*, Center for Research and Advanced Studies of the National Polytechnic Institute

Mono and multilayer Ce-doped hafnium oxide thin films were deposited on silicon wafers and quartz by spin-coating technique using a solution prepared by solgel with hafnium chloride, cerium nitrate, citric acid and ethylene glycol as starting materials. Ce-doped HfO<sub>2</sub> thin films with 1, 3 and 5 layers were annealed in air for 2 h at 500, 700 and 900 °C. The thin films were then characterized for structural, surface morphological and optical properties by means of X-ray diffraction (XRD), Atomic force microscopy (AFM), scanning electron microscopy (SEM) and optical absorption. X-ray diffraction analysis indicated that the cubic HfO<sub>2</sub> films could be obtained by annealing at 500 °C. AFM and SEM images revealed well defined particles which are highly influenced by annealing temperatures.

# Thursday Morning, December 11, 2014

## Biomaterial Interfaces

Room: Milo - Session BI-ThM

## Plasma Bio, Medicine & Agriculture

Moderator: Ellen Fisher, Colorado State University

8:40am **BI-ThM3 Diagnostics of Nonthermal Atmospheric Pressure Plasma Jet and Dielectric Barrier Discharge Sources for Plasma Bioscience and Medicine by Collisional Radiative Model and Stark Broadening Method, Eun Ha Choi, Y.J. Hong, G. Cho, H. Uhm, KwangWoon University, Korea** **INVITED**

Nonthermal biocompatible plasma (bioplasma) sources and their characteristics operating at atmospheric pressure have been introduced and overviewed for plasma bioscience and medicines, especially used in Plasma Bioscience Research Center (PBRC), Korea. The electron temperature and density have been measured, respectively, by the atmospheric collisional radiative model and Stark broadening method in this experiment. The electron temperatures and plasma densities are measured to be  $0.2 \sim 0.7$  eV [1] and  $1 \times 10^{14} \sim 2 \times 10^{15}$  cm<sup>-3</sup>, respectively, for the nonthermal bioplasma jet and DBD plasma sources in PBRC. Herein, we have also introduced the basic generation mechanism of reactive hydroxyl radical OH species and hydrogen peroxide H<sub>2</sub>O<sub>2</sub> by plasma-initiated ultraviolet photolysis of water[1] inside the biological solutions, which are main species of interactions with microbial[2] and mammalian cells resulting in apoptotic cell death [3].

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- [2] Y. H. Ryu et. al., Plos One, 8, e66231 (2013).
- [3] K. Pangomm, et.al., Cell Death & Disease 4, e642 (2013).

9:20am **BI-ThM5 Surface Modification of Drug-Delivery Systems to Optimize Device Performance, Adoracion Pegalajar-Jurado, M.J. Hawker, B.S. Neufeld, M.M. Reynolds, E.R. Fisher, Colorado State University**

Current medical device are often affected by biofouling issues, including blood clot formation and bacterial infection. To combat undesirable side effects and severe medical complications related to the fouling of the devices, a dual approach is required where tuned surface properties and localized delivery of specific biomolecules are combined to enhance device performance. To accomplish this, advanced material platforms are needed to achieve localized therapeutic action and customizable surface properties. Although several wet chemical methods have been explored for surface modification, these methods can produce irreproducible surface modifications resulting from non-uniform coatings and/or can interfere with drug delivery mechanisms. An alternative technique that alleviates many of these issues is plasma surface modification, which offers a tunable and versatile parameter space for tailored and reproducible surface modifications for specific applications while retaining the bulk properties of the material. Herein, we describe the surface modification of a variety of drug delivery systems (including S-nitrosated polymer derivatives) via plasma treatment, resulting in a device that maintained their releasing capabilities (i.e. release of nitric oxide (NO)), but exhibited tailored surface properties for specific applications. As a prototype drug delivery system, we have used S-nitrosated poly(lactic-co-glycolic acid)-based hydrophobic polymer to achieve a material capable of releasing the therapeutic agent NO. The S-nitrosated polymer derivative was modified via H<sub>2</sub>O plasma treatment, resulting in a superhydrophilic material (water droplet spread completely in <100 ms) that retained 90% of its initial S-nitrosothiol content. Under thermal conditions, NO release profiles were identical to controls. Under buffer soak conditions, the NO release profile was slightly lowered for the plasma-treated materials; however, they still result in physiologically relevant NO fluxes. Correlations between this data and those recorded from other plasma treated drug delivery systems will also be discussed.

9:40am **BI-ThM6 Generation and Transport of Reactive Oxygen Species in Plasma Irradiated Liquid, I. Ikuse, Satoshi Hamaguchi, Osaka University**

Numerical simulations of chemical reactions and diffusion of reactive species in water exposed to an atmospheric-pressure plasma (APP) have been performed based on one-dimensional reaction-diffusion equations. When a living tissue is exposed to a low-temperature APP, there is almost always a liquid layer, such as blood, lymph, or other body fluid, that separates the gas phase and the tissue. Therefore charged and chemically

reactive species generated by the plasma are transported through the liquid before reacting with the tissue surfaces. The aim of this research is to understand how and where such chemically reactive species that affect biological matters are generated and transported through a liquid. While a variety of ions, excited atoms and molecules as well as chemically reactive charge-neutral species (including free radicals) are generated in the gas phase, the majority of highly reactive species may decay or be converted to more stable species before reaching the liquid surface. On the other hand, charged species and highly reactive charge-neutral species generated in the gas phase near the plasma-liquid interface are likely to be adsorbed by the liquid surface and to generate highly reactive species in a very thin layer (with a thickness 10 ~ 100 nm) of liquid just below the liquid surface. In the simulation, gas phase species generated by APP are assumed to enter pure water at their thermal velocities and dissolved without any barrier. The model incorporates 37 species and 111 chemical reactions in water at room temperature. The simulation has indicated the presence of such a thin liquid layer (which we call a "reaction boundary layer") at the plasma-liquid interface, only in which highly reactive species such as OH radicals and solvated electrons exist and rapidly generate less reactive species such as H<sub>2</sub>O<sub>2</sub>, which are then transported to the bulk liquid by diffusion.

10:20am **BI-ThM8 Short-Pulsed Uniform Atmospheric Pressure Dielectric Barrier Discharges in Medical and Biological Surface Treatment, Gregory Fridman, Drexel University, USA** **INVITED**

Engineering innovation has produced startling advances in healthcare. Lasers, ultrasound, ionizing and electromagnetic radiation are examples of life saving diagnostics and treatments that originated in engineering disciplines outside of medicine. In this vein, it was demonstrated that specific types of strongly non-equilibrium nanosecond pulsed atmospheric air plasmas have unique therapeutic effects and hold the promise for new medical diagnostic tools. For example, this presentation will be focused on therapeutic effect of plasmas based on their ability to deactivate pathogens directly in the wound bed, stop bleeding without damage to healthy tissue, promote cell migration and proliferation into the wound bed, angiogenesis, growth factor release, stem cell differentiation and specialization, and other effects leading to the improved healing of wounds and diseases. Mechanisms of plasma-tissue interaction through liquid medium, nanosecond plasma uniformity, and generation and control of reactive oxygen and reactive nitrogen species in plasma will be discussed in this presentation, based on results of the current DARPA and NIH-funded projects.

11:00am **BI-ThM10 Plasma Applications to Agriculture: Plasma Farming, Sukjae Yoo, National Fusion Research Institute, Korea, Republic of Korea** **INVITED**

Plasmas have been applied to various fields: The surface modification and thin film deposition, semiconductor and display fabrication, development of new energy sources, and environmental improvements, plasma medical treatments, etc. In addition to the above mentioned fields, the plasma can be well applied to the agriculture and food.

In case of the semiconductor industry, the first technical innovation was caused by invention of the transistor and integrated circuit (IC) based on chemical wet processes, and the second technical innovation with the very large scale integrated circuit (VLSI) has been realized by adopting plasma processes.

We can draw an analogy between the semiconductor industry and agriculture: The traditional agriculture was innovatively replaced by the chemical agriculture with much higher productivity owing to the invention of agricultural pesticides and chemical fertilizers. Due to the pesticide residue, however, the chemical agriculture has been increasingly replaced by the inorganic agriculture which has even the disadvantage of lower productivity. The problems of both the pesticide residue of chemical agriculture and the low productivity of the inorganic agriculture can be innovatively overcome by adopting the plasma technology.

In this paper, a new concept of the plasma application to the agricultural phases, 'Plasma Farming', will be introduced and some case studies of how to apply the plasma technology to the agriculture will also be given

## Energy Harvesting & Storage

### Room: Lehua - Session EH-ThM

## Nanotechnology & Energy

**Moderator:** Jin-Hyo Boo, Sungkyunkwan University, Korea

8:00am **EH-ThM1 Improving the Photoconversion Efficiency of Quantum Dots Sensitized TiO<sub>2</sub> Solar Cells Prepared by SILAR and Electrophoresis Method.** *I. Zarazua*, Centro de Investigaciones en Optica, Mexico, *D. Esparza*, *A. Sanchez*, *A. Cerda*, *T. Lopez-Luke*, *Elder De la Rosa*, Centro de Investigaciones en Optica A.C., Mexico **INVITED**

One of the most studied hybrid-type nanostructured solar cells is the Gratzel or dye sensitized solar cell (DSSC). DSSCs typically consist of TiO<sub>2</sub> NCs acting as a highly porous, wide bandgap semiconductor for electron collection, and dye molecules adsorbed onto the TiO<sub>2</sub> NCs surface acting as sensitizers to harvest solar light. An alternative to DSSC is the utilization of quantum dots (QDs), e.g., CdSe, CdTe, CdS, PbS, PbSe, Bi<sub>2</sub>S<sub>3</sub>, and InP, as sensitizers to replace the expensive ruthenium dyes. QDs have large extinction coefficients in the visible region and, after bandgap excitation, undergo charge separation, injecting electrons to the conduction band of the metal oxide

The quantum dots (QD) has been recently drawing great attention as a material for solar energy conversion. The quantum dots sensitized titanium dioxide (TiO<sub>2</sub>) was synthesized by different chemical methods such as successive ionic layer adsorption and reaction (SILAR), and electrophoresis (EP). Titanium dioxide (TiO<sub>2</sub>) films consisting of a 150 nm compact layer, a 6 μm layer made of 40 nm TiO<sub>2</sub> nanoparticles (NPs) and a 7 μm scattering layer made of 400 nm TiO<sub>2</sub> NPs, were composited with several QDs such as CdS, PbS, ZnS, and Bi<sub>2</sub>S<sub>3</sub> by SILAR and EP. Multisensitized configurations as PbS/CdS/ZnS and CdS/Bi<sub>2</sub>S<sub>3</sub>/ZnS were analyzed obtaining a photoconversion efficiencies of 3.75% and 2.52% respectively. These efficiencies are due to high photocurrents (14.3 and 10.2 Ma/cm<sup>2</sup>, respectively) obtained by the correct combination of near infrared and visible light photoabsorption. Photoconversion efficiency was increased to 5% by combining both sensitizers method in the appropriate way. It also was studied the effect of depositing Gold Nanoparticles (Au NPs) by electrophoresis in CdS SILAR sensitized solar cells, results show that Au NPs slightly reduces the photocurrent (from 8.7 to 7.4 Ma) by reducing the photoabsorption of the CdS QDs, but at the same time strongly increases the FF (from 51 to 58%) and Voc (from 510 to 560 Mv). Electrochemical measurements suggest that Au NPs help to prevent recombination processes in the solar cell. In this paper, a detailed analysis of charge transport on both configurations is presented; taking advantage of impedance spectroscopy (IES) a detailed analysis of each interface is also presented.

We acknowledge financial support from CONACYT through grant 134111, UC-MEXUS program, CEMIE-Sol (P28), and European Community Seven Framework Programme (FP7-NMP-2010-EU-MEXICO) and CONACYT under grant agreements 263878 and 125141, respectively. D. Esparza, Andrea Sánchez and Andrea Cerda acknowledge scholarship from CONACYT.

8:40am **EH-ThM3 Applications of pure ZnO and the Mn-doped ZnO on Dye Sensitized Solar Cells.** *P.X. Feng*, *Xiaoyan Peng*, *Y.M. Li*, UPR, Puerto Rico

Mn-doped ZnO nanopowders have been prepared by the sol-gel technique using zinc and manganese (II) acetates as precursors. The crystalline structural investigations reveal that as prepared nanostructures with low Mn doping concentration have single hexagonal phase and are grown along the preferred c-axis. The chemical bonding structure in Mn-doped ZnO nanopowders was examined using X-ray photoelectron spectroscopy techniques, which indicate substitution of Mn<sup>2+</sup> ions into Zn<sup>2+</sup> sites in ZnO lattice. Temperature-dependent Raman spectra of the nanocrystals displayed suppression of luminescence and enhancement in full width at half maximum in pure ZnO nanocrystals with increase in temperature, which suggests an enhancement in particle size at elevated temperature. Furthermore, the magnetic measurement of Mn-doped ZnO nanostructures exhibits the ferromagnetism at room temperature.

The characteristics of dye-sensitized solar cells (DSSCs) with pure ZnO and Mn-doped ZnO nanopowders have also been investigated. The enhancement of the performance of DSSCs achieved using Mn-doped ZnO nanopowders is attributable to the introduction of the spontaneous polarization direction of ferroelectric materials with the electric field which will efficiently block the back transfer of electron from fluorine doped tin oxide to the I<sub>3</sub><sup>-</sup>/I<sub>3</sub> redox couple.

9:00am **EH-ThM4 Infrared Spectroscopic Study of Adsorption of Carbon Monoxide and Other Surface Reactions at the Ruthenium Dioxide Particle Film Aqueous Solution Interface.** *Jim McQuillan*, *S. Aloi*, University of Otago, New Zealand

Ruthenium dioxide is renowned as a highly active oxidation catalyst as well as a material with supercapacitor properties. Its heterogeneous catalyst behaviour has been extensively studied in surface science using well-defined crystal faces under high vacuum conditions. These studies have led to a good understanding of its active sites and the roles they play in solid/gas interface reactions such as the oxidation of adsorbed carbon monoxide. At the same time, the importance of ruthenium dioxide as an electrocatalyst has led to many electrochemical studies of RuO<sub>2</sub> electrodes immersed in aqueous solutions. These studies, somewhat contrasting with those in surface science, have sought to elucidate the basis of the 'pseudocapacitor' behaviour of hydrous RuO<sub>2</sub> which must involve both faradaic and non-faradaic processes. In spite of extensive efforts the details of the electron and proton transfer processes at RuO<sub>2</sub> electrodes remain obscure and there have been few spectroscopic studies addressing questions about the molecular nature of processes at the hydrous RuO<sub>2</sub> interface.

We have used in situ attenuated total reflection infrared (ATR-IR) spectroscopy to examine hydrous RuO<sub>2</sub> particle films deposited on diamond and ZnSe prisms immersed in flowing aqueous solutions. The adsorption behaviour of oxalate has been shown to be very similar to that of oxalate adsorbing on TiO<sub>2</sub> involving bidentate chelation. Adsorbed carbon monoxide exhibits several peaks indicating a diversity of sites as previously observed in its adsorption to RuO<sub>2</sub> (110) under high vacuum. Adsorbed carbon dioxide/carbonate is formed from the oxidation of adsorbed CO. Both the adsorbed CO and adsorbed carbonate spectra are sensitive to the presence of CO and O<sub>2</sub> as redox agents in solution which suggests that surface ruthenium ions may undergo changes in oxidation state via redox species in solution. These novel *in situ* spectroscopic results are the first from the RuO<sub>2</sub> aqueous solution interface and will be discussed in comparison with those from surface science and electrochemistry.

9:20am **EH-ThM5 Effect of Different Synthesis Routes of NaTaO<sub>3</sub> and the Presence of Metal-Based Nanoparticles as Co-Catalyst on the Hydrogen Production.** *Leticia M. Torres-Guerra*, *I. Juarez-Ramirez*, *C. Gomez-Solis*, *D. Sanchez-Martinez*, *J.C. Ballesteros-Pacheco*, Universidad Autonoma de Nuevo Leon, Mexico **INVITED**

Significant attention has been paid on the investigations of new photocatalysts metal-oxides because of their ability to harness the sun energy to drive fuel-producing reactions, such as water splitting. The compound NaTaO<sub>3</sub> has been studied in the last 10 years as photocatalyst in this reaction. According to the results obtained by several authors, high activity on this reaction was found by using NaTaO<sub>3</sub> material prepared by solid state route. This result is associated with the high crystallinity of the powder. However, there are other factors that also influence the physicochemical properties of semiconductor material such as specific surface area, microstructure, optoelectronic properties among others. Therefore the synthesis of metal-oxides can be carry out by soft chemical methods in order to modify and control the morphology, which allows to increase sites for hydrogen evolution. In our research group we have explored the performance of sodium tantalate, NaTaO<sub>3</sub> and RuO<sub>2</sub>/La:NaTaO<sub>3</sub> prepared by several synthesis methods such as solid state reaction, sol-gel, hydrothermal, ultrasonic, solvo-combustion on photoinduced reactions. The sodium tantalate phase with perovskite structure has been synthesized by solvo-combustion path at low temperature (180°C) and using nanoparticles of RuO<sub>2</sub> as co-catalyst. This material showed considerably high photocatalytic activity for hydrogen production around 9,800 μmol.h<sup>-1</sup>.g<sup>-1</sup>, twice greater than those results obtained when the material was prepared by solid state method. The activity is associated with the material high crystallinity and the presence of the second phase, Na<sub>2</sub>Ta<sub>4</sub>O<sub>11</sub> in small concentration after annealed at 600°C. The formation of nanosteps between NaTaO<sub>3</sub> nanoparticles also contributed to the reaction efficiency. In addition, it was found that the crystalline structure formed by chains enhances mobility among linked octahedra and separation of hole-electron pairs, which increases the photoactivity of the material in these processes. From photoelectrochemical study was proposed the reaction mechanism that occurs during the water splitting on NaTaO<sub>3</sub> single and doped phase. Additionally, experiments of the electrochemical impedance spectroscopy were realized in order to obtain Mott-Schottky plots to determine the flat band potential of NaTaO<sub>3</sub>, RuO<sub>2</sub>/La:NaTaO<sub>3</sub>.

10:20am **EH-ThM8 Tailored Nanomaterials for Electrochemical Applications.** *Vojislav Stamenkovic*, Argonne National Laboratory

Research that is aimed to fundamental understanding of processes for electrochemical energy conversion and storage will be presented. Atomic scale insight at the topmost surface layer is essential in order to understand

and control properties of catalytically active materials. Therefore, well-defined surfaces have been in focus of our research that is executed in ultra-high vacuum (UHV) systems merged with electrochemical cells. Properties such as surface structure, surface and bulk compositions, electronic properties and surface defects are established by UHV surface specific tools. Well-characterized surfaces are then transferred to the ambient pressure electrochemical cell under strictly controlled conditions, and formed electrified solid-liquid interface is being characterized in order to obtain direct correlation between fundamental properties of materials and electrochemical behavior.

Our recent work, has been demonstrated that fine tuning of surface properties can lead towards unprecedented improvements in their functional behavior [1]. This presentation will address unique approach that is capable of utilizing structure-function relationships in the design of multimetallic materials for electrochemical systems. The following topics will be discussed: 1) well-defined materials obtained by varying their surface structure, composition profile and electronic properties in UHV; 2) atomic/molecular insight into formation of the electrified solid-liquid interfaces; 3) identification of the active and the most vulnerable surface sites under reaction conditions; 4) insight into chemical nature between the surface atoms, reactants, and molecular species in the electrolyte; 5) design and synthesis of tailored nanomaterials with desired size, shape and composition profile [2,3]; 6) ex-situ and in-situ characterization of tailored electrochemical interfaces.

This synergistic approach encompasses highly diverse experimental methods that span from UHV to rational synthesis of nanomaterials, has been proven to serve as a foundation in the development of practical materials for electrochemical applications such as batteries, fuel cells and electrolyzers. Reaction rates and durability of tailored nanomaterials for the electrochemical oxygen reduction, hydrogen evolution and hydrogen oxidation are improved over 30-fold compared to state of the art catalysts.

References:

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#### 10:40am EH-ThM9 Photo-Electrochemical Energy Conversion and Storage. A. Hankin, Geoff Kelsall, Imperial College London, UK

Global (mean) power demands of ca.  $1.5 \times 10^{13}$  W, projected to double by 2050, could be provided from the earth's ultimate power source, ca.  $1.2 \times 10^{17}$  W of incident solar radiation, if adequately efficient, robust and economic transducers are developed. However, the diurnal nature of solar power requires that such transducers are coupled to energy storage, preferably in chemical bonds for high specific energy / energy density, and to fuel cells for subsequent conversion to electrical energy. Such systems could decarbonise power sources, manage intermittency of renewable power sources and smooth the dynamics of electrical power demands. This can be achieved if electrons from photovoltaic panels are used, for instance, to electrolyse water to form (oxygen and) hydrogen, which can be oxidised subsequently in fuel cells. Alternatively, solar energy can be used directly, and potentially more cheaply, for photo-electrochemical reduction (and oxidation) of water in an environmentally benign route to hydrogen (and oxygen).

As in photovoltaic cells, a semiconducting material may be used to absorb solar photons with energies ( $h\nu$ ) greater than the semiconductor's band gap, generating electrons in its conduction band ( $e_{CB}^-$ ) and highly oxidising electron 'holes' in its valence band ( $h_{VB}^+$ ). The semiconductor needs to be chosen judiciously, so that: (a) electrons at its conduction band edge have sufficient energy to reduce water to hydrogen, and (b) holes at its valence band edge are sufficiently energetic to oxidise water to oxygen. Though the feasibility of such processes is well established, practical reactor systems have yet to be deployed, because the semiconductors also need to be stable, well-matched to the solar spectrum and achieve acceptable photon-to-hydrogen energy conversion efficiencies. Unfortunately, no single material yet meets all these criteria, to enable such artificial photosynthetic reactors to be: efficient, robust and cheap, of which only any two properties are achievable at present.

200 nm thin films of n-type  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> photo-anodes were produced by automated spray pyrolysis of iron(III) salts dissolved in ethanol onto F-doped SnO<sub>2</sub> coated glass or perforated titanium substrates heated to 450 °C and with an open area of ca. 17 %. These photo-anodes were deployed in laboratory-scale photo-electrochemical reactors, designed initially for photo-assisted electrolysis only, rather than spontaneous photo-electrolysis; a metal cathode supported hydrogen evolution with an electrical energy input.

Results will be reported for the thermodynamic and kinetic constraints on such processes, together with the effects of experimental variables on H<sub>2</sub> production rates.

#### 11:00am EH-ThM10 Gate-Modulated Thermoelectric Characteristics of Silicon Nanowires on Plastic Substrates, Youngin Jeon, Korea University, Republic of Korea, J. Choi, K. Cho, Korea University, S. Kim, Korea University, Republic of Korea

Recently, several novel concepts of thermoelectric technologies have been reported as a promising source of next-generation regeneratable energy. Moreover, silicon nanowire (Si NW) based thermoelectric devices are an attractive research area due to their advantages such as non-toxicity, abundance, and low-cost manufacturing, which can lead to new opportunities in broad areas of commercial electronics. The efficiency of energy conversion has been intensively studied by modulating the dimensionless thermoelectric figure of merit,  $ZT = \sigma S^2 T / \kappa$ , where  $\sigma$  is the electrical conductivity,  $S$  is the thermoelectric power (Seebeck coefficient),  $\kappa$  is the thermal conductivity, and  $T$  is the absolute temperature. Numerous studies indicate that the use of Si NW enables the improvement of  $ZT$  due to their low-dimensional properties. Nevertheless, it is still difficult to achieve high  $ZT$  value because  $\sigma$ ,  $S$  and  $\kappa$  are interdependent. Therefore, the modification of these parameters in Si NW can enhance the thermoelectric properties. Among various methods, the field-effect modulation, applying electric fields on thermoelectric materials, may be one of the prominent ways to modulate the thermoelectric parameters. In this study, we fabricate a gated Si NW thermoelectric device constructed on a thermal-insulating plastic substrate, and examine the field-effect modulation of thermoelectric characteristics.

Figure 1 shows the optical image of our gated thermoelectric device on a plastic substrate. The structure of the device with a NW channel length of 50  $\mu$ m is similar to a NW field-effect transistor. N-type Si NWs with a doped concentration of  $10^{17}$  cm<sup>-3</sup> are present between the electrodes and a gate electrode is located at the middle of the Si NWs. And a heater electrode is used as a heating source. We investigate the seebeck voltage variation of the gated thermoelectric device with the gate bias is applied. Figure 2(a) exhibits the seebeck voltage versus temperature variation characteristics of the device with  $V_{GS}$  from 0 to 5 V. Our device shows the good gate controllability of the channel potential, which implies the capability of the electrical conductivity modulation for the Si NWs. Thus, as  $V_{GS}$  decreases, the conductivity of the Si NWs also decreases accordingly, leading to the increase of the seebeck voltage with the same temperature variation. Therefore, as shown in Figure 2(b), the seebeck coefficient, defined as  $- \Delta V / \Delta T$ , is able to modulate with the gate voltage variation. Our study suggests that the gated thermoelectric device with n-type Si NWs on a plastic substrate reveals its potential use as a next-generation energy harvesting device.

#### 11:20am EH-ThM11 Transition Metals Ion Implantation into AlInN/GaN Thin Films, Abdul Majid, University of Gujrat, Pakistan, Zhu, Chinese Academy of Sciences, Beijing

A lot of work has been done on Mn doping in III-V [1] but work on Mn and other TM ions doping in AlInN is still lacking. Out of III-Nitrides, AlInN is the only ternary alloy which is capable of lattice matching with GaN and is potential candidate for use as distributed Bragg reflectors, cladding layers and several other electronic /optoelectronic devices[2]. Like several other materials, the doping of AlInN with TM elements is expected to produce diluted magnetic semiconductors (DMS) based on it. Realization of AlInN based DMS will be exciting due to wide direct band gap and lattice matching capability at 17% indium content with GaN. This work is one of initial detailed reports on TM doping into AlInN. Transition metals ions of Cr, Mn, Co and V were implanted MOCVD grown wurtzite AlInN/GaN thin films at doses  $5 \times 10^{14}$  to  $5 \times 10^{15}$  and  $5 \times 10^{16}$  ions/cm<sup>2</sup>. The structural properties of the materials were studied by X-ray diffraction and Rutherford backscattering spectroscopy (RBS) techniques. XRD analysis revealed that GaN related peak for all samples remains at its usual Bragg position of  $2\theta = 34.56^\circ$  whereas a shift in AlInN peak taken place from its position of  $2\theta = 35.51^\circ$  for as-grown sample. RBS analysis provided interesting results with clear shift in position of indium related peak pointing to migration of indium atoms towards interface of heterostructures. Moreover this peak has observed to be splitted into two peaks which is indication of depth wise redistribution of indium atoms within the material. The measurements of magnetization versus temperature as well as applied magnetic field measured using SQUID magnetometer indicated room temperature ferromagnetism in the films. The density Functional Theory based calculations of Transition metals doped AlInN predicted that TM ions will preferably substitute In sites in the alloy. In order to model the experimental results and explore the mechanism of ferromagnetic exchange interactions in the materials, detailed density functional theory (DFT) based calculations were performed. The electronic and structural properties of pure and TM doped AlInN were computationally investigated using ADF-BAND program which performs calculations using Kohn-Sham under Local Density Approximation. We modeled 64 atoms supercell with  $3 \times 3 \times 3$  mesh in the form Al<sub>27</sub>In<sub>5</sub>N<sub>32</sub> for pure AlInN and Al<sub>27</sub>In<sub>3</sub>Mn<sub>2</sub>N<sub>32</sub> (2 Mn atoms substitutes 2 In atoms), Al<sub>26</sub>In<sub>5</sub>Mn<sub>1</sub>N<sub>32</sub> (Mn substitutes Al) and

Al<sub>2</sub>In<sub>5</sub>MnN<sub>32</sub> (Mn substitutes Al) supercells for Mn doped AlInN. The literature suggests that Fermi level should lie within spin up Mn band predicting Mn:AlInN to be in half metallic state like other Mn doped III-Nitrides [3]. The calculated results indicate that Mn d band is partially filled for Al<sub>2</sub>In<sub>4</sub>MnN<sub>32</sub> and Al<sub>2</sub>In<sub>3</sub>Mn<sub>2</sub>N<sub>32</sub> whereas completely empty for Al<sub>2</sub>In<sub>5</sub>MnN<sub>32</sub>. It can be said that, either one or two Mn atoms substituting In sites produces expected half metallic AlInN whereas Mn substituting Al sites turns out to be unacceptable option. It is therefore concluded that Mn will preferably substitute indium in AlInN.

[1]. T. C. Schulthess, W. M. Thmmerman, Z. Szotek, W. H. Buler and G. M. Stocks, *Nature materials*, 4, 838 (2005)

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## Thin Films

Room: Makai - Session TF-ThM

## Graphene

Moderator: Suneel Kodambaka, University of California, Los Angeles

8:00am **TF-ThM1 Construction and Characterization of Two Dimensional Atomic Crystals on Transition Metal Surfaces: Graphene, Silicene, Germanene, and Hafnene.** *Shixuan Du*, Institute of Physics, Chinese Academy of Sciences, China **INVITED**

Epitaxy on a transition metal (TM) substrate is a promising method to produce a variety of two dimensional (2D) atomic crystals which potentially can be used in next generation electronic devices. This method is particularly valuable in the case of producing 2D materials that do not exist in 3D forms, for instance, silicene. In this talk, I will present construction and characterization of graphene, silicene, germanene, and hafnium honeycomb lattice on transition metal surfaces (TMS) (for example, Ru(0001), Pt(111), and Ir(111)). Molecular beam epitaxial growth technique is used to form the large scale 2D atomic crystals on TMS. Low electron energy diffraction (LEED) and scanning tunneling microscopy/spectroscopy (STM/S) together with density functional theory (DFT) calculations are employed to confirm the formed structure on the TMS. We expect that on the TMS more new 2D crystals could be found and these materials will show very interesting physical property and its promising potential applications in nanoscale devices.

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3. L. Meng *et al.*, *Nano Lett.* **13**, 685 (2013).
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5. L.F. Li *et al.*, *Adv. Mater.* **26**, 4820 (2014).

8:40am **TF-ThM3 Graphitic Structures on Ru(0001).** *Valeria del Campo*, Universidad Tecnica Federico Santa María, Chile, *R.H. Henriquez*, Universidad Técnica Federico Santa María, Chile, *P.H. Häberle*, Universidad Tecnica Federico Santa María, Chile

Chemical Vapor Deposition (CVD) is one of the most used techniques for growth of graphitic structures. In the case of graphene, this technique allows the growth of large graphene sheets. However, to obtain monocrystalline graphene (millimeter scale) the CVD process is performed in Ultra High Vacuum (UHV). In this work we grew monocrystalline graphene and carbon nanodiscs on Ru(0001) through LP-CVD (Low Pressure CVD).

To grow our samples, first we heat the substrate (ruthenium crystal) in UHV. Once the desired temperature has been reached, the substrate is exposed to ethylene for some minutes. After exposure, the sample is annealed to allow the formation of carbon structures on the substrate. We performed this process with two different sets of parameters, obtaining different carbon structures on the Ru(0001) surface.

With one set of parameters we obtained graphene sheets on the ruthenium surface. With the second set of parameters we also grew a graphene layer, but on top of this layer we grew carbon nanodiscs. The diameters of these discs vary from few to hundreds nanometers, while their height is always below 1 nm.

The growth of carbon nanodiscs could be explained not only by the different set of parameters but also by the presence of impurities on the ruthenium surface. These impurities enable a preferential nucleation around

them. This carbon excess allows the formation of carbon nanodiscs under the CVD conditions used in this experiment.

9:20am **TF-ThM5 On the Wettability of Graphene.** *Akira Akaishi*, The University of Electro-Communications (UEC-Tokyo) and JST-CREST, Japan, *T. Yonemaru*, The University of Electro-Communications (UEC-Tokyo) and JST-CREST, *J. Nakamura*, The University of Electro-Communications (UEC-Tokyo), Tokyo, Japan

While graphite is well known as hydrophobic material, recent studies have revealed that pristine graphitic surfaces are more likely to be hydrophilic. Hydrophobic/hydrophilic nature is closely related to wettability of surfaces. One of the characteristic measures of wettability is a contact angle that is the angle of the edges of a water droplet placed on target surfaces. It has been reported that the contact angle of water on graphite surfaces decreases as removing hydrocarbons on the surface [1,2]. The contact angle estimated by molecular dynamics (MD) simulations, however, varies depending on a choice of the parameters of interaction potentials between a water molecule and graphitic surfaces [3]. The wettability of pristine graphene surfaces remains unsettled.

We have investigated the behavior of water molecules on graphene surfaces with MD simulations by changing empirical parameters. The simulations are prepared with a graphene sheet and a water droplet which is dropped initially on the graphene surface. With increasing the number of water molecules, the droplet covers the surface and the layered-structure of molecules on the surface is formed. This indicates that, at a level of empirical model, a graphene surface is capable of wetting.

The formation of water layers on the surface can be seen by the density profile of water molecules. The density distribution of oxygen and hydrogen atoms of water along the axis perpendicular to the graphene surface indicates the existence of the layers. Moreover, the distinct peaks of the hydrogen atom distributions indicate that the direction of oxygen-hydrogen (O-H) bonds is not randomly distributed but is certainly oriented. The angle distribution of O-H bonds shows that hydrogen bonds are formed between the water layers on the graphene surface. In other words, the water molecules in the layers tend to form the hydrogen bonding only within the layers. The water molecules above the layer have no unpaired hydrogen bonds that are pointing perpendicular to the layer plane.

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9:40am **TF-ThM6 Unbalanced Standing Wave Patterns at a Graphene Junction.** *W.-J. Jang, H. Kim*, Korea University, Seoul, Republic of Korea, *M. Wang, S.K. Jang*, Sungkyunkwan University (SKKU), Republic of Korea, *M. Kim*, SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University (SKKU), Suwon 440-746, Republic of Korea, *S. Lee, S.-W. Kim, Y.-J. Song*, Sungkyunkwan University (SKKU), Republic of Korea, *Se-Jong Kahng*, Korea University, Republic of Korea

Exotic behaviors such as lensing and perfect transmission are expected in graphene p-n junctions, due to lattice-induced chirality of charge carriers, and experimentally studied using charge transport devices with a scale of several tens of nanometers. However, there has not been a study to confirm such behaviors at the atomic scale. Here, we report the experimental evidence for chiral electron reflections at a graphene junction on hexagonal BN/Cu. We performed scanning tunneling microscopy and spectroscopy to observe unbalanced electron standing wave patterns, which only appeared in one region at an energy lower than 100 meV, or at higher than 250 meV in the other region. Such an energy-dependent crossover of regions of standing wave patterns is explained by solving the Dirac equation with a simple potential step model. Our study shows that chirality of the charge carrier is a key component for understanding their reflections in graphene junctions at the atomic scale.

11:00am **TF-ThM10 Synthesis of Graphene via Surface Segregation and Reaction.** *Daisuke Fujita*, NIMS, Japan, *K. Sagisaka, H. Guo*, National Institute for Materials Science, Japan

Single-layer, bi-layer and few-layer thick nanosheets of graphene have been attracting significant amount of attention due to their excellent physical, chemical and mechanical properties. The first isolation of few-layer graphene (FLG) was demonstrated in 2004. However, single-layer graphene (SLG) was first synthesized 40 year ago by *surface segregation*, and was identified by Blakely *et al.* in 1974 using surface sensitive techniques. In 1980s, we initiated the growth and characterization of FLG and h-BN nanosheets using surface segregation and *surface reaction*. For the graphene growth, there are three important steps; surface segregation of doped atoms, surface reaction to form a monolayer phase, and subsequent 3-D growth (*surface precipitation*). Such surface phase transition was demonstrated on



C-doped Ni(111) by *in situ* X-ray photoelectron spectroscopy (XPS) at elevated temperatures, and the growth mode was clarified by inelastic background analysis. Among the three, the surface segregation plays the most important role for the SLG synthesis. The surface segregation approach has been applied to Pt(111) and Pd(111) substrates, where weak coupling is expected, and controllable growth has been demonstrated successfully. As one of the derivatives, we recently proposed a promising method for producing SLG covering an entire substrate at low temperature using a Ni film deposited on an HOPG substrate. By heating the Ni/HOPG in high vacuum, carbon atoms forming graphene are diffused from the HOPG substrate through the Ni template. In this paper, we will put more focus on the effect of competitive surface-site occupation between carbon and other surface-active impurities on the SLG growth. It is known that sulfur is a typical impurity of metals and the most surface-active element. Even with a high purity single crystal, the surface sites are finally occupied by sulfur at the elevated temperatures by surface segregation. In the case of Ni(110) surface, it is confirmed by scanning Auger microscopy (SAM) and scanning tunneling microscopy (STM) that the available surface sites is nearly occupied by sulfur with a centered 2x2 arrangement. When the Ni(110) is doped with carbon, surface segregation of carbon and following graphene growth shall be strongly affected or restricted by the surface active elements such as sulfur. In this situation, we discovered a strongly directional growth of SLG, exhibiting rectangular-like shapes and nearly straight step edges. The detailed characterization at the nanoscale and interesting growth mechanism shall be discussed based on high resolution microscopes like UHV-STM and scanning helium ion microscopy (SHIM).

11:20am **TF-ThM11 Anomalous Enhancement of Seebeck Coefficients for the Graphene/h-BN Superlattices**, *Jun Nakamura*, The University of Electro-Communications (UEC-Tokyo), Tokyo, Japan, *Y. Yokomizo*, The University of Electro-Communications (UEC-Tokyo) and JST-CREST

The thermoelectric conversion has been of interest for many researchers since Hicks and Dresselhaus showed that the introduction of low-dimensional structures such as quantum well structures would significantly enhance the dimensionless figure of merit [1]. Graphene is a two-dimensional, mono-layer material having honeycomb lattice of carbon atoms [2,3]. It has been suggested that the graphene-based device can be a novel thermoelectric material because of its potential giant Seebeck coefficient larger than 30 mV/K [4]. On the other hand, graphene nanoribbon (GNR) is a one-dimensional (1D) material, a strip of graphene, which has also been investigated theoretically as thermoelectric materials. A molecular dynamics study has shown that a high figure of merit can be obtained for the zigzag GNR (ZGNR) [5]. This result implies that the introduction of 1D structural modulation makes graphene into novel thermoelectric materials. We hereby propose, in this study, superlattice models consisting of ZGNR and zigzag BN nanoribbon (ZBNNR) [6,7]. We have investigated the Seebeck coefficients of ZGNR/BNNRs within the Boltzmann transport theory. It has been shown that a ZGNR/ZBNNR marks up to 20 times larger in the Seebeck coefficient than graphene. The Seebeck coefficients of the superlattices increase with decreasing width of the constituent ZGNR. It has been revealed that the giant Seebeck coefficients of the superlattices stem from the so-called pudding mold band with a finite energy gap.

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11:40am **TF-ThM12 All-graphene Gas Sensor Integrated with Sensing Channel and Graphene Heater**, *Choon-Gi Choi*, Creative Research Center for Graphene Electronics, Electronics and Telecommunications Research Institute (ETRI), Republic of Korea

Graphene leading to high surface-to-volume ratio and outstanding conductivity has been applied for gas molecule sensing with fully utilizing its unique transparent and flexible functionalities which cannot be expected from solid-state gas sensors. However, in order to realize the fast responsive and significantly sensitive graphene gas sensor without hampering of both flexibility and transparency, the high quality of sp<sup>2</sup> carbon bonding for sharp sensing response are demanded. In this work, we demonstrate large-scale flexible and transparent gas molecule sensor devices, integrated with a graphene sensing channel and a graphene transparent heater for fast recovering operation. This combined all-graphene device structure enable an overall device optical transmittance that exceeds 90% and reliable sensing performance with a bending strain of less than 1.4%. In particular, we could classify the fast (~14 s) and slow (~95 s) response due to sp<sup>2</sup>-

carbon bonding and disorders on graphene and the self-integrated graphene heater leads to the rapid recovery (~11 s) of a 2 × 2 cm<sup>2</sup> sized sensor with reproducible sensing cycles, including full recovery steps without significant signal degradation under exposure to NO<sub>2</sub> gas.

This work was supported by the Creative Research Program of the ETRI (14ZE1110) of Korea and by a grant (Code No. 2011-0031660) from the Center for Advanced Soft Electronics under the Global Frontier Research Program of the Ministry of Education, Science and Technology of Korea.

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