Nanomaterials
Room Hau - Session NM-MoM

Magnetic Properties
Moderator: Yoshiaki Nakamura, Osaka University, Japan

8:20am **NM-MoM2 Effect of Segregation of sp-Impurities on Surface and Grain Boundary Magnetism in Nanocrystalline Nickel and Cobalt***, **Mojmir Sob**, M. Vsianska, H. Vemolova,* Masaryk University, Czech Republic

We present a systematic ab initio study of segregation of 12 non-magnetic sp-impurities (Al, Si, P, S, Ga, Ge, As, Se, In, Sn, Sb and Te) at Σ5(210) grain boundary (GB) and (210) free surface (FS) in fcc nanocrystalline ferromagnetic cobalt and nickel and analyze their effect on structure, magnetic and mechanical properties. In nanocrystalline nickel, most of the above impurities nearly kill or substantially reduce the magnetic moments at the FS and, when segregating interstitially (i.e. Si, P, S, Ge, As, Se), also at the GB so that they provide atomically thin magnetically dead layers which may be very desirable in spintronics. We demonstrate that the existence of magnetically dead layers is a common phenomenon at the sp-impurity-decorated GB and FS in nickel. It is caused by a strong hybridization of sp states of the impurities with the d states of nickel and a redistribution of electron states in both majority and minority bands. Reduction of magnetic moments at the Σ5(210) GB in fcc nanocrystalline cobalt is, in absolute values, very similar to that in nickel. However, as the magnetic moment in bulk cobalt is higher, we do not observe magnetically dead layers here. It turns out that by focused impurity segregation we can generate atomically thin magnetic layers with tailored magnetization, which can contribute to a new development of technologically important materials.

8:40am **NM-MoM3 Reversible Single-Molecular Manipulations of Spin Trans-Effect in Co-porphryin/Au(111) with Conserved Spin Moment***, M.H. Chang,* Korea University, Republic of Korea*; Y.H. Chang,* orea Advanced Institute of Science and Technology (KAIST), Korea*; H. Kim,* Korea University, Republic of Korea*; S.-H. Lee,* Korea University*; Y.-H. Kim,* Korea Advanced Institute of Science and Technology (KAIST), Korea*; **Se-Jong Kahng**,* Korea University, Korea

Controlling spin interactions in magnetic-molecules/metal is essential for spintronic molecular device applications. It has been considered that small molecule coordination to magnetic-molecules/metal can be used to reset molecular spins from 1/2 to zero and from zero to 1/2. However, the study on the control of spin interactions without changing spin moment of magnetic-molecules has been rare. Here, we demonstrate that spin interactions in Co-porphyrin/Au(111) can be controlled while spins being conserved, by coordination and de-coordination of small gaseous molecules, using scanning tunneling microscopy and spectroscopy (STM and STS). With small moleculecoordination, we observed that a zero-bias peak at Co-porphryin, a signature of Kondo effect in STS, remained but was clearly showed reduced width i.e. Kondo temperature, and that it could be reversibly retrieved by single molecular STM manipulations. Based on our density functional theory calculation results, the reduced Kondo temperature is explained with the relocation of unpaired spins in d_z2 orbitals of Co-porphyrin by vertical coordination of small molecules. Our study shows that with conserved spin moment in magnetic-molecules/metal, spin version of trans-effect can be directly probed through Kondo effect with STS.

9:00am **NM-MoM4 Current-induced Magnetic Domain Wall Motion and its Application***, **Teruo Ono**,* Kyoto University, Japan **INVITED**

Current-induced magentic domain wall motion has been attracted much attention both from scientific and technological points of view [1]. When a magnetic DW is driven by electric current via adiabatic spin torque, the theory predicts a finite threshold current even for a perfect wire without any extrinsic pinning [2]. We have shown that this intrinsic pinning determines the threshold current, and thus that the adiabatic spin torque dominates the DW motion resulting in DW motion along electron flow direction, in a perpendicularly magnetized Co/Ni system sandwiched by a symmetric capping and seed layers [3-9]. On the other hand, current-induced DW motion against electron flow direction has been observed in ultrathin magnetic films in which the structural inversion symmetry (SIA) was broken [10, 11]. Recently, this DW motion against electron flow direction has been explained by the combination of a chiral DW and spin Hall torque [12, 13].In this presentation, I will show the systematic investigation by changing thickness of Co/Ni layer and discuss the contribution of adiabatic spin transfer torque, and spin Hall torque in the current-induced DW motion. I will also discuss possible applications using the current-induced DW motion.

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9:40am **NM-MoM6 Reconfigurable Nano-Structured Magnetic Metamaterials for Magnonic Logic***, **Andrei Slavin**, I.V. Lisenkov, V.S. Tyberkevych,* Oakland University, USA

Artificial magnetic metamaterials formed by arrays of dipolarly coupled magnetic nanodots are promising candidates for applications in microwave signal processing. It has been shown recently, that an array of magnetic dots can be used as a reconfigurable magnonic metamaterial (RMM), since its metastable static state (and the corresponding microwave characteristics) can be switched by application of a pulse of a bias magnetic field [1-3].

In this work we present a theory of switching of a metastable static state in a magnetic metamaterial formed by an array of identical dipolarly coupled nanodots under the action of a short (duration of the order of 10-100 ns) magnetic field pulse. It is shown that a large array of magnetic dots cannot be switched into a perfect periodic antiferromagnetic state (AFM). Instead, the final state of an array after the end of the switching pulse comprises a set of clusters with the local AFM periodicity. The properties of the array's final state strongly depend on the duration of the trailing front τ_f of the switching field pulse. In particular, the average size of the AFM clusters in the final state increases as $A\sim \tau_f^{2/3}$. This increase in the regularity of a final state is limited by the thermally activated dot magnetization reversals that become possible if the switching field decreases too slowly. In particular, our results show that the distance of the signal propagation in a chain of magnetic dots may be increased by application of a clock pulse having a long trailing front. It is also demonstrated that using magnetic metamaterials it is possible to design of a magnonic phase shifter operating without an external bias magnetic field. The phase shifter uses a localized collective spin wave mode propagating along a domain wall "waveguide" in a dipolarly-coupled magnetic dot array with a chessboard antiferromagnetic (CAFM) ground state. It is also demonstrated numerically that the remagnetization of a single magnetic dot adjacent to the domain wall waveguide introduces a controllable phase shift in the propagating spin wave mode without significant change to the mode amplitude. Thus, it is possible to realize a logic XOR gate in the same system.

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Nanomaterials
Room Hau - Session NM-MoE
Nanocatalysis

Moderators: Ryan Richards, Colorado School of Mines, USA, Brian Trewyn, Colorado School of Mines, USA

6:00pm **NM-MoE2 Electrocatalysis - Ensemble versus Single Nanoparticle Investigations***, **Kristina Tschulik**,* Ruhr-Univ. Bochum, Germany **INVITED**

Nanomaterials play a crucial role in catalysis thanks to their large surface-to-volume ratio and the possibility to adjust their electronic structure, i.e. reactivity. As it provides several promising routes to sustainable energy, electrocatalysis is a strongly expanding research topic to date. It provides a route to both, the production of sustainable fuels by water electrolysis or CO_2 reduction, and to their environmentally friendly utilization in hydrogen or alcohol fuel cells. The fact that these reactions occur at the solid liquid interface and that electronic and ionic charge carriers are involved, make the characterization of nano-electrocatalysts a challenging task. The overlapping effects of altered mass transport at nanoparticle modified surfaces and of changed electronic connection add to the changes in reaction kinetics. Hence, it is difficult to directly extract kinetic information from experimental data.

To overcome the obstacles of poor electronic conductivity and slow diffusional mass transport, nanomaterials are typically mixed with a conductive binder and thick films of this mixture are immobilized on rotating disc electrodes for electrocatalysis studies. However, this conventional procedure fails if porous films result or the influence of the binder material is not known. Thus, new methods for binder-free electrocatalyst characterization are being developed to enable fast and reliable electrochemical characterization of new catalyst materials. Two new approaches are presented that facility binder-free testing of electrocatalysts either using (sub-)monolayer films of nanomaterials [1] or single nanoparticle impact studies. In the first case, ensembles of nanoparticles on an electrode are produced [1], while the latter approach utilizes the Brownian motion based impacts of nanoparticles at an electrode to study their [2] electrocatalytic performance [2]. Both methodologies avoid thick films and convection. Hence, conductivity effects are minimized, while changes in the mass transport of reactants can be quantified using numerical simulations of the diffusional processes at nanoparticle modified electrodes. Accounting for these overlapping effects, the experimental electrochemical response during electrochemical reduction of CO_2, O_2 or H^+, can be deconvoluted to reveal the true kinetic performance of novel catalysts. These methods may thus enable a more rational design and testing of new catalyst materials in the future.

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6:40pm **NM-MoE4 Formation and Migration of a Au-CO Complex in Gold-assisted Catalysis***, **Monica McEntee**,* University of Virginia, USA*; J. Wang,* Oak Ridge National Laboratory, USA*; W. Tang, M. Neurock,* University of Virginia, USA*; A.P. Baddorf, P. Maksymovych,* Oak Ridge National Laboratory, USA*; J.T. Yates, Jr.,* University of Virginia, USA

Fabrication of highly active, stable and selective nanocatalysts requires an understanding of the mechanisms that control charge transfer and the activation of adsorbate interactions at specific surface sites. Here I report on the nature of low coordinated Au sites (likely to be on Au nanoparticles) by creating nano-pits on a Au (111) single crystal surface using scanning tunneling microscopy (STM). At room temperature, CO molecules adsorb on Au atoms and form Au-CO complexes, which allow for Au atom extraction from dislocation sites of the herringbone reconstruction. These complexes migrate and form Au clusters on elbows and edges of the Au surface. In conjunction with STM, transmission infrared (IR) spectroscopy and density functional theory (DFT) calculations were used to understand this new mechanistic motif. The mechanism for the Au atom extraction involves electron transfer from CO to Au forming positive charge on CO that creates stronger bonding with Au atoms of lower coordination number. Nanocatalysts involving Au nanoparticles with an abundance of low coordinated Au sites likely exhibit similar properties and these studies could foster future enhanced catalysts.

7:00pm **NM-MoE5 Advanced Nanostructures as Electrocatalysts for Energy Applications***, **Vojislav Stamenkovic**,* Argonne National Laboratory, USA

Electrocatalysis is a subclass of heterogeneous catalysis that is aimed towards increase of the electrochemical reaction rates that are taking place at the surfaces. Real-world electrocatalysts are usually based on precious metals in the form of nanoparticles due to their high surface-to-volume ratio, which enables better utilization of employed materials. Ability to tailor nanostructure of an electrocatalyst is critical in order to tune their electrocatalytic properties. Over the last decade, that has mainly been achieved through implementation of fundamental studies performed on well-defined extended surfaces with distinct single crystalline and polycrystalline structures. Based on these studies, it has been demonstrated that performance of an electrocatalyst could be significantly changed through the control of size, composition, morphology and architecture of employed nanomaterials. This presentation will outline the most important in development of an efficient electrocatalyst: 1) electrochemical properties of well-defined surfaces, 2) synthesis and characterization of different electrocatalysts, and 3) correlation between physical properties (size, shape, composition and morphology) and electrochemical behavior (activity and durability). In addition, a novel research platform in the development of functional nanomaterials for energy conversion and storage applications such as fuel cells electrolyzers and batteries will also be presented.

Besides activity, our results have demonstrated that durability of an electrocatalyst can also be tailored by manipulating the catalyst structure. For instance, in order to address this issue a core-shell electrocatalyst where an Au core was coated by a multilayered MPt_3 shell was developed. Such core-shell Au/MPt_3 electrocatalysts showed negligible activity loss after 60,000 cycles between 0.6 – 1.1 V (vs. RHE). In the most recent example, an entire gold core was replaced by Ni core which was coated by gold and then encapsulated by Pt-bimetallic shell, creating a core-interlayer-shell structure with unique electrochemical properties. In addition, a highly functional hollow type multimetallic structures will be discussed as efficient electrocatalysts for oxygen reduction, hydrogen oxidation and evolution reactions.

Common ground for all systems relies on distinguished approach that includes collection of fundamental knowledge from well-defined highly crystalline systems and connects them to the real world nanomaterials.

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7:40pm **NM-MoE7 Metal Nanoparticles Intercalated in Mesoporous Silica as Robust Catalyst Platforms***, **Ryan Richards**, S. Gage, Y. Ji, M. Menart, M. Davidson, S. Pylypenko, B. Trewyn,* Colorado School of Mines, USA

Metal nanoparticles have been in the research spotlight for decades for their activity as efficient and highly selective heterogeneous catalysts. Similar to many nanoscale metal particles, the catalytic activity of for example Pd and Au NPs also depends on particle size. At high temperatures however the particles often undergo aggregation and sintering resulting in an increase in particle size and a corresponding loss in activity. In order impart robustness to Pd and Au NPs catalysts, supporting NPs on another material is a common approach. Amongst support materials, silica is attractive for its relative chemical inertness and thermal stability. Here, we present a sol-gel process by which we intercalated Pd and Au into the wall framework of mesoporous silica yielding a catalytic material termed PdMS or GMS here (Pd or Au in the walls of mesoporous silica). The PdMS material has been shown to be stable (maintaining both porous silica framework and Pd nanoparticle size) at temperatures as high as 650 °C making them attractive for high temperature processes.

8:00pm **NM-MoE8 Development of Noble-metal Free and Durable Nanoporous Catalysts for Exhaust-Gas Conversion***, **Takeshi Fujita**,* Tohoku University, Japan

Precious metals (Pt and Pd) are typical materials for heterogeneous exhaust-gas catalysts in automotive systems. During a catalytic reaction in conventional nanoparticulate systems, such as Pt, active nanoparticles (typically less than 5 nm) aggregate, resulting in a significant reduction of performance. In addition, their limited resources and high market-driven prices are principal issues in realizing the path toward a more sustainable society.

Herein, we developed an earth-abundant nanoporous NiCuMnO catalyst by leaching Mn from a CuNiMn precursor. The developed catalyst was catalytically active and durable for NO reduction and CO oxidation. During catalytic reactions, the nanostructure self-transformed into a more active nanostructure; in particular, the Cu/CuO regions derived from the nanostructure were very active, and further significant coarsening was not observed without the loss of activity, as these regions were tangled with a stable nanoporous NiMnO network. The self-transformed nanostructure successfully completed a long-term durability test for NO reduction at 400 °C for 10 days. The *in situ* TEM under NO reduction clearly provided evidence for the instant reaction-induced self-transformation of the nanostructure. This result demonstrates an important implication of this work: even when nanoporous alloys are coarsened to significantly greater than 100 nm, as long as the metal phase is entangled and sustained within a stable nanoporous network of oxides, geometrically necessary surface defects can be retained as catalytically active sites and further enhanced catalytic performance exhibited because of the metal-oxide interfaces (i.e. perimeter); thus, catalytic activity can be retained with durability.

Although the nanoporous NiCuMnO catalyst requires more improvement at low temperatures, the temperature of the catalyst bed in an automobile system is typically higher than 400 °C, where nanoparticles become significantly unstable. Production of the nanoporous catalysts can be easily scaled up, and they may be a rational alternative to traditional precious-metal catalysts for automotive systems in the near future [1].

References

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Nanomaterials
Room Hau - Session NM-TuM
Nanofabrication and Nanodevices I

Moderator: Adam Schwartzberg, Lawrence Berkeley Lab, USA

8:00am **NM-TuM1 Fabrication of Nanoplasmonic Pore on the Pyramid for Single Molecule Analysis*, SeongSoo Choi*,** *M.J. Park, C.H. Han, S.J. Oh, T. Yamaguchi,* Research Center for Nanobio Science, SunMoon University, Republic of Korea*; Y.S. Kim,* Sungkyunkwan University, Korea, Republic of Korea*; N.K. Park,* School of Electrical Engineering, Seoul National University, Republic of Korea

There have been tremendous interests about the portable single molecule sensor device by using nanopore detection techniques. Recently the portable genome sequencing device based on the electrical detection technique was fabricated, however, the very high error rate during detection process was reported. In this report, we will report the nanoplasmonic Au nanopore fabrication by using diffusion of atoms, or drilling a freestanding thin film under high electron beam irradiation. For diffusion techniques, the Au apertures with ~ 100 nm diameter were fabricated by using focused ion beam technique followed by electron beam irradiations. The Au nanoclusters were formed on the diffused membrane several months later under the room environment after electron beam irradiations. In addition, drilling a freestanding 40 nm thick Au membrane was successfully carried out. Due to unstable electron beam irradiation on the nanoscale spot, we observed a crescent shape aperture with 0.75 nm width on the freestanding Au film. The fabricated nanopore surrounded with periodically patterned grooves can enhance the optical transmission and enhance the optical intensity due to plasmonic hot spot at the pore area. The controlled nanopore can be utilized as single molecule translocation and analysis by using optical detection and optically driven technique.

8:20am **NM-TuM2 Reversible Diels-Alder attachment of Organic Molecules to Single Atoms on Hydrogenated Semiconductors*, Szymon Godlewski*,** *M. Kolmer,* Jagiellonian University, Poland*; M. Engelund,* Donostia International Physics Center, Spain*; H. Kawai,* Institute of Materials Research and Engineering*; R. Zuzak,* Jagiellonian University, Poland*; A. Garcia-Lekue,* Donostia International Physics Center, Spain*; A.M. Echavaren,* Institute of Chemical Research of Catalonia*; D. Pena, D. Perez, E. Guitian,* Universidad de Santiago de Compostela*; C. Joachim,* CEMES-CNRS, France*; D. Sanchez-Portal,* Donostia International Physics Center, Spain*; M. Saeys,* Ghent University, Belgium*; M. Szymonski,* Jagiellonian University, Poland

In recent years the on-surface, local chemistry attracts growing attention, inspired by the interest in fundamental processes occurring on surfaces, as well as by potential technological applications. In particular, the controlled and reversible bonding between single molecules and atoms could be advantageous in construction of prototypical molecular switches, rotors and electronic circuits. To control the electronic properties of organic species the isolation from the underlying substrate is required. This could be achieved by application of passivated surfaces that enable retention of originally designed properties [1-3]. Hydrogen passivated silicon and germanium surfaces are of particular interest enabling creation of atomic scale defects – hydrogen vacancies that could interact with organic molecules and form artificial wiring [4-5].

In the presentation we will demonstrate reversible Diels-Alder attachment of prototypical three-branch conjugated molecules to paired surface dangling bonds. We will show that molecules initially undergo the [4+2] cycloaddition forming chemical bonds with the unsaturated surface dangling bonds [6]. Further, it will be discussed that the bonds could be broken and restored using the low temperature scanning tunnelling microscope. We will demonstrate that at low temperature the molecules located on surface dangling bonds could be switched between the chemisorbed configuration and the physisorbed one held by van der Waals interactions only. Interestingly, the molecules adsorbed in the latter configuration could be controllably switched rotationally with the STM tip, which constitutes the first molecular switch on a passivated surface. Further it will be shown that by tuning the structure of the molecules the attachment geometry could be controlled with high selectivity. Finally we will introduce prospects for utilization of the control over connecting individual molecules with surface single atoms.

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8:40am **NM-TuM3 Full Color Light Emitting Diodes using Perovskite Quantum Dots as Emissive Materials**, *Y.-H. Suh,* Ulsan National Institute of Science and Technology (UNIST), Republic of Korea*; J.-W. Chio,* Gwangju Institute of Science and Technology (GIST), Republic of Korea*; T. Kim,* Ulsan National Institute of Science and Technology (UNIST), Republic of Korea*; S.-H. Han,* Mokpo National Maritime University, Republic of Korea*; J. Park,* Ulsan National Institute of Science and Technology (UNIST), Republic of Korea*; **Chang-Lyoul Lee**,* Gwangju Institute of Science and Technology (GIST), Republic of Korea

The cesium lead halide ($CsPbX_3$, X = Cl, Br, and I) based perovskite quantum dots (QDs) were synthesized using precipitation and hot-injection methods. And also, the device performance of QD-LEDs using inorganic perovskite ($CsPbX_3$) as emissive layer was characterized. The $CsPbX_3$ showed excellent properties, such as high quantum yield (>~80%), easily tunable band gap, and high color purity as well as high stability. The PL spectra of $CsPbX_3$ were varied by changing the composition of halides. The inverted structure QD-LEDs consisted of ITO/ZnO/poly-electrolyte/PeQDs/MoO_3/Ag showed the high color purity EL (Blue : ~480 nm, Green: ~510 nm, Red : ~680 nm) and high brightness (Blue : ~200cd/m^2, Green: ~1,200cd/m^2, Red : ~300cd/m^2).

9:00am **NM-TuM4 Nanoarchitecture Design for Independent Control of Carrier and Phonon Transports*, Yoshiaki Nakamura,*** Osaka University, Japan **INVITED**

Thermoelectric (TE) conversion has been expected to be one of the ideal energy sources, where waste heat is converted to be usable electrical energy. Therefore, TE performance enhancement had drawn much attention. TE performance is related to dimensionless figure of merit, $ZT=S^2\sigma T/\kappa$, where S is Seebeck coefficient, σ is electrical conductivity, κ is thermal conductivity, and T is absolute temperature. This means that the materials with high S, σ, and low κ are required. However, high σ and low κ are difficult to achieve simultaneously because they are correlated. Therefore, the identical control of σ and κ has been a vital goal in thermoelectric study for long.

We proposed the nanoarchitecture where phonon was scattered effectively at the nanostructure interfaces, but carriers could go through them using ultrasmall epitaxial nanodots (ND) with well-controlled interfaces. Herein, carriers feel that nanomaterials are single crystal because crystals of NDs are oriented. On the other hand, the interfaces of ultrasmall NDs scatter phonon. In this study, we use our original technique for forming epitaxial ND structures. We achieve the identical control of phonon and carrier transports using the above nanoarchitecture design.

Clean Si surfaces were oxidized at 500°C at the O_2 pressure of 2×10^{-4} Pa to form ultrathin (~0.3 nm) SiO_2 films. Si or Ge was then deposited to form epitaxial Si or Ge NDs grown on Si substrates with ultrahigh density of ~10^{12} cm^{-2} as the following. At first stage of Si of Ge deposition, nanowindows were created in the ultrathin SiO_2 films through the reaction of $Si+SiO_2 \rightarrow 2SiO\uparrow$, or $Ge+ SiO_2 \rightarrow GeO\uparrow+SiO\uparrow$. By subsequent deposition, Si or Ge NDs formed on the ultrahigh density nanowindows. In the case of Ge NDs, Si layers were formed on Ge NDs at 400°C. The above formation of Si NDs or Si layer/Ge NDs and the oxidization process were repeated to fabricate the ND stacked structures.

The formation of the epitaxial nanoarchitectures including NDs was succeeded. The κ values were measured by 2ω method. The smallest κ value of stacked Si NDs with 3 nm diameter was close to the amorphous value. In the case of Ge NDs, the κ values were also drastically reduced compared with bulk Si. The σ of Ge ND structures was enhanced to be a similar value to the bulk Si cases by the interface designing, indicating the independent control of κ and σ. This demonstrates the possibility of our nanostructure as a Si-based thermoelectric material with high ZT.

This work was partially supported by JSPS KAKENHI Grant Number 16H02078 for Scientific Research (A) and 15K13276 for Challenging

Exploratory Research. In part, this work was supported by CREST-JST program.

9:40am **NM-TuM6 DNA self-assembled Nanostructures using a Scaffold with a Minimum Size*, Enrique Samano,*** Universidad Nacional Autónoma de México, México*; T.H. LaBean,* North Carolina Central University, USA

Artificial DNA nanostructures such as DNA origami have garnered significant interest as templates for sub-20 nm assembly of materials because their design allows for the incorporation of binding sites to assemble nanocomponents with 6nm resolution. The DNA origami strategy for assembling designed supramolecular complexes requires ssDNA as a scaffold strand. A system is described that was designed using approximately one third of the M13 bacteriophage genome as a scaffold. Folding of the short 2404-base ssDNA scaffold into a variety of two-dimensional origami shapes (rectangle, triangle, and circle) with high assembly yields is demonstrated. DNA origami templates, modified to have DNA binding sites with a uniquely coded sequence, can be used to produce complex metallic nanostructures of programmable design. Gold nanoparticles functionalized with a complementary DNA sequence were attached to specific binding sites on the scaffold in a highly controllable manner to form a predesigned metallic array on two nanostructures.

10:20am **NM-TuM8 Feedback-Controlled Electromigration (FCE) Method with Automatically Optimized Parameters*, Noriaki Numakura,*** *Y. Iwata, J. Shirakashi,* Tokyo University of Agriculture & Technology, Japan

Feedback-controlled electromigration (FCE) has been used as a useful technique for fabricating quantum point contacts (QPCs) and nanogaps [1]. The conventional FCE method is performed on a general-purpose operating system (GPOS). In contrast, real-time operating system (RTOS) is specifically designed to run applications with precise timing and reliability. Hence, we have previously reported the FCE method using RTOS, in order to run FCE algorithms time-deterministically and to control quantized conductance of Au nanowires, at room temperature in ambient air [2]. In this report, we propose a new FCE system with automatically optimized parameters for the improvement of control performance of FCE using RTOS.

In this system, we designed the FCE algorithms with randomly varying parameters. First, FCE experiments for the Au nanowires were repeatedly performed to obtain various FCE experimental data. Then, the FCE parameters were evaluated using cost functions, and stored in a database. Finally, we performed the FCE experiments with a suitable set of evaluated FCE parameters, which was generated using the stored data. As a result, the conductance of Au nanowire was successfully quantized and decreased without catastrophic break. Therefore, it is considered that the FCE system based on automatically optimized parameters can show the conductance quantization of Au nanowires even at room temperature in ambient air.

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10:40am **NM-TuM9 Controlled Switching and Charge State Alteration of Surface Dangling Bond Nanostructures, Realization of a Quantum Hamiltonian Boolean Logic Gate***, S. Godlewski, **Rafal Zuzak**,* Jagiellonian University, Poland*; M. Kolmer,* Jagiellonian University, Poland*; M. Engelund,* Donostia International Physics Center, Spain*; H. Kawai,* Institute of Materials Research and Engineering, Singapore*; G. Dridi,* CEMES-CNRS, France*; A. Garcia-Lekue,* Donostia International Physics Center, Spain*; C. Joachim,* CEMES-CNRS, France*; D. Sanchez-Portal,* Donostia International Physics Center, Spain*; M. Szymonski,* Jagiellonian University, Poland

In recent years we observe an increasing interest in the precise atomic-scale fabrication of surface nanostructures. This is because the miniaturization of various electronic devices has pushed many fundamental research efforts toward creating atomic-scale circuits [1]. Among different substrates, the hydrogen passivated silicon and germanium surfaces are regarded as the promising ones due to the fact that they allow precise fabrication of complex dangling bond (DB) nanostructures, which introduce new electronic states within the intrinsic band gap of the substrate [2]. These structures could be further utilized in fabrication of atomic scale devices [3] or may be directly applied in quantum circuitry.

In the presentation we will describe fabrication of various surface DB nanostructures. Their geometrical and electronic properties will be analysed on the basis of scanning tunnelling microscopy/spectroscopy (STM/STS) measurements corroborated by density functional theory (DFT) calculations. We will show that upon electron/hole injection dangling bonds exhibit dynamical behaviour, which due to the high frequency of oscillations leads to smooth STM appearance. A new imaging model, based on a dynamical two-state rate equation, which allows detailed reproduction of observed STM pattern will be introduced [4]. Moreover, the influence of single dangling bond charging on the STS spectra will be analysed [5]. We will further envision that our new model might be applied to simulate other bi-stable systems where fluctuations arise from transiently charged electronic states. Finally, we will present successful design and construction of the first prototypical QHC (Quantum Hamiltonian Computing) atomic scale Boolean logic gate operated by the STM tip [6].

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11:00am **NM-TuM10 Synthesis of Transition Metal Dichalcogenide Heterostructures and Nanodevices by Atomic Layer Deposition*, Christoph Kastl,*** *C.T. Chen,* Lawrence Berkeley National Laboratory, USA*; B. Shevitski,* University of California, Berkeley, USA*; T.R. Kuykendall, S. Aloni, A.M. Schwartzberg,* Lawrence Berkeley National Laboratory, USA

Interest in layered transition metal dichalcogenides (TMDs) has been renewed since the discovery of emergent properties when reduced to single two-dimensional layers. The current state-of-the-art fabrication of heterostructures involves exfoliation from bulk crystals and subsequent manual stacking of the atomic layers. The lack of reproducible and large scale synthetic methods for high quality, consistent TMD samples has become a major bottleneck to research on and application of these materials.

The following two-step process involving atomic layer deposition (ALD) and chalcogenization can be used as a scalable and highly versatile method for TMD synthesis. First, high quality transition metal oxide films are deposited by ALD. Second, the transition metal oxide films are converted into layered TMDs by chemical chalcogenization, i.e. annealing under H2S atmosphere in a high temperature furnace. [1] We leverage the particular advantages of ALD to further develop this approach into a fabrication process for encased nanodevices and heterostructures. Planar films of MoO3 and/or WO3 are deposited on the growth substrate, and SiO2 is used as an inert capping layer. Then, device structures are defined by photolithography and reactive ion etching. In the subsequent conversion step, the nucleation starts at the exposed cross sections of the heterostructure, and the TMD growth proceeds laterally from the nucleation site. Cross-sectional TEM reveals that this lateral growth mode forms highly crystalline MoS2 (WS2) layers which are aligned parallel to the substrate. We characterize the optical and electronic properties of the encased heterostructures by photoluminescence spectroscopy, ultrafast transient absorption spectroscopy, and field effect measurements. Furthermore, controlling the extent of the lateral growth via annealing time and temperature, we show that encased TMD nanoribbons can be fabricated with lateral dimension down to ~10 nm.

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11:20am **NM-TuM11 Growth and In situ Electronic Transport and Scanning Probe Studies of Topological Materials Bi_2Se_3 and Na_3Bi*, Michael Fuhrer,*** Monash University, Australia **INVITED**

Topological materials are fascinating novel electronic phases with important device implications. Topological insulators are insulating in their interiors but conduct on their boundaries; two-dimensional topological insulators can realize dissipationless conduction along their one-dimensional edges. Topological Dirac semimetals lie at the boundary between conventional and topological insulators, and can be pushed toward one or the other by electric or magnetic fields, realizing new types of switches.

I will discuss the development of a novel experimental capability combining the growth of topological materials by molecular beam epitaxy (MBE) with *in situ* magnetotransport and low-temperature scanning tunneling microscopy at 5 K. This capability has been used to study the transport properties of topological insulator Bi_2Se_3 *in situ* during MBE growth, monitoring the carrier concentration and mobility as a function of film thickness[1]. More recently, topological Dirac semimetal Na_3Bi thin films have been prepared on α-$Al_2O_3(0001)$ substrates with low temperature charge carrier mobilities exceeding 6000 $cm^2V^{-1}s^{-1}$ with n-type carrier densities below 1×10^{18} cm^{-3}, comparable to the best single crystal values[2]. Perpendicular magnetoresistance at low field shows the perfect weak-antilocalization behaviour expected for Dirac fermions in the absence of intervalley scattering. Our ongoing efforts to tune the carrier density using physical and chemical schemes to realize topological devices will also be discussed [3].

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Nanomaterials
Room Mauka - Session NM-TuP
Nanomaterials Poster Session

NM-TuP1 On the Possibility of the Development of Vicinal Superlattices in Quantum Wires on Semiconductor Low - Index Surfaces*, **Victor Petrov,* Institute of Radio Engineering & Electronics, Russian Academy of Science,Moscow,125009,Russia, Russian Federation

As is well known, vicinal superlattices (VSLs) are realized in 2D electron systems on semiconductor high-index Miller surfaces. The possibility of existence of such VSLs was predicted theoretically (V.A.Petrov, 1977) [1,2]; simultaneously and independently they were realized (T.Cole et al.1977) [3]. At the present time, all these VSLs are developed only in 2D systems.

In this work we suggest a new method of development of the VSL in the quantum wires (QWR).where superlattice effects should be maximal. The special feature of this method is the combination of the main properties of the VSL - the separation in the system by some way of the long translation period A - with the possibility of developing this situation in the QWR on semiconductor low - index surfaces. It is easy to see that this situation is possible when the axis of the QWR which lies on the low - index surface will be oriented at the necessary angles to the basic translation vectors along the surface. In this case the translation symmetry of the QWR will be determined by its orientation on the crystal surface since the possibility of a free motion only along the axis of the wire selects in the initial two - dimensional translation group along the surface a one - dimensional translation subgroup along the wire with the basic period A. Thus, in the one-dimensional VSL the period A is selected by the orientation of the wire on the surface. For example, if the QWR is realized in the MOS system with the use of a narrow gate (V.A.Petrov 1978)[4] then the orientation of the wire will be determined simply by the appropriate orientation of the gate.

The analytic expressions of the new periods A were obtained as a function of the angles which determine orientation of the QWR for the different low-index surfaces GaAs and Si. The positions of minigaps in the one-dimensional k-space were determined. It is should be noted that in the region of the particle wave function localization in the QWR there are many crystallographic planes which form a superlattice energetic spectrum of the particle. Illustrative estimates of the magnitude of the minigaps for the QWR of the rectangular cross-section made in the weak coupling approximation demonstrate their dependence on the geometric parameters of the cross-section, on the period A as well as on the crystal potential.

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NM-TuP2 Influence of Electron Interference Effects on Reflection of Electron Waves From Potential Barrier in 2D Semiconductor Nanostructures*, **Andrey Nikitin**, V.A. Petrov,* Institute of Radio Engineering & Electronics, Russian Academy of Science,Moscow,125009,Russia, Russian Federation

The influence of the interference of electron waves in the case of their reflection from potential barrier on the spatial distribution of the density of quantum-mechanical current $ej_x(x,z)$ (e – electron charge) in 2D semiconductor nanostructure which is represented by rectangular narrow ($x < 0, QW_1$) and wide ($x > 0$, QW_2) quantum wells (QWs) sequentially oriented along the direction of the propagation of electron wave has been studied theoretically. It is supposed that the wave falls from the narrow QW_1 on the semi-infinite potential barrier V_0 in height in the wide QW_2, the energy of the falling wave being less than V_0. Differing widths of QW_1 and QW_2 provide the non-orthogonality of wave functions of particles in these regions and the corresponding existence of electron interferential effects in this kind of nanostructure. In particular cases these effects lead to the appearance of spatially inhomogeneous distributions $ej_x^{(1)}(x,z)$ in QW_1 and $ej_x^{(2)}(x,z)$ in QW_2. It has been analytically demonstrated that in case of an electron wave falling along the first (lower) quantum-dimensional subband in QW_1 and its kinetic energy E_x being less than the energy positions of all the other subbands in QW_1 (*i.e.*, the undamped propagation of the wave reflected from the barrier with real quasi-momentum is possible only along this lower subband) $ej_x^{(1)}(x,z)$ and $ej_x^{(2)}(x,z)$ are equal to zero. However, if a particle has such an energy that the refection of the wave with real quasi-momenta is possible along more than one (lower) subband, then the situation completely changes due to the interference of the reflected waves. In this case the interference leads to an existence of a complicatedly oscillating spatially inhomogeneous distribution $ej_x^{(1)}(x,z)$, and under the barrier in QW_2 it provides the appearance of exponentially damped at $x \rightarrow \infty$ and possessing a coordinate dependence of leakage $ej_x^{(2)}(x,z)$ under the barrier. Besides, three regions of the symmetric along z axis propagation $ej_x^{(2)}(x,z)$ are formed under the barrier. They are the central one, in which the current is directed in axis x positive direction, and two side regions in which the current is directed in negative direction. The presence of the regions of that kind provides the charge flow from under the barrier. The numerical calculations of $ej_x^{(1)}(x,z)$ and $ej_x^{(2)}(x,z)$ have also been made taking into account 31 subbands. It should be noted that these kinds of effects have a general nature and exist in 1D and 2D nanostructures with arbitrary profiles of QWs and barriers.

NM-TuP3 Understanding Ligand-Surface Passivation of Cation-Rich Colloidal Quantum Dots: First-Principles Study*, J.-H. Ko, D. Yoo, **Yong-Hyun Kim**,* Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea

Colloidal quantum dots (CQDs) are attractive nanomaterials for optoelectronic and photovoltaic applications because they are useful for mass production and easy to tune optical and electronic properties by controlling the size of CQDs. Generally, stable CQDs with good ligand-surface passivation are essential for such CQD applications. Yet, microscopic understanding how CQD surfaces are stabilized with passivating ligands is not clear in the colloidal environment. In this study, we performed first-principles density-functional theory (DFT) calculations for understanding ligand-surface passivation of cation-rich surfaces of IV-VI, II-VI, and III-V CQDs. Calculation results indicate that while non-polar surfaces of CQDs are self-passivated, polar surfaces of cation-rich CQDs, i.e., (100) and (111) for zinc blende semiconductors, have reactive surface dangling electrons that should be properly coordinated with passivating anionic ligands. We will discuss how such polar surfaces of CQDs could be stabilized by organic and inorganic ligands based on electron counting rule and coordination chemistry.

NM-TuP4 Ar Plasma Treated Transparent Silver Nanowire Electrodes for Flexible Quantum Dot Light-Emitting Diodes*, J-W. Kim,* Korea Electronics Technology Institute (KETI), Republic of Korea*; **Jiwan Kim**,* Kyonggi University, Republic of Korea

A smooth, ultra-flexible, and transparent electrode was developed from Ag nanowires (AgNWs) embedded in a colorless polyimide (cPI) by utilizing an inverted film-processing method. The resulting AgNW-cPI composite electrode is highly transparent and has an ultra-smooth surface with a low sheet resistance. The thickness of this conductive composite film was reduced to less than 100um with extreme flexibility. This film exhibited mechanical durability up to a bending radius of 5 mm. Green quantum dots light-emitting diodes (QLEDs) were fabricated using these composites as bottom electrodes (anodes). Hole-injection in QLEDs was poor, because AgNWs were largely buried beneath the composite's surface. Thus, we used a simple plasma treatment to remove the thin cPI layer overlaying the nanowires without introducing other conductive materials. As a result, we were able to finely control the flexible QLEDs electrical/optical properties using the enlarged conductive pathways. The fabricated flexible devices showed only slight performance degradation after a repeated bending test.

NM-TuP5 High-throughput Synthesis of Emissive Glass Microcomponents via Contact Flow Lithography*, **Jiseok Lee**,* Ulsan National Institute of Science and Technology, Republic of Korea

We report a high-throughput synthesis of emissive microcomponents with rare-earth-doped upconverting nanocrystals (UCNs) using a contact flow lithography. Upconverting nanocrystals were synthesized using hydrothermal reaction and used as anti-Stokes emitters that absorb near-infrared (NIR) light and emit in visible spectrum. We utilized contact flow lithography for massive production of nonspherical composite microcomponents. Emissive composite microcomponents with a variety of shapes was synthesized and corresponding glass microcomponents were obtained through polymer burn-off. The synthesized particles with UCNs are stable at high temperature and have great potential to use as anti-counterfeiting platform.

NM-TuP6 Effect of Redox-Induced Conformational Changes in Charge Transport Characteristics of a Ferrocene-Alkanethiolate Molecular Device: Temperature-Dependent Transition Voltage Spectroscopy Analysis*, **Hyunhak Jeong**, Y. Jang, D. Kim, W.-T. Hwang, J.-W. Kim, T. Lee,* Seoul National University, Republic of Korea

The ultimate aim of molecular electronics is to overcome the limit of the conventional silicon based solid-state electronics by utilizing either single molecules or a bundle of molecules as an active electronic device component. For example, Nijhuis et al. recently reported a robust molecular diode using ferrocene-alkanethiolate self-assembled monolayers (SAMs) and eutectic Ga and In (EGaIn) electrodes.[1] They demonstrated a large rectification ratio of up to ~1000 and reported that the strong asymmetric electrical characteristics could be interpreted by hopping assisted tunneling transport arising from the ferrocene-alkanethiolates and the electrodes.

Similar to these studies, we have also examined the possibility of the electronic device application by fabricating a large number of molecular devices based on ferrocene-alkanethiolate (denoted as FcC) SAMs using a conventional solid-state device fabrication technique both on rigid and flexible substrates.[2] Specifically, we observed a distinctive temperature dependence on the electrical characteristics; that is, the current density decreased as the temperature increased in a certain temperature range when a sufficient voltage was applied with a certain voltage polarity. This behavior was in contrast to the usually expected thermally activated charge transport in the molecular device junction or other device junctions in which, most times, the current density increases as the temperature increases. In that study,[2] we suggested the unusual thermal characteristics are probably due to the redox-induced conformational changes of the FcC in the molecular junctions. While the analysis was quite reasonable and consistent with the experimental results, further evidence was needed to support our suggested explanation. We also performed temperature-dependent transition voltage spectroscopy (TVS) analysis based on a multibarrier tunneling model, which supports the occurrence of the proposed redox-induced conformational changes in the FcC molecular junctions.[3]

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NM-TuP7 High Elastic Modulus, High Extensibility Nanorods Constructed of pH-Responsive Cyclic Peptide Polymer*, **Kenan Fears**, M. Kolel-Veetil, D. Barlow, N. Bernstein, C. So, K. Wahl,* US Naval Research Laboratory, USA

Due to their ability to self-assemble into supramolecular nanorods in solution, cyclic β -tripeptides (CBTPs) have been used as molecular scaffolds that predictably display functional groups along the axis of the assembly. To enhance the mechanical strength and processability of such nanostructures, we synthesized a linear polymer of amide-bonded CBTP subunits using previous computational analysis on the conformational stability and tunability as guidance. Two amino acids in each subunit (β -HLys or β -HGlu) form “hinges” with neighboring subunits, and electrostatic repulsions between the third, β -HOrn, forced the polymer to adopt a disordered conformation when protonated. When deprotonated, atomic force microscopy revealed rigid nanorods exhibiting an elastic moduli (51.3 GPa) stiffer than any report peptide-based material. The hinges also allow the nanorods to elongate under tension which should impart the polymer with high extensibility and resilience. Nanorods were decorated with Au nanoparticles to demonstrate the ease in functionalizing the polymer, greatly expanding its potential applications beyond a structural material. The solubility and structural control achieved by combining covalent bonds, non-covalent bonds, and electrostatic interactions suggest the polymer may not only exhibit excellent processability but also mimic toughness and elasticity found in nature.

NM-TuP8 Growth and Optical Properties of Catalyst-free Ga(In)N Nanorods with Different Top Shapes*, **Moon-Deock Kim**, B.-G. Park, J.-W. Hwang,* Chungnam National University, Republic of Korea*; W.-C. Yang, D.-Y. Kim, K.-B. Chung,* Dongguk university, Republic of Korea

In this work, we have investigated the kinetic process and adatoms mechanism of four different top shapes of catalyst-free Ga(In)N nanorods (NRs) namely flat, taper, hammer, and mushroom structures were grown in holes of a patterned Si (111) substrate by plasma-assisted molecular beam epitaxy. Arrays of nano-holes with diameter of 80 nm on the Si substrate were obtained by using of self-assembled silica nanospheres as a nano-hole mask. The silica nanospheres coated on the Si substrate and then spread using a spin-coating method. A 10 nm-Ti deposited after dry etching to sizes control and then removed silica nanospheres by chemical etching. Different top shapes of Ga(In)N were obtained by varying the growth conditions namely growth temperature and N2 plasma power, and the morphology evolution was explained based on the interrelation between sidewall diffusion and direct impingement during the NRs growth. GaN NRs grown at the growth temperature (T_g) and *Ga* flux of 650 °C and 5x10^{-7} Torr, respectively, were used as the buffer for the subsequent growth of GaN NRs with different top shapes. GaN NRs with flat top (Fig. 1(a)) was obtained without altering the growth conditions that was used for the buffer growth. When the T_g was increased gradually from 590 °C to 650 °C under *Ga* flux of 1x10^{-7} Torr, we obtained GaN NRs with top tapered shape (Fig. 1(b)). On the other hand, hammer shaped GaN NRs (Fig. 1(c)) were obtained when the T_g was reduced gradually to 570 °C, while keeping the Ga flux 1x10^{-7} Torr during the growth of GaN NRs. Furthermore, mushroom shaped Ga(In)N nanostructure (Fig. 1(d)) on top of GaN NRs were obtained when introducing *In* flux of 1x10^{-7} Torr at T_g ~ 350 °C under the same Ga flux. The variations in the shape of GaN NRs are explained by the interrelation of sidewall diffusion and the supersaturation of adatoms at the top surface [1, 2]. Photoluminescence measurements revealed higher light emission for tapered GaN when compared to non-tapered structure. APSYS simulations were further conducted to theoretically confirm the observed experimental results. We believe that our results can provide crucial information for the shape controlled growth of GaN NRs with diverse nanostructures and promising approach for the realization of high brightness LEDs.

Fig. 1 SEM images of GaN NRs with different top shape (a) flat, (b) tapered, (c) hammer and of GaInN with (d) mushroom

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NM-TuP9 Semi-green Synthesis and Characterization of Superparamagnetic Fe_3O_4-MNPs with Aqueous Extracts from C. Verum and Natural Extract from V. Planifolia*, A.L. Ramírez-Núñez,* Doctoral Program in Nanosciences and Nanotechnology CINVESTAV-IPN, Mexico*; **Jaime Santoyo-Salazar**,* Nanosciences and nanotechnology, CINVESTAV-IPN, México*; L.F. Jiménez-García,* Faculty of Sciences, UNAM, México*; G. Goya Rossetti,* Instituto de Nanociencia de Aragón, Spain

Recently biosynthetic methods employing either biological entities or plant extracts have emerged as an easy, fast and economical alternative to chemical and physical síntesis procedures for the production of safer nanomaterials for human use. An eco-friendly semi-green method was used in order to obtain magnetite magnetic nanoparticles (Fe_3O_4-MNPs). Besides the know effect of polyphenols as therapeutical agents in cancer diseases, biomolecules from aqueous extracts can act as capping and reducing agents wich effectively replace toxic chemical reductans. Plant extracts with a rich mixture of active biological phytochemicals (i.e. polyphenol compounds, tannins, saponnins, flavonoids) control and shape the growing nanoparticles. Superparamagnetic properties have been studied extensively due to their potential use in hyperthermia in cancer treatment. The green synthesis of Fe_3O_4-MNPs with aqueous extracts represent a major advantage in the synthesis of superparamagnetic materials for biomedical usage, due to their diminished toxicity to biological organisms and more efficient drug delivery carriers for specific cancer diseases. In order to explore the diversity of biomolecules in the obtention of Fe_3O_4-MNPs, in this work an aqueous extract from *Cinnamomun verum* and *Vanilla planifolia* (natural pods and synthetic extract) were used during the synthesis of magnetite.

The Fe_3O_4 MNPs obtained were identified by XRD (PDF-19-0629) corresponding to an inverse spatial group *Fd3m* (227) inverse spinel FCC structure, *a*= 8.355 Å in synthetic vanilla and a=8.362 Å in vanilla pods extract (*V. planifolia),* and *a*=8.366 Å in *C. verum*. IR peaks at 576 cm^{-1} correspond to Fe-O bonding formation; vibrational peaks at 576-1641 and 3415 cm^{-1} suggest phenol molecules involved in bio-reduction process. XRD and HRTEM diffraction patterns overlap with the corresponding Fe_3O_4 peaks (220),(311),(400),(511),(440). The *d* spacing 2.4 Å in *V. planifolia* and 2.7 Å in *C. verum* match the main diffraction plane 35° (311). The particle size calculated by Scherrer´s equation by Scherrer´s equation *(t=Kl/b cos Θ)* in *V. planifolia* was 12 nm and 14 nm in *C. verum*. AFM-MFM data show a monodomain arrangement of 2-3 nm in *V. planifolia* and 5-6 nm in *C.*

verum. VSM data indicate that magnetization increases rather using *C. verum* extract (64.89 emu/g) than *V. planifolia* (46.6 emu/g). The SPA values suggest that vanilla pods extract has an advantageous performance during Fe_3O4-MNPs synthesis due to their increased heating capability (64.51 W/g). The bio-synthesis of Fe_3O_4 MNPs obtained by aqueous plant extracts are commensurable to those obtained by a chemical method with a better performance than synthetic extract.

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NM-TuP10 Nanostructure Surface Design for Increased Photovoltaic Responses in Ethanol Photochemical Fuel Cells*, K. Hirakawa, D. Rodriguez, K. Anderson,* ***Yong Gan,*** California State Polytechic University Pomona, USA

Electro-spun Titanium nanofibers can be applied to the surface of photoanode to create a multi-catalyst anode. The electrospinning process is considered in this study and found that it is as one of the simplest ways to create nanofibers with varying diameters ranging from 50 to 500 nm. When combined with a polyvinylpyrrolidone (PVP) composite, titanium oxide creates a nanofiber with high surface area while containing the intrinsic semiconductor properties of . The effects of using silicon nanowires (SiNW) on the surface of doped silicon as a substrate was also studied in this work. SiNWs create a porous surface feature due to the electrodeposited silver on silicon. Silver has a plasmonic effect which allows free electrons to oscillate on the surface of the metal when exposed to light. This plasmonic effect allows Silver to be used as a photocatalyst. Silicon can also be easily etched which creates another photocatalyst . The porous SiNWs enhances the phonon scattering about the interfaces of the nanowires due to its high anti reflectivity causing higher absorption. The functionality of a PEC cell is driven by many factors. nanotubes are the primary interest in this research. The purpose of this work is to determine the effects of type of the surface modified nanostructured photocatalyst anode, the ethanol concentration levels, on the response time of the photoelectrochemical (PEC) reaction when exposed to UV light source. Over a short period of UV irradiation exposure, the response time influences how much the potential difference changes between the anode and cathode. Creating multi-catalyst anodes using doping techniques, electrospinning applications, and electrodeposition methods change the photocatalytic properties. Varying the concentration of the fuel by lowering the energy density present in the electrolyte also effects the response time of the photoanode. By inspecting the various response times, the efficient photoanode in this study is identified.

NM-TuP11 Microfluidic Capacitive Sensors Using Ionic Liquid Electrodes and CNT/PDMS Composites for Multimodal Sensing Applications*,* ***SunGeun Yoon****, S.M. Lee,* Chung Ang University, Republic of Korea

There are many studies of demonstrating capactive sensors for various purposes such as detecting pressure, body motions, and temperature variation. However, its perfoming principle is mainly dependent on physical and geometrical changes of dielectric layers. In this study, we developed a new class of microfluidic capacitive sensors with utilizing ionic liquid serving as electrodes and CNT/PDMS composites (CPCs) as a dielectric layer. The working principle of our microfluidic sensors was investigated with geometrical changes of microfluidic channel and variations of electric double layer (EDL) capacitance. Our microfluidic capacitive sensors showed detection of localized pressure, lateral pressure movement, and even temperature variations with high sensitivity. By using multimodal capability, the microfluidic capacitive sensor was successfully performed as a keypad and applied to a bottle and human skin. This microfluidic capacitive sensors could offer great opportunity of development for future stretchable and flexible electronic devices such as wearable electronics, soft robotics, electronic skin, and human healthcare systems.

NM-TuP18 Adsorption and Thermal Processes of NO with Silicene on ZrB_2/Si(111)*,* ***Jun Yoshinobu,*** ISSP, Univ. of Tokyo, Japan*; K. Mukai, H. Ueda, S. Yoshimoto, C. Lee, T. Ozaki,* Univ. of Tokyo, Japan*; A. Fleurence, Y. Yamada-Takamura,* Japan Advanced Institute of Science and Technology, Japan

We investigated the adsorption and thermal processes of NO with silicene on ZrB_2/Si(111) using synchrotron radiation X-ray photoelectron spectroscopy (XPS) and density-functional theory (DFT) calculations. NO is dissociatively adsorbed on the silicene surface at 300 K. The substitutional adsorption of a nitrogen atom to a silicon site in the silicene honeycomb predominantly occurs. An oxygen atom is most probably inserted between two Si atoms of the silicone honeycomb. With increasing NO exposure, the honeycomb structure of silicene is destroyed and three dimensional silicon oxinitride may be formed. By heating above 900 K, the oxide species start to desorb from the surface most probably as SiO species. After heating to 1053 K, no oxygen is observed by XPS; nitrogen species remain on the surface. At the same time, the bare silicene domains are restored. The substitutional nitridation of silicene including $Si_3{\equiv}N$ species may provide a two-dimensional SiN honeycomb sheet on the surface.

NM-TuP19 Cellulose Nanowhiskers Topography & Young's Modulus Imaging Using Atomic Force Microscopy*, B. Kim,* ***Gerald Pascual****, P.. Kondapani, K. Lee,* Park Systems Corporation

Carbon nanotubes (CNTs) are a popular sample for various nanotechnology studies. However, they are very difficult to synthesize en masse. As a result, researchers have started looking at alternatives with similar properties. One of the candidates to replace CNTs in some nanocomposite materials is cellulose nanowhiskers (CNWs), structures that can be readily produced from plant sources. To determine the feasibility of substituting CNWs for CNTs, it is important to verify the two materials have similar morphologies and nanomechanical properties. One must first establish a baseline for comparison by accurately characterizing CNW properties at nanoscale . To this end, three CNW samples were examined using an atomic force microscope (AFM) with non-contact AFM mode and an AFM-based fast nanomechanical mode. The target properties for evaluation were the samples' topography to determine the nanowhiskers' size and shape and their Young's modulus values. The ensuing AFM measurements yielded topography data showing the nanowhiskers ranging from 100 to 1000 nm in length and 1 to 3 nm in width. Nanomechanical property data acquired with the AFM in fast nanomechanical mode demonstrated the CNW samples had a modulus value of approximately 180 GPa . Not only do these measurements establish a baseline CNW to CNT comparison for topography and a specific nanomechanical property, but they also demonstrate the viability of AFM as an effective tool for dimensional nanometrology and quantitative property measurements of novel nanocomposite components.

NM-TuP20 Dynamics of Carbon Monoxide Adsorbed on Tungsten (310) Surface of Cold Field Electron Emitters*,* ***Soichiro Matsunaga****, Y. Suwa, K. Kasuya, S. Katagiri,* Hitachi Ltd, Japan

We investigated a tungsten (310) surface, which has been widely used as electron emitting surface of cold field emitters (CFE). The intensity of electron beams emitted from a CFE rapidly decreases even under an ultra-high vacuum (UHV) environment of 10^{-8} Pa [1]. There has been a recent report that a stable operation region with high current angular density appeared by operating a CFE under an extreme-high vacuum (XHV), from 10^{-9} to 10^{-10} Pa[2]. That study revealed that the decreasing of the emitted beam is caused by residual hydrogen gas in CFE gun chambers, and they used a non-evaporative getter (NEG) to evacuate the hydrogen gas from the gun chamber. In the stable operation region of a NEG-evacuated CFE, we have observed unexpected increasing and step-wise shifting of the beam current.

In order to understand the mechanisms behind the unexpected beam fluctuations, we performed electron emission experiments and computational simulation of the emission surface. Results showed that the step-wise fluctuation is related to the adsorption of a single carbon monoxide (CO) molecule onto the W(310) surface. We performed a first principle calculation of the CO-adsorbed W(310) surface in order to understand the mechanism behind the step-wise fluctuation. To study the site of electron emission on the single-CO-molecule-adsorbed surface, we developed a calculation method to evaluate the heterogeneous potential barrier height of the surface under strong electric fields. On the basis of these experimental and calculation results, we propose that the adsorption and diffusion of a single CO molecule on W(310) surface cause the step-wise fluctuations of the current.

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Nanomaterials
Room Hau - Session NM-TuE

Nanofabrication and Nanodevices II

Moderator: Adam Hitchcock, McMaster University, Canada

5:40pm **NM-TuE1 Surface and Screening Effects on Optical Properties of Carbon Nanotubes*, Yuichiro Kato,*** RIKEN, Japan **INVITED**

Screening is limited in single-walled carbon nanotubes because of their one-dimensional nature, and the strong Coulomb interactions result in optical spectra dominated by excitons with binding energies lager than half an eV. Also because of the limited screening, a charged carrier can be bound to an exciton to form a trion that is stable at room temperature. Adsorption and desorption of molecules on the surface of nanotubes can readily modulate such interactions.

Here we discuss experiments aimed at highlighting the behaviors of excitons and trions in individual suspended carbon nanotubes. Simultaneous photoluminescence and photoconductivity spectroscopy show evidences for spontaneous dissociation of excitons [1], despite the expectation that free carrier generation from such a tightly-bound state would be difficult. As the field is increased, we observe an emergence of new absorption peaks in the excitation spectra, which can be explained by electrical activation of dark excited states [2]. Although trion formation has been thought to be difficult in suspended nanotubes due to low exciton-carrier scattering rates, we have succeeded in identifying trion emission under an application of gate voltages [3]. More recently, we have observed optical bistability of exciton emission, which is attributed to resonance shifts caused by molecular adsorption and desorption.

Work supported by KAKENHI, The Canon Foundation, The Asahi Glass Foundation, and the Photon Frontier Network Program of MEXT, Japan.

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6:20pm **NM-TuE3 Low-temperature Localized Growth of High Aspect-Ratio Multi-Wall Titanium Dioxide Nanotubes for Orthogonal Frequency Coded SAW Gas Sensors*, William Clavijo,*** *C. Castano,* Virginia Commonwealth University, USA*; W. Wilson,* NASA Langley Research Center, USA*; G. Atkinson,* Virginia Commonwealth University, USA

We expand the potential application and sensitivity of solid acoustic wave (SAW) gas sensors by incorporating ultra-high surface area, multi-wall TiO_2 nanotubes into orthogonal frequency coded (OFC) SAW gas sensors. This process relies on synthetization of multi-wall tube-in-tube polycrystalline TiO_2 nanotubes utilizing nanoporous anodic aluminum oxide (AAO) templates in a thin (2.5µm) aluminum film deposited on a lithium niobate substrate. We have demonstrated this method by integrating multi-wall nanotubes onto the delay line of an OFC SAW device to form an integrated sensor structure. The multi-wall TiO_2 nanotube growth uses a combination of multi-stage aluminum anodization, alumina barrier layer removal, TiO_2 and Al_2O_3 atomic layer deposition (ALD), and wet release etching. This growth process selectively forms TiO_2 nanotubes on the delay line while the aluminum film remains intact for interdigital transducers (IDT) and reflector banks. The self-assembled high density AAO template was selectively formed in an ultra-smooth (R_a=1.5nm) 2.5 µm thick aluminum layer deposited through e-beam evaporation. The resulting AAO template consists of nanopores of 100 nm in diameter and 1.5 µm in height with an aerial density of 1.3 x 10^{10} nanopores/cm^2. This AAO template was then filled with successive ALD nanotubes by alternating Al_2O_3 sacrificial spacers and TiO_2 at 200 ˚C. The alumina template and Al_2O_3 sacrificial spacers were then removed, leaving free standing multi-wall coaxial TiO_2 nanotubes of 1.5 µm in height and 100 nm in diameter, offering an increase in 112X the surface area over a standard flat TiO_2 film for sensing applications. The TiO_2 nanostructures were characterized by SEM, and TEM to examine internal structure, composition, and verify crystal structure. In addition, the OFC SAW gas sensor with a center frequency of 229 MHz and 3 reflectors on each side of the IDT was tested using 200 ppm NH_3 to demonstrate functionality and measure sensitivity. Mass loading induced by the NH_3 gas absorbed onto the multi-wall TiO_2 nanotube resulted in amplitude shift of 0.027 dB upon exposure to 200 ppm NH_3 at room temperature during interrogation of the 3rd reflector in sensitive channel. The sensor shows a promising room temperature operation with reproducible performance. Furthermore, OFC SAW gas sensors may be coded and implemented both passively and wirelessly in addition of taking advantages of the benefits of SAW technology.

6:40pm **NM-TuE4 Epitaxial Graphene Based Sensors for Gigahertz Detection*, Anthony Boyd,*** US Naval Research Laboratory, USA*; A. El Fatimy, P. Barbara,* Georgetown University, USA*; A. Nath, PM. Campbell, M. Currie, R.L. Myers-Ward, K.M. Daniels, D.K. Gaskill,* US Naval Research Laboratory, USA

There is a clear need for fast, high efficiency, and broadband sensitive detectors. Graphene demonstrates great promise to fill this void, possessing high room temperature carrier mobility, up to 60000 cm^{2}V^{-1}s^{-1}, and absorption of incoming radiation, ~2.3%. This absorption is impressive considering graphene is a single atomic layer thick. In the gigahertz (GHz) frequency range, the absorption is enhanced due to the Drude contribution of the free carriers. Synthesizing epitaxial graphene (EG) on SiC has the advantages of wafer scale size, low defect density, and being single crystal.[1] Growing high quality, conformal dielectric films with Atomic Layer Deposition (ALD) on EG is challenging due to the lack of dangling bonds which serve as nucleation sights for film growth. Researchers at this laboratory have developed a fluorine functionalization approach to overcome the challenge without negatively impacting graphene's morphology and electronic properties to enable ALD of high-κ dielectrics onto EG for gated devices.[2]

We investigate two types of GHz detectors fabricated on EG. The first is an antenna coupled device. It utilizes two dissimilar contact metals, one for the source and the other for the drain, and the metal work function difference translates into asymmetric Seebeck voltages at each contact. We fabricated these devices with two types of EG: 1) a quasi-free standing bilayer graphene (QBLEG) and 2) a standard one monolayer EG (1ML). The second device is a field effect transistor constructed using 1ML EG with an asymmetric top gate that creates a PN junction and facilitates tuning the photovoltaic response . Both device types were fabricated using a lift off resist-based clean lithography process, have low contact resistance [3] and use metal work function asymmetry for detection, consistent with recent studies of the photothermoelectric effect mechanism.[4]

The devices were electrically characterized and then irradiated with a Backwards Wave Oscillator from 100 to 177GHz. The antenna coupled devices response varies with frequency, incident power, and demonstrates a distinct antenna coupling. The QBLEG shows a 3 to 4X increase in response over the standard 1ML. The response of the PN junctions depends on the radiation frequency and the gate voltage. At a fixed frequency, the device response can be doubled by tuning the gate voltage, consistent with the known dependence of the Seebeck coefficient with charge concentration.

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7:00pm **NM-TuE5 Structural and Electrical Properties of Electromigrated Au Nanogaps*, Tomoyuki Ito,*** *K. Inoue, J. Shirakashi,* Tokyo University of Agriculture & Technology, Japan

Au nanogaps have been attractive for the fabrication of single-molecule devices. For this reason, many different approaches of Au nanogaps have been reported, including electromigration [1], break junction [2] and electroplating [3]. We have already reported on fabricating narrower Ni nanogaps by controlling tunnel resistance of the nanogaps using field-emission-induced electromigration. We call this method "activation" [4, 5]. In this report, the application of activation to Au nanogaps is investigated in comparison with that of Ni nanogaps.

Under room temperature and vacuum condition, the activation was applied to initial Au nanogaps with a separation of around 50 nm. The initial Au nanogaps showed high tunnel resistance of more than 500 TΩ. After performing the activation with the preset current I_s of above 300 nA, the tunnel resistance of Au nanogaps gradually decreased to less than 10 MΩ. Activation properties of Au nanogaps are quite similar to those of Ni nanogaps ever reported [4, 5]. Thus, the results imply that the tunnel resistance of Au nanogaps can be controlled in the same way as that of Ni nanogaps using activation.

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8:00pm **NM-TuE8 Investigation of Electromigration Induced by Field Emission Current Flowing through Au Nanogaps in Ambient Air***, **Kazuki Inoue**, T. Ito, J. Shirakashi,* Tokyo University of Agriculture & Technology, Japan

We have proposed a simple method for the fabrication and control of nanogaps, called "activation" [1]. In the activation scheme, electromigration (EM) is induced by field emission current passing through the nanogaps. Hence, the control of tunnel resistance of Ni nanogaps was achieved using the activation method [1, 2]. As expected, the activation method has been applied to Ni nanogaps in vacuum conditions. On the other hand, controlled EM technique is generally applicable to Au nanowires in ambient air conditions [3]. Here, we investigate activation properties for Au nanogaps in ambient air conditions, from the point of view of practical use of activation method. First, initial nanogaps of Au, separated by several tens of nanometers, were fabricated on SiO_2/Si substrate by electron-beam lithography and lift-off process. Then, the activation method was performed in ambient air at room temperature. The tunnel resistance of the Au nanogaps after performing the activation became smaller than that of before performing the activation, resulting in a decrease in the separation of the Au nanogaps. Thus, these results suggest that the activation method can be applied to Au nanogaps even in ambient air conditions.

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8:20pm **NM-TuE9 Nanoparticles and Nanostructures Synthesis by High-Power Pulsed Hollow Cathode Sputtering***, **Ulf Helmersson**, S. Askari, N. Brenning, S. Ekeroth, R. Gunnarsson,* Linköping University, Sweden

The use of high-power pulses for synthesis of nanoparticles in the gas phase is of interest because of the effective ionization of the supplied gases and the sputtered source material. The advantage of ionizing the source material is the effective trapping of positive ions onto the negatively charged nanoparticles in the plasma resulting in a significant increase in growth rate and utilization of material. A cylindrical metal hollow cathode was used where sputtering occurs on the internal surface of the cylinder. Apart from that a cathode configuration with a linear slit was employed suitable for roll-to-roll deposition. The sputtered material of ions and neutrals is ejected from the cathode due to the the pressure buildup by the high voltage pulse, due to the outward directed ambipolar electric field structure at the hollow cathode opening and due to the flow of the gas through the cathode. This results in rapid expansion of the sputtered material and it leads to nucleation and growth of nanoparticles. A range of materials has been synthesized by this technique including Fe, Cu, Ti, Ag, Mo, In and Zn. By adding a reactive gas to the process nanoparticles containing Ti-O, Ti-N Zn-O and In-N has been synthesized. Several process parameters were identified to affect the size, size distribution, shape and structure of the nanoparticles. These parameters include pulse power, pulse frequency, sputtering gas composition, gas pressure and geometry of the setup. By tuning these parameters, the nanoparticle size can range from a few nm to more than 250 nm in diameter. Depending on the employed process parameters, the crystal structure of nanoparticles varies from a single crystal with well-defined crystallographic faces to polycrystalline and amorphous cauliflower structures consisting of randomly oriented agglomerates of nano-crystals. In the presentation it will also be shown that the nanoparticles can be used for assembling of different nanostructures.

8:40pm **NM-TuE10 Out of the Plane: Graphene-based Vertical Transistors for Realistic Applications***, **Anindya Nath**,* George Mason University, USA*; B.D. Kong, A. Koehler,* US Naval Research Laboratory, USA*; V.R. Anderson,* U.S. Naval Research Laboratory, USA*; V.D. Wheeler,* US Naval Research Laboratory, USA*; E.R. Cleveland,* US Naval Research Laboratory,USA*; A.K. Boyd, K.M. Daniels, R.L. Myers-Ward, D.K. Gaskill, K.D. Hobart, F.J. Kub, G.G. Jernigan,* US Naval Research Laboratory, USA

The graphene gold rush for electronic applications has been subdued due to the lack of an energy-gap in the graphene band structure which impedes utilization of graphene-based lateral field effect transistors for switching applications. Alternatively, graphene based vertical devices, such as hot electron transistors (GHETs), have been proposed to overcome the band-gap bottle neck. HETs utilize high energy tunneling injected electrons (hot electrons) to achieve high performance. High on-off ratio can be achieved by biasing the emitter-base and collector-base junctions. For traditional metal-based HETs, the cut-off frequency are limited by base transit time (for thick base metal) or high RC delay (for thin base metal). Graphene offers the ideal solution for HETs due to its ultimate thinness and high conductivity. Epitaxial graphene grown on conducting SiC is an attractive choice for GHETs due to the naturally occurring Schottky barrier between SiC-graphene interface, which can be exploited as the collector barrier. The integration of an emitter-base junction dielectric, however, possess significant challenges due to the low wettability of the graphene sp^2 structures. Previous efforts to integrate ultra-thin dielectric layer often lead to metal rich seed layers with pinholes, graphene lattice damage, restricted ALD growth temperature or the inability of wafer scale process integration.

In this work, the amphiphilic nature of graphene oxide is exploited as a seed layer to facilitate ultrathin and conformal high-κ metal oxide deposition on epitaxial graphene by atomic layer deposition at growth temperatures as high as 300°C. Three different high-κ metal oxides (Al2O3, HfO2 and TiO2) with various thicknesses (4 -20 nm) were grown on ultrathin (1.5 nm) GO seed layers on EG. The uniformity and stoichiometry of the films were confirmed by atomic force microscopy and X-ray photoelectron spectroscopy. Additionally, metal-insulator-graphene tunnel devices were fabricated and temperature dependant tunneling behavior is studied. No defect/trap assisted conduction behavior was observed, and a transition from direct to fowler-nordheim tunneling was observed at low temperatures. For graphene field effect transistors (GFETs) with metal oxide on GO seed layer demonstrated high on-state current, low gate leakage current and good channel modulation. Capacitance voltage measurement of the GFETs exhibited low hysteresis and nearly ideal dielectric constants for respective dielectrics. These results demonstrate a simple yet cost-effective universal way of wafer-scale ultrathin high-κ dielectrics deposition on epitaxial graphene by ALD.

Nanomaterials
Room Hau - Session NM-WeM
Nanocharacterization

Moderator: Kristina Tschulik, Ruhr-Univ. Bochum, Germany

8:00am **NM-WeM1 Nanoscopic Analysis of Semiconductor Heterointerfaces by Kelvin Probe Force Microscopy***, F. Yamada, T. Kobayashi, K. Takabayashi, K. Shimomura, Y. Zhang,* ***Itaru Kamiya,*** Toyota Technological Institute, Japan

The electronic structure of heterointerfaces is known to determine the performance of semiconductor devices. This led to the series rigorous studies on interfaces, *i.e.,* Fermi level pinning or Schottky barrier formation, for decades. However, such studies were not easy and hence the results not conclusive, due to factors such as the reproducibility in preparing identical interfaces or limitation in the availability of tools that could characterize the interfaces on an atomic scale. Kelvin probe force microscopy (KFM) is an atomic force microscopy-based technique that provides us with the opportunity to tackle such problems by mapping the surface potential and topograph on nanometer scale simultaneously. Here, we report the application of KFM for the study of 1) InAs quantum dots (QDs) grown on GaAs(001) and 2) Si heterojunction (SHJ) solar cell structure.

We previously reported that the I-V characteristics of the InAs QD on GaAs(001) vary as a function of QD size, and that the interface may be ohmic-like when the QD diameter is about 100 nm while it exhibited Schottky diode-like behavior when the diameter is about 20 nm [1]. The phenomenon was naively interpreted in terms of a balance between Fermi level pinning in the conduction band of the InAs eventually overcoming that at mid gap for GaAs surrounding the InAs QD as its size is enlarged. Here, we performed KFM on QDs whose diameters are around 20-30 nm. We observe that a ring-like dip of surface potential is formed at the peripheral of the QDs (Fig.1) in agreement with previous work [2]. We converted the surface potential map into band alignment by using the known electron affinity of the bulk materials, as a function of depth from the surface. We find that the Fermi level of the dip region lies in the conduction band suggesting the presence of a source of electric contact, while the Fermi level in the wetting layer and the majority of the QD lies in the band gap (Fig.2).

We also performed KFM measurements on the cleaved interfaces of SHJ solar cell and related structures. The SHJ structure we employed is ITO/*p*-aSi/*i*-aSi/*n*-cSi(001). We observe that while the workfunction, and thus the band alignment, of *i*-aSi/*n*-cSi(001) interface is abrupt, *p*-aSi/*i*-aSi is not, and also that ITO/*p*-aSi interface may be blurred as a result of interdiffusion (Fig.3). This is in strong contrast from the reference sample Ag/Si(001) from which we observe a nearly ideal Schottky-like band alignment.

We will discuss the possible mechanisms and implication of these results.

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8:20am **NM-WeM2 Defect Mediated Material Properties of 2-D Transition Metal Dichalcogenides studied by using Parallel Ultra High Resolution AFM and STS Mapping***, A. Weber-Bargioni,* ***Sebastian Wickenburg,*** Lawrence Berkeley National Laboratory, USA

In this presentation we show how individual atomic defects and linear mirror twin boundaries in 2- D MoSe 2 , identified with super resolution atomic force microscopy, alter the electronic wave function, imaged via Scanning Tunneling Spectroscopic mapping, leading along mirror twin boundaries to charge density waves and solitons.

Hierarchically ordered defects or adsorbents in two dimensional transition metal dichalcogenides modify the local electronic states in terms of energy and geometry of the electronic wave functions at length scales of individual wave functions, inducing novel functionality. Due to their 2-D nature, 2-D TMDs are an excellent model system to directly access, visualize and determine the effects of defect mediated electronic wave function tuning using high resolution AFM and differential conductance mapping.

We focused on studying various defect classes in 2-D MoSe2. We identified individual Se vacancies – on both, the SPM facing and the substrate facing surface. Both result in particular electronic wave function related to states localized at the atomic defect [1]. These defect states form atomically sharp type 1 hetero junctions with the surrounding pristine MoSe2, and form an excellent test bed to study catalytic activity with atomic precision.

We also identified hierarchically ordered defects in from of Mirror Twin Boundaries (MTB) in MoSe2, which form truly 1-D metal channels embedded in the surrounding semiconductor. At low temperatures these 1-D metallic states open a band gap at the Fermi level of 100meV. The new band gap frontier states exhibit a spatial modulation along the channels with a periodicity of three times the lattice constant. Density Functional Theory calculation confirm that the observed charge modulation is a result of the formation of a charge density wave [2]. Charging up the charge density wave we observe the creation of solitons – a self-reinforcing wave - and are able to measure its' energetic dispersion [3].

These results demonstrate how defects can not only modify the local electronic wave function, but directly alter the material properties and opens up a large playground to study the effects of linear defects, hierarchically ordered defects or adsorbents.

1 Maps of Electronic Wave functions associated with various atomic defects in MoSe2, S. Barja, S. Wickenburg, , A.Weber-Bargioni et al. *submitted*

2 Charge density wave order in 1D mirror twin boundaries of single-layer MoSe2, S. Barja, S. Wickenburg, A.Weber-Bargioni et al. *accepted in nature physics*

3 Formation of Charge Density Wave Solitons in Mirror Twin Boundaries embedded in MoSe2, S. Wickenburg, S. Barja, A.Weber-Bargioni et al. submitted

8:40am **NM-WeM3 Solution Phase Synthesis, Electron Microscopy Characterization and Catalytic and Medical Applications of Nanoparticles***,* ***Richard Tilley,*** University of New South Wales, Australia **INVITED**

Liquid phase synthesis is a powerful method for the formation of uniform sized nanoparticles and nanoparticles with a faceted morphology. General strategies for the formation of nanoparticles and through chemical synthesis will be outlined. The results presented will include the formation of catalytic metals such as gold core palladium shell nanoparticles, below and branched nanostructures of gold, palladium and ruthenium. The growth mechanism of how the particles form will also be presented along with HRTEM observations. Biomedical and catalytic applications will be discussed.

9:20am **NM-WeM5 Atomic Species Identification at the (101) Anatase Surface by Simultaneous Scanning Tunnelling and Atomic Force Microscopy***, O. Stetsovych,* NIMS, Japan*; M. Todorović,* Universidad Autonoma de Madrid, Spain*; T.K. Shimuzu,* NIMS, Japan*; R. Perez,* Universidad Autonoma de Madrid, Spain*;* ***Oscar Custance,*** NIMS, Japan

Titanium dioxide (TiO_2) is an important material in a number of energy-related applications such as photocatalytic water splitting, and the conversion of solar energy to electricity. Most of these applications rely on nano-crystalline TiO_2 samples that consist principally of two polymorphs: anatase and rutile. In some commercial TiO_2 samples, anatase nano-crystals account for up to 75% of the product, and anatase is generally regarded as having a higher surface reactivity than rutile.

Despite the pivotal role of anatase as reactive component in TiO_2 samples used as the active phase in commercial catalysts, there is still a relatively scarce amount of experimental studies on anatase surfaces in comparison with rutile. More research is required to better understand the surface properties that define anatase as such a good photocatalyst. In particular, the real space characterization of anatase substrates at the atomic scale is essential to elucidate the basic principles that govern the photocatalytic and photovoltaic applications of this TiO_2 polymorph.

In this contribution, we combine atomic force microscopy (AFM) and scanning tunneling microscopy (STM), supported by first-principles calculations, for the simultaneous imaging and unambiguous identification of atomic species at the (101) anatase surface [1]. By using single water molecules as atomic markers, we demonstrate that AFM images the topmost oxygen atoms of the surface, while the main contribution to the STM signal comes from the titanium atoms at the third atomic layer. We show that the STM signal is sensitive to sub-surface defects, and that simultaneous AFM-STM allows the acquisition of STM images with atomic resolution within the surface band gap, where standard STM imaging is challenging.

Based on key distinguishing features extracted from experiments and first principles calculations, we identify candidates for the most common surface defects of the (101) anatase surface and characterize the surface local chemical reactivity with the AFM probe at atomic scale.

The findings reported here provide the foundation for future work on anatase, and pave the way for the study of more complex anatase systems related to water splitting and organic photovoltaics, including the adsorption geometries and binding sites of photoactive molecules as well as metal dopants to enhance hydrogen production.

[1] O. Stetsovych et al. Nature Communications 6, 7265 (2015)

9:40am **NM-WeM6 Electrochemically-generated Nanomaterials Studied by In situ Flow Spectro-electrochemical Scanning Transmission X-Ray Microscopy**, ***Adam Hitchcock***, *V. Prabu,* McMaster University, Canada; *S.M. Rosendahl,* Canadian Light Source, Canada; *M. Reynolds, H. Hosseinkhannazer,* Norcada Inc, Canada

We are using soft X-ray scanning transmission X-ray microscopy (STXM) [1] to investigate Cu thin film and dendritic electrochemical growth on a Au surface under variable pH conditions. Electrochemical reduction of Cu(II) under acid conditions is commonly used to deposit copper for integrated circuit interconnects, and in many other technologically important applications of thin films and nanoscale Cu metal. Improved understanding of the fundamental steps of the reaction and how to control undesirable phenomena such as dendritic growth is needed to further optimize this process. The reduction of Cu(II) to Cu(0) proceeds via a Cu(I) intermediate, which can be detected under weakly acidic to neutral conditions. We have developed a novel device for *in situ* STXM studies of electrochemical reactions which can operate under flow or static conditions [2]. The ability to change electrolyte during an experiment is being used to better understand the role of Cu(I) species in the deposition process. Spectromicroscopy at the Cu 2p and O 1s edges is used to analyze initial and final states, follow the process *in situ*, and search for intermediate species. The apparatus and techniques for spectro-electrochemical-microscopy will be described and results will be presented from deposition & stripping of copper from $CuCl_2$(aq) and $CuSO_4$(aq) electrolytic solutions as a function of pH.

STXM performed using BL10ID1 at CLS and BL 5.3.2.2 at ALS . Research supported by NSERC and the Catalyst Research for Polymer Electrolyte Fuel Cells (CaRPE-FC) network.

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10:20am **NM-WeM8 Structural and Chemical Study of the Stability of Pt-based Fuel Cell Electrocatalysts via 3D Electron Tomography**, ***Karren More***, *D.A. Cullen, B.T. Sneed,* Oak Ridge National Laboratory, USA

Polymer electrolyte membrane (PEM) fuel cell performance and materials degradation, particularly associated with the cathode catalyst layer (CCL), can be directly attributed to the structure and chemistry of individual material components, as well as their uniformity/homogeneity within a CCL. The individual material constituents used to form the CCL within the membrane electrode assemblies (MEAs), e.g., the electrocatalyst (Pt or Pt-alloys), catalyst support (C-based), and ionomer films (proton conductor), and especially the critical interfaces that are formed between these various constituents, are critically importance in controlling fuel cell performance. Understanding the specific microstructural characteristics of the individual materials within the CCL, and how the materials interact during fuel cell operation/aging, is important for identifying materials optimization parameters that can significantly enhance performance and durability.

Research efforts at Oak Ridge National Laboratory are focused on the high-resolution microstructural and microchemical characterization of MEAs fabricated using different Pt-based electocatalysts and catalyst loadings, carbon-based support materials, and ionomer solutions, as well as the same MEAs subjected to accelerated stress tests (ASTs) designed to degrade specific MEA components and assess durability. High-resolution analytical microscopy methods are used to study the distribution and chemistry of materials and interfaces within CCLs, which are combined with high-resolution imaging and 3D electron tomography techniques to provide unprecedented insight into the structure and interfaces (ionomer/support, ionomer/catalyst, catalyst/support, ionomer/pore) in "real" MEAs before and after aging. This presentation will focus on understanding materials distributions within the CCL as a function of processing variables, e.g., initial ionomer and/or ink chemistry, electrocatalyst (type, loading, and dispersion), and the type of carbon support used. The stability of the ionomer films, electrocatalyst, and support structures in CCLs after ASTs will be evaluated.

Research sponsored by (1) the Fuel Cell Technologies Office, Office of Energy Efficiency and Renewable Energy, U.S. Department of Energy and (2) Oak Ridge National Laboratory's Center for Nanophase Materials Sciences (CNMS), which is a U.S. Department of Energy, Office of Science User Facility.

10:40am **NM-WeM9 Challenges in Synthesis and Characterization of Non-precious Transition Metal Carbide/Nitride Catalysts**, *S. Gage, M. Davidson, C. Ngo, C.A. Cadigan,* Colorado School of Mines, USA; *D. Esposito,* Max-Planck Institute for Colloids and Interfaces; ***Brian Trewyn***, *R. Richards, S. Pylypenko,* Colorado School of Mines, USA

Metal carbides/nitrides have demonstrated unique properties for various catalytic reactions and are attractive as earth-abundant alternatives to precious group metals (PGM). However, synthesis of nanoscale transition metal carbides and nitrides has proven difficult, and obtaining structures with high surface areas and controlled morphologies have been elusive. Additional challenges arise from the complex nature of these nanomaterials and there is limited characterization available in the literature. Through unique synthetic approaches, we have created a wide array of unsupported and supported nickel-based nanomaterials, and utilized bulk and surface characterization techniques to identify synthesis-composition-property relationships.

11:00am **NM-WeM10 Stacking of AlOOH Nano-Rods and Plates: The Effect of Surface Termination Chemistry on the Preferential Interacting Crystal Zones in Solution**, ***Michele Conroy***, *J. Soltis, S. Chatterjee, E. Buck,* Pacific Northwest National Laboratory, USA

Aluminum oxyhydroxide (boehmite) nanoparticles are used for a wide variety of applications including catalysis and adsorption. It has been shown that boehmite nanoparticles with 010 plane as the largest exposed surface area have increased catalysis and adsorption rate, due to the relatively high OH density of this plane. Additionally synthesizing these nanoparticles in a hierarchical structures instead as mono-dispersed, has been reported to increase the reactivity even further. In this study we utilize cryo-transmission electron microscopy (TEM) and in-situ liquid TEM to achieve fundamental insights into the mechanisms of nanoparticle aggregation and reactivity. Although there is a lot of theoretical debate around the preferential interacting zones of AlOOH crystalline nanoparticles in solution, there has been no experimental confirmation to date. Our initial results show that the particles aggregate along a preferred crystal orientation (the main flat (010)), irrespective of pH and solution content, forming large stacked agglomerates and decreasing the exposed surface area.

Aluminum oxide nanoparticles formed by the dehydration of boehmite are also widely used in industrial catalysis including petrochemical, chemical, and automotive due to their stability at high temperatures. Although the shape of the nanoparticle during the thermal treatment of boehmite remains the same the terminating planes of course change with the removal of water. This enabled us to study any change in the aggregation due to the terminating chemistry without the shape of the nanoparticle itself being a possible variable.

11:20am **NM-WeM11 Nanoscale Chemical Imaging with Photo-induced Force Microscopy*, Sung Park,*** Molecular Vista, USA

Infrared Photo-induced Force Microscopy (IR PiFM) is based on an atomic force microscopy (AFM) platform that is coupled to a widely tunable mid-IR laser. PiFM measures the dipole induced at or near the surface of a sample by an excitation light source by detecting the dipole-dipole force that exists between the induced dipole in the sample and the mirror image dipole in the metallic AFM tip. This interaction is strongly affected by the optical absorption spectrum of the sample, thereby providing a significant spectral contrast mechanism which can be used to differentiate between chemical species. Due to its AFM heritage, PiFM acquires both the topography and spectral images concurrently and naturally provides information on the relationship between local chemistry and topology with sub 10 nm spatial resolution on a variety of samples. PiFM spectral images surpass spectral images that are generated via other techniques such as scanning transmission X-ray microscopy (based on synchrotron source), micro confocal Raman microscopy, and electron microscopes, both in spatial resolution and chemical specificity. The breadth of the capabilities of PiFM will be highlighted by presenting data on various polymer systems. By enabling imaging at the nm-scale with chemical specificity, PiFM provides a powerful new analytical method for deepening our understanding of nanomaterials and facilitating technological applications of such materials.

11:40am **NM-WeM12 CNC Modification for the Development of Active Food Packaging*, Monique Lacroix,*** INRS-Institut Armand-Frappier, Canada

Irradiation treatment of CNC was performed at doses of 5-20 kGy followed by reaction with a redox group of ascorbic acid (AA) and hydrogen peroxide in order to promote the formation of radicals on the macromolecule to enhanced the interaction of CNC with gallic acid. Our results have demonstrated that both of these pre-treatments induce the formation of carboxylic acid groups on CNC surface by conductometric titration. Derivates of carboxylic acid are known as food stabilizers and preservers due to their antiradical and antimicrobial effects. Since gallic acid has carboxilic acid groups, it was found that its interaction with pre-teated CNC with gamma-irradiation in the presence of redox group (CNC-g-GA) can impart to native CNC antiradical properties. A solution of 20% of CNC-g-GA was then added to a 1% (w/w) gellan in order to produced antiradical gellan-based film packaging. A significant improvement of the tensile strength (TS), the tensile modulus (TM) and the elongation at break (EB) and the water resistance was observed when CNC-g-GA was added to the film packaging formulation ($p \leq 0.05$). These results bring to a new application of antiradical film packaging or coatings which could be applied for food industry to preserve fruit and vegetables during storage.

Nanomaterials
Room Mauka - Session NM-WeP
Nanomaterials Poster Session

NM-WeP1 Quantum Confinement Effect and Photocatalytic Properties of Cu_4SnS_4 and Cu_4SnS_4-Au Quantum Dots*, Wenchao Liu,* Nanjing Tech University, China

We developed an improved hydrothermal method with water-oil two-phase reaction system to synthesize size-controllable and oil-soluble Cu_4SnS_4 (CTS) quantum dots (QDs). The formation and growth mechanism of CTS QDs was proved to proceed via three steps: nucleation of $C_{31}S_{16}$ nanoparticles, diffusion of Sn^{4+} into $Cu_{31}S_{16}$ nanoparticles and formation of regular hexagonal nanoprisms via Ostwald ripening. The water-oil interface plays an important role in controlling nuclei process and growth speed of CTS QDs. The average size and size distribution of CTS QDs can be controlled efficiently through adjusting the solvent ratio of toluene/water. Nearly monodisperse CTS QDs can be synthesized when the toluene volume is larger than 30 mL. More importantly, this improved hydrothermal method is a general and low cost method to synthesize not only chalcogenide based QDs but also other complex compound QDs. The blue-shift of absorption edge and broadening of Raman bands were observed due to the quantum confinement effect. The exciton Bohr radius of CTS QDs was calculated to be 3.3-5.8 nm by using the first principle calculation. We further use the CTS quantum dots as seeds to produce CTS-Au heterostructured nanoparticles. Such heterostructured nanoparticles are shown to have excellent photocatalytic properties.

NM-WeP2 Magnetic Strain Imaging of a Main Pole Tip and an Upper Shield in a Hard Disk Drive*, Kenta Butsugan,* Kansai University, Japan

Hard disk drives (HDDs) play an important role as large-scale information storages. Currently, in perpendicular recording, the main pole is keenly confined to apply magnetic fields to a finite portion. Therefore, remanent magnetization tends to appear at the pole tip. The magnetic fields produced by the remanent magnetization erase data recorded on magnetic media. The head-induced data erasure, especially erase-after-write, is a serious problem for the single-pole writer. We observed a head to reveal the erase-after-write phenomenon using magnetic strain imaging.

Scanning probe microscopes (SPMs) can sensitively detect changes in the gap between the tip and sample, with high in-plane resolutions. Strain imaging, based upon the excellent capabilities of SPMs, detects changes in the gap induced by the modulation of a physical property to be imaged, and images the modulated property of the sample together with its topography. Strain imaging was applied to observe the piezoelectric/ferroelectric properties of samples, and then magnetic observation was presented.

When a magnetic sample is subjected to a magnetic field, strains are generated in the sample. Because the strains involve factors that depend on the magnetization of each domain, we can observe the magnetic domain structures by imaging the strains via an SPM. We pointed out magnetostriction, magnetic forces, and electromagnetic interaction between the magnetization and eddy currents as the causes of the strains. Any magnetic probe is not required with this method, because domain structures are imaged by the detection of surface displacements. The applied magnetic fields are well-estimated and precisely controllable, while the stray fields from the magnetic probes used in magnetic force microscopy are not controllable and not easy to estimate.

Our observed samples were heads having the main pole tips of 60-nm and 30-nm width. One of them was multilayer pole tip. We observed magnetic imaging of the tips with respect to the write coil currents. We present these results.

NM-WeP3 Electrical and Optical Properties of Barium Titanate Nanoparticles Contained in Mesoporous Silicate Thin Film*, Atsushi Kohno,* *T. Tajiri,* Fukuoka University, Japan

Integration of size-controlled nanoparticles into thin films is attractive for applications to functional materials and devices owing to their unique properties related to the reduced size. We have synthesized the nanoparticles of dielectric materials in the one-dimensional pores of mesoporous silicate SBA-15 thin films formed on silicon and quartz substrates and have investigated the characteristics of nanoparticles. Ferroelectric nanoparticles are attractive for memory application especially as ultra-small scale devices, and the ferroelectricity of nanoparticle is interesting from the viewpoint of materials sciences. In this research we focus on the nanoparticles of perovskite-type ferroelectric materials. The synthesis of barium titanate ($BaTiO_3$) nanoparticles in the pores of SBA-15 thin film were developed, and the electrical and optical properties of the nanoparticles have been investigated.

Mesoporous silicate SBA-15 has been synthesized using Ethylene oxide/propylene oxide/ethylene oxide triblock copolymer and tetraethylorthosilicate. The mixture solution was coated on p-Si(100) and quartz substrates by spin-coating, and then the coated samples were dried and sintered. The SBA-15 thin film samples were dipped in $BaTiO_3$ precursor solution. The SBA-15 films which contained $BaTiO_3$ precursor solution in the pores were sintered in a furnace at 700 °C for crystallization. In the case of electrical measurement Au electrodes were made on the films.

X-ray diffraction showed that the one-dimensional pores in SBA-15 thin film were aligned parallel to the surface and stacked keeping well-ordered hexagonal symmetry. The pore diameter was estimated to be about 5 nm from the analyses of X-ray diffraction and reflectivity, as detail of the evaluation method was reported elsewhere. It was confirmed that the stacked pore structure was never affected by the synthesis of $BaTiO_3$ nanoparticles. The elemental composition and chemical states of $BaTiO_3$ nanoparticles in the thin films were checked by XPS measurement as compared with the bulk material. The optical absorption of $BaTiO_3$ nanoparticles was clearly observed and the absorption edge is estimated to be about 3.7 eV which is much larger than the bandgap of the bulk material.

The clockwise hysteresis was clearly observed in the capacitance-voltage characteristics of Au/$BaTiO_3$-containing SBA-15/p-Si capacitor and the hysteresis voltage width was increased and saturated as increased the applied voltage. These results suggest that the hysteresis was caused by ferroelectricity of $BaTiO_3$ nanoparticles. The properties of the $BaTiO_3$ nanoparticles will be discussed in the conference.

NM-WeP4 Structural Analysis of Hydroxyapatite Nanoparticles by Rietveld Refinement and Electron Diffraction*, Magdalena Méndez-González,* ESFM-National Polytechnic Institute of México*; G.M. González,* UPIBI-National Polytechnic Institute of México*; M.M. Méndez,* ESFM-National Polytechnic Institute of México

It was studied by Rietveld refinement and electron diffraction structural behavior of hydroxyapatite nano-particles, synthesized by chemical precipitation under normal temperature and pressure. Rietveld refinement using the data applied to XRD structural parameters of the nano-particles, its crystal size and the crystalline phases were obtained. Electron diffraction semi spherical and slightly elongated morphology, defined in relation to time and aging temperature used in the synthesis, distinguishing normal hexagonal prism morphology observed in natural hydroxyapatite crystals micrometer size was observed.

NM-WeP5 Fe_3O_4@$Zn_3K_2[Fe(CN)_6]_2$ for Cesium Removal from Radioactive. Aqueous Waste Solutions: A Mössbauer and XPS Study*, Arely Cano,* CICATA Legaria, National Polytechnic Institute, México*; A.A. Lemus-Santana,* CICATA Legaria, National Polytechnic Institute, Mexico*; J. Tóth, L. Kövér,* Institute for Nuclear Research (ATOMKI), Hungarian Academy of Sciences, Hungary*; E. Reguera,* CICATA Legaria, National Polytechnic Institute, México

$Zn_3A_2[Fe(CN)_6]\cdot xH_2O$ with A= Na^+, K^+, Rb^+ shows a high ability for Cs^+ removal from aqueous solutions by ionic exchange.These solids have a porous framework formed by six large ellipsoidal cavities per hexagonal unit cell with dimensions close to 15.5x11.1x7.9 Å. The neighboring cavities remain connected by elliptical windows of about 6.8x8Å. Within a given cavity two charge balance cations A^+ are found. These cations are located close to N corners of the ZnN_4 tetrahedron [1]. For Cs^+ the ionic exchange is highly favorable due of its large volume [2], the Cs^+ ion is found interacting with two N neighboring atoms. This explains that when $Zn_3A_2[Fe(CN)_6]_2\cdot xH_2O$ is immersed in an aqueous solution containing Cs^+, the ionic exchange is quantitative. On the other hand, the iron oxides nanoparticles have attracted attention as simple, efficient and economical materials for pollutant removal, including heavy metals. Their physicochemical properties as large surface areas, surface reactivity and strong adsorption capability can be modified and enhanced to obtain effective adsorbents materials. In addition, the iron oxide behaves as ferrimagnetic or ferromagnetic material; such property can be used to allow the separation process using an applied magnetic field. This is the case of the system under study in this contribution. In this study, paramagnetic magnetite nanoparticles were synthesized and covered with a thin shell of $Zn_3A_2[Fe(CN)_6]_2$, then the shell was progressively growing at the surface. The nanocomposi tes obtained were evaluated for Cs^+ removal from aqueous solutions. For evaluation, the nanocomposites were prepared with different iron oxide particles sizes and $Zn_3A_2[Fe(CN)_6]$ thin shell . The structural study was carried out from XRD powder patterns and Electron Microscopy data.

The interactions at the interface between the core of magnetite nanoparticles and the zinc hexacyanoferrate shell were studied by X-ray Photoelectron Spectroscopy (XPS) and Mössbauer spectroscopy. The nanocomposites studied were prepared by two different successive adsorption cycles of shell growth, $Fe_3O_4@[Fe(CN)_6]^{4-}$ and Zn^{2+}. The quantitative analysis by XPS allows determine the shell thickness using an appropriate model and supported with Mössbauer data which allows the identification of species formed and their interactions at the interface.

NM-WeP6 Subwavelength Color Printing with Wide Viewing Angle*,* *HuiJoon Park*, Ajou University, Republic of Korea

Color filter has been considered as an essential component of various display technologies such as LCDs and OLEDs, because the quality of image and resolution of those displays are significantly affected by the performance of color filters. Existing color filter systems, however, utilize colorant pigments or dyes, whose properties are easily affected by numerous factors including constant UV illumination, longstanding heat exposure and moisture, thus causing the performance degradation of display devices in a relatively short period of time. Furthermore, their low stability with respect to diverse processing chemicals and complicated patterning processes for creating individual pixels are also the biggest concern of the traditional color filter systems.

As an alternative to the present color-generating systems, a structural color filter scheme, which exploits a physical interaction of light with nano- and micro-structures (*e.g.* photonic and plasmonic resonances), has been widely investigated due to their potential advantages such as ultra-compactness, long-standing stability and simple manufacturability as compared to the conventional color filters.

Particularly, with the growing popularity of high-definition devices, the ability of attaining high spatial resolution by tightly localizing the light energy into neighboring gaps at the deep subwavelength scale, thus being able to create color pixels beyond the diffraction limit, has been another key feature of the structural color filter system. Therefore, in recent years, with the rapid developments of large-scale nanofabrication techniques such as nanoimprint lithography, colloidal self-assembly and laser interference lithography, substantial amount of attention has been given to the various nanostructure-based color filtering systems, which could provide unique and distinct possibilities for enabling a color printing with sub-diffraction resolution. However, there have been great difficulties in retaining optical resonances at the same wavelength over a wide angular range and simultaneously creating vivid full colors in a pixel unit through a one-step process.

Here, an angle-insensitive structural color filtering scheme based on strong interference effects in ultrathin subwavelength semiconductor gratings on metallic substrates is introduced. The proposed color filter devices, which are fabricated over a large area using nanoimprint lithography, produce distinctive colors that are easily tuned by altering a width of the nanostructured gratings even with the fixed thickness of the structure, thus allowing all the individual color pixels to be patterned via one-step fabrication.

NM-WeP7 Ultrasonic Assisted Preparation of Liposomes using Supercritical Carbon Dioxide*,* *Chiho Uemori*, Nagoya University, Japan*; W. Diono,* Nagoya University*; T. Kon,* Shalom Co.*; H. Kanda,* Nagoya University*; M. Goto,* Nagoya University, Japan

A liposome is a spherical vesicle having single or multiple lipid bilayers. Liposomes are generally composed of phospholipids. Lipophilic or hydrophilic compounds can be encapsulated in liposomes either in the phospholipid bilayer or in the inner aqueous phase. Liposomes are prepared conventionally by the Bangham method, the detergent depletion method, the reverse phase evaporation method, and emulsion method. Recently, supercritical carbon dioxide has been applied to produce liposome instead of organic solvent.

In this work, liposomes were produced utilizing supercritical fluid technology with ultrasonic mixing. Since no organic solvent was used in this process, solvent-free liposomes were prepared. As a lipid, we used sphingomyelin or phosphatidylcholine. Phospholipids and water were charged in high pressure vessel. Then, pressurized carbon dioxide was pumped into the vessel. The vessel was placed in thermostatted water bath and applied ultrasonic power to mix phospholipids, water, and carbon dioxide phase in order to produce liposome structure. The obtained liposomes were identified as multi-lamella form by TEM analysis. The effects of operation parameters such as ultrasonic frequency, pressure, and temperature, particle size of liposomes were studied.

NM-WeP8 Method development and Determination of Trace Metal Impurities in Silicon Based Nanopowder in Solvent Mixture by Inductively Coupled Plasma Mass Spectrometry*,* *Mohsina Islam*, *S. Liu,* Chemtrace Analytical Testing and Solutions

In Semiconductor industry, the silicon based nanoparticles showed great promises in various applications like thin- film transistors for liquid crystal displays (LCD TFTS), solar cells and printed semiconductor materials because of its superior properties such as feasibility of surface functionalization, size dependent multicolor light emission and stability against photobleaching.

In this work a novel analytical method was developed for the determination of trace metal impurities in silicon based nanoparticles dispersed in solvent mixture using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). For this purpose silicon nanoparticles with metal dopants, e.g, phosphorous and boron dopant nanoparticles dispersed in various solvents like Isopropyl alcohol, PGMEA and Terpineol were studied. The sample was prepared by evaporation to solvent boiling point followed by Silicon dissolved and digestion with mixed acid solution. The trace metal (TM) residue was dissolved and reconstituted in dilute acid solution which is analysed through ICP-MS. Following the same method, a spiked sample was prepared with known TM level in the range of 3.0 to 6.0 ppb. The spike recoveries with this method is in the range of 75 to 125% for all elements. The dopant levels were measured as 0.05-0.3 wt.% for B and P following the dissolution and dilution of sample in mixed acid solution. The method detection limit as low as 0.1 to 10 ppb were achieved for different TM contaminants.

NM-WeP9 Optical and Morphological Characterization of ZnSe Nanoparticles Processed by Laser Ablation in Liquid*,* *Patricia Maldonado-Altamirano*, *R.Y. Ponce-Cano, L.A. Martinez-Ara,* ESFM-IPN, México*; M.A. Hernandez-Perez,* ESIQIE-IPN, México*; J.R. Aguilar-Hernandez,* ESFM-IPN, México

In this work we present results and analysis concerning the processing of semiconducting ZnSe nanoparticles obtained by laser ablation of diluted ZnSe powder in acetone. A Nd-YAG pulsed laser was used for ablation, tuned at the first harmonic, 1064 nm, 50 Hz frequency repetition during 60 minutes. The experiment was performed as a function of the laser power intensity. UV-Vis and Raman spectroscopies were used to characterize the ZnSe particles, whereas scanning electron microscopy, transmission electron microscopy and X ray diffraction were used to determine the morphology and size of the particles. According to the UV-Vis results it was confirmed a shift of the band gap towards high energy (blue shift) from 2.7 to 3.3 eV. Raman spectroscopy show the LO phonon at 250 cm^{-1} and also the so called surface mode at 230 cm^{-1}, for the case of the smaller particles, approximately 10 nm, which was estimated through SEM and TEM images. The cristalline planes were also observed in the TEM images. X-Ray diffractograms confirmed that the particles show the wurtzite structure. A deep analysis of the results is presented and discussed.

NM-WeP10 New Method Of Synthesis Of Graphene From Cvd In Steady State*,* *Alejandra Moreno-Barcenas*, Centro de Investigacion y de Estudios Avanzados Del Intituto Politecnico Nacional, Mexico*; J.F. Perez-Robles, A. Garcia-Garcia,* Centro de Investigacion y De Estudios Avanzados Del Intituto Politecnico Nacional, Mexico*; L.M. Avilez-Arellano,* CINVESTAV Querétaro México, Mexico*; Y.V. Vorobiev,* CINVESTAV-Unidad Queretaro, Mexico

The Graphene is a material used in a wide range of applications due to its unique structure and excellent electronic, optical, mechanical and thermal properties. Currently, several techniques are being developed to obtain graphene, one of this techniques that has highlighted which chemical vapor deposition (CVD) technique is the most reported. The fastest progress in graphene methodology in recent years have been obtained by this way. In this sense, the aim of the investigation in graphene is to increase the graphene production by CVD with high quality and at low cost. However, usually to produce graphene, it is necessary to use high vacuum equipment and temperatures about 1800 °C, which represents a very high cost. In this paper a new method is proposed to obtaining monolayer graphene with good quality and low cost operation. Using acetylene and nitrogen as precursors by CVD is possible to obtained monolayer graphene by CVD, instead of methane and argon. Also a mix of nitrogen:hydrogen (90:10, respectively) was used instead pure hydrogen. All the components are subjected to temperatures about 1000 °C and atmospheric pressure, on polycrystalline copper foil. The synthesis of the graphene is carried out in steady state, reducing the synthesis time around a minute. The amount of gas flow is determined taking into account the reactor volume per unit mass. The presence of graphene is shown by transmission electronic microscopy and Raman spectroscopy confirmed the monolayer of graphene.

NM-WeP13 High Temperature Shift Reaction without Pre-reduction over Metal Substituted Spinel Ferrite Catalysts prepared by Assisted Sol-Gel Method*, Dae-Woon Jeong,* Changwon National University, Republic of Korea

The purpose of this study was to prepare directly the magnetite of spinel ferrite catalysts using glycine assisted sol-gel combustion method and to compare the catalytic activity of Ni, Co, Mn, Mg, and Zn substituted spinel ferrite catalysts for the high temperature shift reaction. Selected metal ions (Ni, Co, Mn, Mg, and Zn) were introduced into iron oxide (spinel lattice) and the resulting materials screened for catalytic performance for the high temperature shift reaction using waste-derived synthesis gas. The active phase of spinel ferrite catalysts was directly prepared by the glycine assisted sol-gel combustion method under a reducing atmosphere. Among the prepared nano catalysts, $NiFe_2O_4$ catalyst exhibited the highest CO conversion (X_{CO}=81%) with long term stability even at a very high gas hourly space velocity of 40,057h^{-1}. This result was mainly due to the inverse spinel structure and easier reducibility of $NiFe_2O_4$ catalyst. The properties of metal ferrite spinel have been analyzed by Brunauer-Emmett-Teller (BET) method, X-raydiffraction (XRD), and temperature programmed reduction (TPR).

NM-WeP14 Temperature Dependence of the PTFE Surface Morphology Irradiated by an Ar^+ Ion Beam*, Yuki Yamashita,* *I. Takano,* Kogakuin University, Japan

Recently, the application of polytetrafluoroethylene (PTFE) spreads to various fields. PTFE is a macromolecular material that has the repetition of two fluorine atoms combined to a carbon atom. Because these atoms are strongly combined, PTFE has variously excellent characteristics such as a heat-resistant, an electrical insulation, a chemical stability, a low friction, etc. The significant characteristic among them is the high water-repellency which is well known as the coating of a cookware. The improvement of the water-repellency by modifying the PTFE surface morphology has been carried out by using the ion beam or the plasma treatment. In this case, the morphological change of the PTFE surface is caused by the heat and sputtering.

In the present study, the temperature dependence of the PTFE surface morphology irradiated by an Ar^+ ion beam was investigated. Two kinds of PTFE were used. They are the adhesive tape type (T-PTFE; Nitto Denko Corporation.) and the sheet type (N-PTFE; NICHIAS Corporation). The irradiated ion species were Ar^+ ions with 10 kV in an acceleration voltage at 40 μA/cm^2 in a current density. The temperature of PTFE substrates was controlled by the both of liquid nitrogen cooling and the heater heating, and was kept with -50, -25, 0, 25 and 50 degrees. The surface morphology was observed by the laser microscope (OLS4500 OLYMPUS) and the SEM (JSM-5310LV JEOL). The modified surface was evaluated about the water-repellency which was measured by the water-contact-angle meter (Kyowa Interface Science Co, Ltd.) using the θ/2 method. The surface chemical state was investigated using X-ray photoelectron spectroscopy (SHIMADZU Co.Ltd.).

In the same condition of the ion beam irradiation, the T-PTFE surface morphology changed by the T-PTFE substrate temperature. In the case of -50 degrees the surface change was hardly observed, while the needle-like structure was clearly observed in the substrate temperature of 50 degrees. It was considered that the surface morphology was strongly influenced by the substrate temperature than by sputtering of the ion beam. In addition, the atomic concentration measured by the X-ray photoelectron spectroscopy showed that fluorine atoms decreased and carbon atoms increased with a lower temperature, because the preferential sputtering was caused. On the other hand, oxygen atoms increased with a lower temperature because free bonds generated by the removed fluorine atoms from T-PTFE absorbed oxygen atoms in the atmosphere.

It was confirmed that the change of the PTFE substrate temperature in ion irradiation influenced the surface morphology and the atomic content.

NM-WeP15 Large-Area Multi-layer Hexagonal Boron Nitride*, SooMin Kim,* Korea Institute of Science and Technology, Korea

Chemtrace Analytical Testing and Solutions

NM-WeP19 Photocatalytic CO_2 Reduction on Particulate Metal-ion-doped CeO_2*, Hideto Furuno,* *N. Saito, K. Sato, M. Nishikawa,* Nagaoka University of Technology, Japan

1. Introduction

In recent years, the issue of global warming caused by a greenhouse effect gas such as CO_2 has been becoming deeply. Fossil fuels are exhaustible resource, and CO_2 is released into the atmosphere by their combustion. In order to solve these problems, artificial photosynthesis using photocatalyst is one of promising approach. We have been studied photocatalytic overall water splitting into H_2 and O_2 on CeO_2, and showed that proper metal-ion-doped CeO_2 has a sufficient ability to split water by UV irradiation.[1] Although hydrogen is expected as the clean energy source, some problems such as storage and transport remains to be solved. On the other hand, CH_4 has attracted much interest as useful fuel because of their conventional chemical properties. In this study, we payed attention to convert CO_2 to CH_4 by artificial photosynthesis on Pt-loaded Sm-doped CeO_2 photocatalyst.

2. Experimental

Sm-doped CeO_2 was prepared by heating of Sm_2O_3 and CeO_2 mixtures at 1373 K for 16 h in air. Pt was deposited on the as-prepared Sm-doped CeO_2 surface by photodeposition method as a co-catalyst. Prepared Pt-loaded Sm-doped CeO_2 was characterized by X-ray diffraction (XRD) and field emission scanning electron microscope (FE-SEM). Photocatalytic CO_2 reduction was carried out by a hand-made closed gas circulation apparatus directly connected to a gas-chromatograph equipped with BID detector. Photocatalyst was dispersed in distilled water and irradiated by a UV-lamp. CO_2 gas was filled with vessel before light irradiation.

3. Results and discussion

In XRD measurements, the as-prepared Sm-doped CeO_2 showed well-defined fluorite crystal structure with significant peak shift corresponding to Sm doping into their lattice. SEM images indicated that Pt was highly dispersed on CeO_2 surface after photodeposition. As products for photocatalytic reaction, CH_4 and H_2 were detected without producing CO. It is interesting that CO that is a major product for CO_2 reduction was not detected. It is well known fact that Pt has an ability to adsorb CO strongly. These results indicate that Pt-loading plays an important role for CO adsorption and lead to selective CH_4 production for photocatalytic CO_2 reduction.

4. Conclusions

Photocatalytic CO_2 reduction on Pt-loaded Sm-doped CeO_2 was investigated. Pt-loaded Sm-doped CeO_2 showed selective CH_4 production. This results indicate that metal-ion-doped CeO_2 become a suitable material for photocatalytic CO_2 reduction, and the combination between metal-ion-doped CeO_2 and co-catalyst will be an important factor for selective CH_4 production.

References

[1] H. Kadowaki, N. Saito, H. Nishiyama, Y. Inoue, *Chem. Lett.* 36, 440-441 (2007).

NM-WeP20 Effects of Surface Acid Treatment on Mg-doped GaN for Photocatalytic Overall Water Splitting*, Takahiro Inoue,* *N. Saito, M. Nishikawa,* Nagaoka University of Technology, Japan

1. Introduction

H_2 has received attention as a next-generation energy alternative to fossil fuels. In the past four decades, photocatalysts have payed attention to energy conversion materials for water splitting into H_2 and O_2. Recently, we have discovered that Mg-doped GaN has an ability to decompose water when depositing RuO_2. [1] However, synthesized as-prepared Mg-doped GaN has an impurity phase such as MgO, and showed unstable activities at an initial stage of reaction, suggesting that an unstable layer soluble in water exists on as-prepared Mg-doped GaN. Therefore, it is necessary to remove them for improving the activity of photocatalytic water splitting. In this study, we investigated changes in photocatalytic activities by surface acid treatment.

2. Experimental

A precursor of Mg-doped GaN was obtained by co-precipitation method using $Ga(NO_3)_3$ and $Mg(NO_3)_2$ in alkaline solution. The precursor was heated at 1273 K for 15 h under NH_3 atmosphere. The obtained Mg-doped GaN was treated by stirring in 0.1 M HCl solution. RuO_2 was deposited by impregnation method in range from 1 to 5 wt% as a promoter. Photocatalytic water splitting was performed by closed gas circulation apparatus. A 300 W Xe lamp was used for photo-irradiation.

3. Results and discussion

As an impurity phase, an imperceptible peak for MgO was detected on as-prepared Mg-doped GaN. MgO was completely removed by surface acid treatment. For photocatalytic water splitting, RuO_2-loaded as-prepared Mg-doped GaN evolved H_2 and O_2 with N_2 at an initial stage of reaction, then N_2 generation disappeared at the several runs of reaction, indicating that the outermost surface of the as-prepared Mg-doped GaN was dissolved in water by photo-irradiation. On the other hand, acid treatment gave stable and high activities for H_2 and O_2 evolutions compared to that of the as-prepared Mg-doped GaN without N_2 production. The optimum amount of RuO_2 on Mg-doped GaN changed from 3.5wt% to 2.0wt% after acid treatment.

4. Conclusions

Effects of acid treatment on Mg-doped GaN for photocatalytic water splitting were investigated. This work indicates that removal of surface impurity phase and unstable layer on Mg-doped GaN is promising approach.

References

[1] N. Arai, N. Saito, H. Nishiyama, Y. Inoue, K. Domen and K. Sato, *Chem. Lett.*, 35, 796 (2006)

Nanomaterials
Room Hau - Session NM-WeE

Nanocomposites

Moderator: Richard Tilley, University of New South Wales, Australia

5:40pm **NM-WeE1 Nanocrystal-in-Glass Composite Thin Films for Electrochromic Smart Windows***, **Delia Milliron**,* University of Texas at Austin, USA **INVITED**

Degenerately doped metal oxide semiconductors, like ITO, exhibit plasmonic resonance at near and mid-infrared wavelengths tunable by varying their composition. Nanocrystals of many such materials have now been synthesized and applications are emerging that leverage the responsiveness of their localized surface plasmon resonance (LSPR) to electronic charging and discharging. In this talk, I'll focus on how we are applying this concept to develop electrochromic glass that can dynamically control heat loads and daylighting in buildings. We demonstrated that dual-band electrochromism (voltage control over near infrared and visible light transmittance independently) is achievable by embedding plasmonic ITO nanocrystals in a redox-active niobium oxide glass matrix. To develop a practical technology on the basis of this concept, the component materials and their mesoscale architecture can both be optimized so that we now can modulate a large fraction of incident solar radiation on demand. To enable low-cost manufacturing, we have recently developed low-temperature processing strategies and have now fabricated complete dynamic glass prototypes. The materials innovations needed to enable this progress will be emphasized.

6:20pm **NM-WeE3 Functionally Graded Nanocarbon-reinforced Metal Matrix Composite Materials***, **Hansang Kwon**, G.J. Park,* Pukyong National University, Republic of Korea*; S. Lim, J.H. Park,* Next Generation Materials Co., Ltd, Republic of Korea

Functionally graded nanocarbon particles reinforced aluminium (Al) matrix composites have been successfully fabricated by solid-state spark plasma sintering process [1]. The multiwalled-carbon-nanotubes (MWCNT) were used as a main reinforcement and the MWCNT were well dispersed in the Al particles using high energy ball milling process. Several different types of MWCNT were used in the same volume. The ball milled Al-MWCNT powder mixtures were fully densified and demonstrated good adhesion with no serious micro-cracks and pores within a multilayer composite. Each multilayer contained different amounts of the MWCNT, showed different microstructures and mechanical properties. It is possible to control the mechanical, thermal and electrical properties of the functionally graded multilayer composite through the efficient design of an MWCNT reinforced gradient layer.

[Reference]

[1] KWON, H., LEPAROUX, M. & KAWASAKI, A. 2014. Functionally Graded Dual-nanoparticulate-Reinforced Aluminum Matrix Bulk Materials Fabricated by Spark Plasma

6:40pm **NM-WeE4 Boron Nitride Nanotube-Titanium Alloy Nanocomposites***, **John-Andrew Hocker**,* NASA Langley Research Center, USA*; S-H. Chu, V. Yamakov,* National Institute of Aerospace, USA*; J. Newman, S. Messina, E. Judd,* NASA Langley Research Center, USA*; C. Rohmann, D. Bernhardt,* The University of Queensland, Australia*; C. Park, C. Fay,* NASA Langley Research Center, USA

Titanium alloys, such as Ti-6Al-4V, are used in aerospace applications that require light weight, high strength and corrosion resistance. Boron nitride nanotubes (BNNT) are a unique high strength, high aspect ratio, neutron absorbing nanomaterial with good thermal and chemical stability. Adding low density BNNT enables structural mass savings and may impart multifunctional capabilities such as the piezoelectric effect, and increased thermal conductivity. Recent theoretical studies indicate that BNNTs should exhibit a stronger interfacial binding with titanium than they do with aluminum or copper. Guided by those results, a series of nanocomposites was fabricated to experimentally investigate the reinforcing effect of BNNTs on the Ti-6Al-4V alloy. BNNT-Ti-6Al-4V nanocomposites were prepared by first consolidating the powder/BNNT blends at several loadings, 0.01 to 10 weight percent BNNT, in a circular die at elevated temperature and pressure. These consolidated specimens were then placed in a furnace and sintered under vacuum at ~1300°C. The resulting physical and mechanical properties of the metal matrix nanocomposites will be discussed, and compared with morphological results from X-ray diffraction, and optical, scanning electron, and scanning probe microscopies.

7:00pm **NM-WeE5 Fabrication and Applications of Nanocomposites Based on Anodic Aluminium Oxide***, **Jinghua Fang**,* University of Technology Sydney, Australia

Engineering a new class of nanocomposite-metamaterials can achieve ultra-sensitive sensors for bio-imaging, gas detection, air and food contamination control. This is critical to meet the global challenges of environmental conservation and efficient use of energy and mineral resources, especially for point-of-use applications. Using anodic aluminium oxide (AAO), here we report the fabrication of metamaterials with different metal nanostructures, we also investigate the applications of these fabricated metamaterials based on AAO templates.

7:40pm **NM-WeE7 Graphene-based Nanocomposite Hydrogels for Contaminant Removal***, **Nathalie Tufenkji**, N. Yousefi, K. Wong, A. Angulo,* McGill University, Canada

Due to its exceptionally high specific surface area and abundance of surface functional groups, graphene oxide (GO) is of great interest as a high performance sorbent for dyes, heavy metal ions, oils, toxins and organic solvents from contaminated waters. However, recovery of GO after the water treatment process is difficult due to its high stability in water. Thus, self-assembly of GO sheets into porous 3D macrostructures such as hydrogels has been explored as a technique to exploit their high surface area while facilitating easy recovery from treated water. Nonetheless, creating mechanically robust hydrogels with acceptable adsorption capacities is not straightforward. We report a simple method for preparation of ultra-strong nanocomposite GO hydrogels at low pressure using vitamin C as a natural cross-linker. The structure and chemical compositions of the hydrogels are examined using microscopy and spectroscopy techniques. We demonstrate that hydrogels with high storage moduli can be used to effectively remove model dyes such as methylene blue, heavy metal ions and emerging contaminants such as the pharmaceutical products diclofenac and sulfamethoxazole from aqueous solutions. We will describe the novel aspects of the hydrogel synthesis that give rise to its exceptional mechanical strength and adsorption capacity.

8:00pm **NM-WeE8 Towards Producing Bulk Monolithic Core/Shell Nanocomposites***, B.N. Feigelson, **James Wollmershauser**, K. Manandhar,* U.S. Naval Research Laboratory, USA

With designed bulk nanostructured solids, one could potentially combine properties that are mutually exclusive in a single bulk material, and, as a result, dramatically improve the desired performance. However, a major research challenge and roadblock is how to produce 3D nanostructured materials consistently with the required phases arranged in designated spatial order that are at the same time fully dense without porosity and detrimental phases. Known state-of-the-art techniques for producing bulk nanostructures cannot simultaneously meet all these requirements. As a result, the inherent properties of such bulk monolithic nanostructured materials are greatly unknown and unexplored.

We developed an Enhanced High Pressure Sintering (EHPS) process to consolidate oxide, metal, and semiconductor nanoparticles into 3-dimensional monolithic nanostructured materials. EHPS incorporates stringent environmental control and utilizes high pressures to break agglomerates while simultaneously exploiting the increased pristine surface potential of nanoparticles for surface-energy-driven densification without microstructural changes. Using this approach, monolithic nanocrystalline transparent ceramics with grain size bellow 30 nm are demonstrated. Such ceramics exhibit a 30% increase in hardness over a corresponding order of magnitude reduction in grain size and suggest that Hall-Petch type (strengthening via grain size reduction) relations exist in ceramics at least down to 30nm [1].

Core/shell nanoparticles offer fundamentally new means for nanostructured solids design and tailoring basic properties of these artificial materials. To provide flexibility in core/shell nanoparticles design, a particle atomic layer deposition (pALD) reactor was incorporated in the EHPS facility. The new setup allows to controlling environment during all stages of the nanoparticles processing, atomic layer deposition and sintering. Spinel/alumina core/shell nanoparticles were the first material system tested for producing the first core/shell ceramic nanocomposite. Alumina shell was grown on spinel nanoparticles, and then core/shell nanoparticles sintered under pressure without exposing to atmospheric air. The developed nanocomposite

ceramics demonstrated better hardness and fracture toughness than pure nanocrystalline spinel.

[1] Wollmershauser, J. A.; Feigelson, B. N.; Gorzkowski, E. P.; Ellis, C. T.; Goswami, R.; Qadri, S. B.; Tischler, J. G.; Kub, F. J.; Everett, R. K., *Acta Materialia*, 69 , 9-16 (2014).

8:20pm **NM-WeE9 Nanoscale Bioinspired Interfaces in Carbon Fibre Reinforced Polymer Composites***, **Bronwyn Fox**,* Swinburne University, Australia

Carbon fibre composites, where bundles of carbon fibres are embedded in a polymer matrix, offer enormous design flexibility due to the ability to tailor properties such as strength and modulus. They are used to lightweight aerospace and automotive structures and are seeing an exponential increase in demand with the global market predicted to grow to $36 billion by the year 2020. The Achilles heel of these materials lies in their ability to withstand damage from impact loads. Once damaged, the ultimate strength of the material is reduced via the formation of microcracks that lead to delamination failure. The microcracks are often found to originate at the interface between the fibre and the matrix, yet interfacial adhesion in composite materials is poorly understood and still hotly debated in the literature. The relative influence of fibre grade (standard, intermediate or high modulus), fibre surface roughness and chemistry in interfacial adhesion and therefore microcracking is required. This new knowledge will lead to the development of engineered interfaces in composites for improved performance. There are many examples of tailored interfaces in nature from which we can draw inspiration. Nacre (mother of pearl) is a natural high-performance composite comprising nanocrystals of CaCO3, aragonite, embedded in a multi-layered, multi-component soft organic matrix. The CaCO3 crystals do not bind directly to the organic chitin layer, but are separated by an intermediate protein layer. This intermediate phase creates a soft/soft/hard interface that can be likened to an engineered interphase in carbon fibre composites. Commercial carbon fibres are usually electrolytically oxidised and then coated with either an epoxy or a polyurethane sizing to protect the fibre during processing and to facilitate handling. The nature and presence of this sizing may influence the chemistry of the surrounding polymer matrix to create an interphase region. We have explored a range of strategies to tailor the fibre surface roughness and chemistry to ensure compatibility with the polymer matrix. The electrolytic treatment was systematically varied to ensure that the fibre surface was free of amorphous carbon debris, a range of chemical treatments were used including the attachment of small molecules to the fibre surfaces. Novel sizing systems and plasma polymer coatings have also been applied to the fibres. This paper will describe our recent results on the effect of a range of fibre treatments to improve interfacial performance in carbon fibre composites.

8:40pm **NM-WeE10 Photo-stability Enhancement of Colloidal CdSe/ZnS QDs Passivated in Al_2O_3 using Atomic Layer Deposition***, **Chih-Yi Cheng**, C.-H. Chen, M.-H. Mao,* National Taiwan University, Taiwan, Republic of China

Colloidal quantum dots (QDs) have many advantages, such as the tunability of emission wavelength during synthesis and easy integration.[1] However, they are very sensitive to environment conditions because of high surface to volume ratio. Photo-oxidation of QDs is one of the critical problems. It creates defect states and decreases the quantum yield.[2] Strong photo-degradation was observed even in the core/shell structure under laser excitation.[3] Recently we reported the method of passivating QDs in Al_2O_3 using atomic layer deposition (ALD) and systematically studied the time-resolved photoluminescence (PL) of QDs.[4] In this work, we took a further step to investigate the impact of laser excitation on QD PL intensity by applying the ON/OFF cycles (5 min each). One unpassivated and one passivated QDs samples were prepared with details described elsewhere.[4] The STEM image shows a clear single QDs layer uniformly passivated by an Al_2O_3 layer. Both samples were studied under a 532 nm continuous wave laser excitation with a power density of 407 kW/cm^2. The unpassivated QDs showed rapid PL degradation due to strong photo-oxidation. Moreover, the PL intensity did not recovery after OFF periods indicating an irreversible process. In contrast to the sever photo-degradation of the unpassivated QDs, the passivated QDs were found to remain stable. It is interesting that both samples show small PL recovery at the beginning of each ON period. This can be explained by photo-ionization of QDs. During the ON period, the electrons are ejected from QDs and form an electrostatic barrier which leads to PL intensity reduction due to Coulomb blockade.[5] The ionized QDs can be neutralized during the OFF period and then the PL intensity can be recovered to some extent. However, the PL recovery of unpassivated QDs is gradually reduced after several cycles because more and more QDs photo-oxidized. Since the passivated QDs didn't suffer from photo-oxidation, it shows similar amount of PL recovery in every ON period. In conclusion, we demonstrated the photo-stability enhancement of QDs by Al_2O_3 passivation using ALD technique. This method can provide good encapsulation of QDs and the application of this technique for other types of QDs, such as PbS, will be also presented in this study.

Reference:

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