

# Monday Morning, December 8, 2014

## 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 act 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

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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  $4 \times 4$  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.

## 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**, *Sylvia Ptasinska, 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 an 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].

The research described herein was supported by the Division of Chemical Sciences, Geosciences and Biosciences, Basic Energy Sciences, Office of Science, United States Department of Energy through grant number DE-FC02-04ER15533.

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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 absorbed 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 absorbed 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 200and 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.

#### References:

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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.

# Tuesday Morning, December 9, 2014

## 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**, *Waqqar 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 instant, 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. Lymparakis, J. Neugebauer,* Max-Planck Institut für Eisenforschung GmbH, Germany, *P. Caroff,* The Australian National University, Australia, *R.E. Dunin-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.

## 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.

Research carried out at the Canadian Light Source, which is supported by NSERC, CIHR, NRC and the University of Saskatchewan. Research funded by NSERC, Canada Research Chair.

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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*<sub>0</sub> (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, Hyongkeun 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  $sp^2$  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  $I_{on}/I_{off}$  and on-state current are achieved compared with pristine graphene. Notably, the hybrid film had a sheet resistance of  $300 \Omega/\text{sq}$  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- $\text{In}_2\text{Ga}_2\text{ZnO}_7$  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  $\text{In}_2\text{Ga}_2\text{ZnO}_7$  (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 ( $L_g$ ) of  $\sim 500$  nm for the top TFT (t-TFT) and  $\sim 400$  nm for the bottom TFT (b-TFT). Heavily doped p-type silicon was used as the substrate and gate of b-TFT ( $G_b$ ). A 100-nm-thick  $\text{SiO}_2$  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 ( $G_t$ ). Then, the poly-Si/ $\text{SiO}_2$ /Si structure was dry etched sequentially to form the gates. Then, a 100-nm-thick  $\text{SiO}_2$  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  $\sim 40$  nm for the t-TFT, and  $\sim 50$  nm for the b-TFT on the side walls of the  $\text{SiO}_2$ . 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 ( $\text{MoS}_2$ ,  $\text{WS}_2$ ,  $\text{WSe}_2$ ,  $\text{MoSe}_2$ ,  $\text{NbS}_2$ ,  $\text{NbSe}_2$ , 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  $\text{MoS}_2$  and  $\text{WS}_2$  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 ( $\sim \text{cm}^2$ ) single-, bi-, and few-layer  $\text{MoS}_2$  and  $\text{WS}_2$  using a two-step process.  $\text{MoO}_x$  and  $\text{WO}_x$  thin films were deposited onto a Si/ $\text{SiO}_2$  substrate, and these films were then sulfurized under vacuum in a second step occurring at high temperatures ( $750^\circ\text{C}$ ). The synthesized  $\text{MoS}_2$  and  $\text{WS}_2$  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, Hugo R. 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  $1100 \mu\text{mol/g}$ . We obtain values of TCR in the range of  $-1.7$  to  $-3.0 \text{ \% K}^{-1}$  for non-functionalized CNTs and from  $-0.4$  to  $-5.4 \text{ \% K}^{-1}$  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, José Luis 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 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 this 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)-16x2 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)-16x2 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)-16x2 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)-16x2 disappears when it is exposed to atmospheric air. In this study, we investigated a water-terminated Si(110)-16x2 SD surface with XPS and Auger-photoelectron coincidence spectroscopy. Si-2p 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)-16x2 surface is exposed to water from 1.0 L to 5.0 L, there is little change in these Si-2p intensity ratio. This result indicates that clean Si(110)-16x2 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)-16x2 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)-16x2 SD surface is inactivated by water dissociative-adsorption. On the other hand, Si-L<sub>23</sub>VV-Si-2p 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)-16x2 surface is shifted to deeper binding energy side in comparison with that of clean Si(110)-16x2 surface. The water adsorbed Si(110)-16x2 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  $L_1VV$  Auger peaks, experimental determination of the branching ratio of the Si  $L_1L_{23}V$  and Si  $L_1VV$  Auger decays, and competition between the delocalization of the valence hole and the Si  $L_{23}V-VVV$  Auger decay are, to the best of our knowledge, largely unexplored. In this paper, we report on the decay processes of Si 2s core holes in a clean Si(111)-7×7 surface studied using coincidence measurements of the Si Auger electron and the Si 2s 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- $L_{23}VV$ -Si-2p 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  $L_{23}VV$  Auger electrons emitted in the decay processes of Si 2p 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 2s photoelectrons (Si-Auger-Si-2s APECS spectrum). The maximum peak position and shape of the Si-Auger-Si-2s APECS spectrum in the AeKE = 50–92 eV region are almost identical to those of the Si- $L_{23}VV$ -Si-2p APECS. Therefore, we assigned these Auger peaks to Si  $L_{23}VV$  Auger processes. This is direct evidence of Si  $L_{23}VV$  Auger processes being induced by Si 2s ionization.

The peaks of Si-Auger-Si-2s APECS in the AeKE = 20–50 regions were assigned to Si  $L_1L_{23}V$  Auger decays, while the peaks of Si-Auger-Si-2s 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  $L_{23}VV$  Auger decay, while the second is Si  $L_1VV$  Auger decay. From the integrated intensity of the normalized Si  $L_{23}VV$  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-Irisson, 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.

# Tuesday Afternoon, December 9, 2014

## 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  $\sim 5.5$  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  $C_{60}$  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 (Eloc) 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 Yacaman*, 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 Ramirez*, Grupo de Fisica Teórica y Computacional, Escuela de Fisica, 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.

# Wednesday Morning, December 10, 2014

## 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 absorbents is EM impedance matching of the absorbents. 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 absorbents. 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 alumina, aluminum nitride, boron nitride, CNT and graphene, recently. Among them, boron nitride(BN) and aluminum nitride(AlN) ceramics are promising candidate for high thermal conductivity with electrically insulating filler materials. This work presents an enhance 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**, *Nayeli 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 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.

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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, TriSilanolsooctyl 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 Trisilanolsooctyl 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 were 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.

[1] T. Yoshitake et al., *Jpn. J. Appl. Phys.* 48, 020222 (2009).

[2] S. Ohmagari et al., *Jpn. J. Appl. Phys.* 50, 035101 (2011).

## Nanomaterials

Room: Mauka - Session NM-WeP

### Nanomaterials Poster Session

**NM-WeP1 Facile Preparation of  $(\text{NH}_4)_2\text{SiF}_6$  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 ( $(\text{NH}_4)_2\text{SiF}_6$ ) particles as one of the fluorescence materials using a chemical route with good productivity. These  $(\text{NH}_4)_2\text{SiF}_6$  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  $(\text{NH}_4)_2\text{SiF}_6$  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  $(\text{NH}_4)_2\text{SiF}_6$  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  $(\text{NH}_4)_2\text{SiF}_6$  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  $(\text{NH}_4)_2\text{SiF}_6$  with space group of  $Fm\bar{3}m(225)$ . For the FTIR characterization, the absorption peaks related to the  $\text{SiF}_6^{2-}$  and  $\text{NH}_4^+$  ions in addition to N-H mode were also observed. These results demonstrate that the  $(\text{NH}_4)_2\text{SiF}_6$  particles are not only maintained high crystallinity but also composed of ammonium and silicon fluoride as major ingredients. Such  $(\text{NH}_4)_2\text{SiF}_6$  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  $(\text{NH}_4)_2\text{SiF}_6$  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  $\text{TiO}_2$ ,  $\text{Ta}_2\text{O}_5$ , or  $\text{LaTaO}_4$  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  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  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  $\text{NH}_3$  (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  $\mu\text{m}$  in long axis and about 1  $\mu\text{m}$  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 ( $E_2$ ,  $A_1(\text{TO})$ ,  $A_1(\text{LO})$ ,  $E_1(\text{TO})$ , and  $E_1(\text{LO})$ ) were clearly observed for all samples. In addition to the above, new peak was observed at 582  $\text{cm}^{-1}$  on N-containing ZnO rod which is attributed to the  $E_2(\text{Zn-N})$  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  $\text{NH}_3$  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  $\text{TiO}_2$  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

$\text{TiO}_2$  is actively studied as photocatalyst with environmental applications effected on photocatalytic performance by adjusting many factors in the structure. Recently,  $\text{TiO}_2$  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,  $\text{TiO}_2$  monolith was synthesized with various heating temperatures, and its photocatalytic activity was investigated under visible light.

Porous  $\text{TiO}_2$  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  $\text{CuCl}_2$  (molar ratios of  $\text{Cu}/\text{TiO}_2 = 1.0 \times 10^{-3}$ ) 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  $\text{Cu}(\text{II})$ -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.

[1] T. K. Kim, E. D. Jeong, C. Y. Oh, M. H. Hyun, M. S. Lee, H. K. Moon, J. P. Kim, O. S. Jung, F. N. Nawaz, J. S. Jin, *Chem. Pap.* 65(4), 2011, 495

**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.

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Kim, H.: NM-TuP5, **7**  
Kim, H.T.: NM-WeM5, **13**  
Kim, I.: NM-MoM9, 2  
Kim, J.S.: NM-TuP9, 8  
Kim, J.S.Kim.: NM-TuP10, 8  
Kim, J.-W.: NM-TuP14, 9  
Kim, K.: NM-WeM9, 13; NM-WeP18, 16  
Kim, S.: NM-WeM9, **13**  
Kim, S.M.: NM-TuP14, 9  
Kim, Sean.: NM-TuP3, **7**  
Kim, U.K.: NM-TuP9, **8**  
Kim, Y.Kim.: NM-TuP10, 8  
Kitazawa, S.: NM-WeP1, **15**  
Ko, Y.H.Ko.: NM-TuP10, 8  
Krüger, P.: NM-TuP1, 7  
Kubo, M.: NM-MoM4, 1  
Kunisada, Y.: NM-TuP15, **9**  
Kwon, H.: NM-WeM9, 13; NM-WeP18, 16  
Kwon, J.H.: NM-TuP19, **10**; NM-WeP2, 15

## — L —

Lee: NM-WeP20, 16  
Lee, C.Y.: NM-TuM10, 6  
Lee, D.-W.: NM-WeP21, 16  
Lee, H.: NM-MoM9, 2  
Lee, J.: NM-WeP18, **16**  
Lee, J.-I.: NM-TuP21, 10  
Lee, N.-E.: NM-WeP21, 16  
Lee, S.J.: NM-TuP9, 8  
Lee, S.Y.: NM-TuP14, **9**  
Lee, T.: NM-TuM2, **5**  
Lee, T.M.: NM-MoM9, 2  
Leparoux, M.: NM-WeM9, 13  
Leung: NM-MoM1, 1  
Lim, K.J.: NM-TuP19, 10; NM-WeP2, 15  
Liu, S.Y.: NM-MoM7, 2  
Lympirakis, L.: NM-TuM12, 6

## — M —

Maldonado, A.: NM-MoE3, 3  
Malstrom: NM-MoM1, 1  
Martinez-Alanis, P.R.: NM-MoM8, **2**  
Mase, K.: NM-TuP17, 9; NM-TuP20, **10**  
Matsushita, N.: NM-WeP3, 15; NM-WeP4, 15  
Miao, X.L.: NM-MoM3, 1  
Miranda: NM-TuP22, 10  
Miura, Y.: NM-TuP6, **7**  
Miwa, K.: NM-TuE3, 11  
Morante, J.R.: NM-MoM8, 2; NM-TuE5, 11  
Moreno, C.: NM-TuE4, 11  
Moriyama, K.: NM-TuM4, 5

Myung, S.: NM-TuP7, 8

## — N —

Nagaoka, S.: NM-TuP17, 9  
Nahm, S.: NM-WeM5, 13  
Naragino, H.: NM-TuP16, **9**; NM-WeP16, 16  
Navarro Contreras, H.R.: NM-TuP11, **8**  
Neugebauer, J.: NM-TuM12, 6  
Nishiura, S.: NM-TuP17, 9  
Nys, J.P.: NM-TuM12, 6

## — O —

Ogashiwa, Y.: NM-TuP20, 10  
Ogura, S.: NM-MoE2, 3  
Ohmagari, S.: NM-WeM12, 14  
Ohno, S.: NM-MoE2, 3; NM-TuP20, 10  
Okada, K.: NM-WeP3, 15; NM-WeP4, 15  
Okudaira, K.: NM-TuP20, 10  
Okusawa, M.: NM-TuP20, 10  
Otsuki, A.: NM-MoE10, **4**  
Ozawa, N.: NM-MoM4, 1

## — P —

Papst: NM-MoM1, 1  
Park, C.-Y.Park.: NM-TuP10, **8**  
Park, D.K.: NM-TuM10, 6  
Park, J.S.: NM-TuP19, 10; NM-WeP2, **15**  
Park, S.-H.Park.: NM-TuP10, 8  
Park, W.K.: NM-TuP5, 7  
Patriarche, G.: NM-TuM12, 6  
Patscheider, J.: NM-WeM3, **13**  
Pei: NM-MoM1, 1  
Pérez, L.A.: NM-TuP22, **10**  
Ptasinska, S.: NM-MoE1, **3**

## — Q —

Quang, D.V.: NM-WeP21, **16**  
Quintana Ruiz, M.: NM-TuP11, 8

## — R —

Ramírez, Y.: NM-TuE10, **11**  
Reparaz, J.S.: NM-TuE5, 11  
Rha, S.H.: NM-TuP9, 8  
Roache: NM-MoM1, 1  
Roldan Cuenya, BRC.: NM-MoE4, **3**  
Ryu, J.H.: NM-TuP21, **10**

## — S —

Saito, T.: NM-TuM5, 5  
Sakaguchi, N.: NM-TuP15, 9  
Sakaue, M.: NM-TuE3, **11**  
Santana, G.: NM-MoM8, 2  
Santhosh, P.: NM-WeP5, 15  
Sato, K.: NM-WeP1, 15  
Satoh, T.: NM-TuP6, 7  
Sekiba, D.: NM-TuP20, 10  
Shim, W.: NM-MoM6, **1**  
Shimizu, T.K.: NM-TuE4, **11**  
Shirakashi, J.: NM-TuM4, 5; NM-TuM5, 5  
Shohata, N.: NM-TuP20, 10  
Son, M.J.: NM-MoM9, **2**  
Song, W.: NM-TuP7, 8  
Srituravanich, W.: NM-MoE9, 4  
Stetsovych, O.: NM-TuE4, 11  
Strover: NM-MoM1, 1  
Sumitani, K.: NM-TuP16, 9

## — T —

Takano, Y.: NM-TuP20, 10  
Takeda, K.: NM-WeP16, 16  
Takeichi, S.: NM-WeM12, 14  
Takikawa, K.: NM-TuM4, 5  
Tanaka, M.: NM-TuP20, 10  
Thumrongthanyaluk, B.: NM-MoE9, **4**  
Tominaga, A.: NM-TuP16, 9; NM-WeP16, **16**  
Toyonaka, T.: NM-TuM4, 5  
Travas-Sejdic: NM-MoM1, 1  
Trejo: NM-TuP22, 10  
Trung, T.Q.: NM-WeP21, 16

— **U** —

Umek, P.: NM-TuP1, 7

— **V** —

Valencia, F.: NM-WeM11, 14  
van Ruitenbeek, J.M.: NM-TuM8, 5  
Venkata, T.: NM-MoE3, 3  
Vera Reveles, G.: NM-TuP11, 8

— **W** —

Wagner, M.R.: NM-MoM8, 2; NM-TuE5, 11  
Wang, P.: NM-MoM3, 1  
Wason: NM-MoM1, 1

Watanabe, T.: NM-WeP3, 15  
Wei, F.F.: NM-MoM3, 1  
Wilde, M.: NM-MoE2, 3  
Williams, DE.: NM-MoM1, 1

— **X** —

Xu, T.: NM-TuM12, 6

— **Y** —

Yacaman, M.J.: NM-TuE7, 11  
Yagi, M.: NM-TuM5, 5  
Yamamoto, M.: NM-WeP4, 15  
Yanase, K.: NM-TuP20, 10  
Yang, S.S.: NM-MoM9, 2

Yang, W.S.: NM-TuP5, 7

Yoshitake, T.: NM-TuP16, 9; NM-WeM12, 14;  
NM-WeP16, 16

Yu, D.: NM-TuE1, 11

Yun, W.S.: NM-TuM10, 6

— **Z** —

Zhang, C.W.: NM-MoM7, 2

Zhang, X.: NM-TuP4, 7

Zhang, XQ.: NM-MoE1, 3

Zhou, L.H.: NM-MoM3, 1

Zhu, X.: NM-TuP1, 7