Biomaterial Surfaces & Interfaces
Room Naupaka Salon 6-7 - Session BI-MoM

35 Years of NESAC/BIO I

Moderator: David Castner, University of Washington

8:00am **BI-MoM-1 Adventures in Biointerface Engineering Inspired by NESACBio – Combining and Integrating Techniques to Gain Insight into Biointerfaces (and Most Instruments Wins!)**, ***Sally L. McArthur,*** Swinburne Institute of Technology, Australia **INVITED**

Control and the ability to elicit specific responses from a biological system lies at the heart of most bioengineering. We want to immobilize proteins on biosensors but ask them to as sensitive as they are in solution or in the body, stimulate cells to assemble into tissues, reconstructing our bodily functions. We want methods that prevent bacteria forming biofilms and better still we would like them to stop bacteria attaching to surfaces full stop. But biology is soft and normally has lots of water associated with it, so how and why would you want to use vacuum based techniques to create coatings or characterise these systems?

This talk will explore how in my group and our collaborators, have tackled the challenges associated with interfacing vacuum deposited plasma polymers with water, proteins, lipids and cells to create a wide number of model systems and devices. At the same time, we have developed methods for chemically characterising these systems in vacuum, integrating XPS and ToF-SIMS with a range of other surface analytical and biological tools to gain insight into the materials we create and their interactions with biological systems.

8:40am **BI-MoM-3 ToF-SIMS Label Free Chemical Imaging of Surface Modifications in Materials with Extreme Topography**, ***Michael Taylor,*** *D Graham, L Gamble,* University of Washington

ToF-SIMS is uniquely suited towards high spatial resolution imaging of surface modifications in materials with structure. While imaging 2D “flat” surfaces is relatively simple, working with three-dimensional (3D) “rough” surfaces is challenging due to the topography. This topography interferes with the ability to extract spatio-chemical differences in the sample and results in image shadowing and decreased mass resolution. In 3D depth profiling, topography can cause differential etching as the sputtering beam can impact the surface at different heights and angles. In many cases the combination of these factors prevents acquiring high quality imaging data since features associated with surface chemistry can be obscured. Multivariate image analysis methods have been used to assess the impact of topography on ToF-SIMS data, and AFM has been applied for topographical correction. However, the former method only assesses the impact, while the latter is time consuming and does not mitigate the effects of surface topography entirely. We propose an alternate methodology for imaging topographic samples with ToF-SIMS, demonstrating that through a simple polymer embedding methodology, topographic materials, ill-suited for ToF-SIMS analysis can be transformed into surfaces where topographical effects are minimized and high spatial resolution label free imaging of chemical modifications can be performed in topographic materials[1]. Imaging surface modifications in the pores of biopolymer scaffolds will be presented, using a highly focused Bi_3^+ LMIG beam for analysis in 2D, and the addition of an Ar_{1500}^+ sputter beam for depth profiling the pore in 3D.

FC (fluorocarbon) modification of PCL pores will be imaged, showing FC film deposits in the scaffold pore, and its distribution can be imaged in 3D. Water plasma hydrolyzed PCL scaffolds, modified with bovine serum albumin (BSA) through EDC/NHS bioconjugation chemistry can similarly be imaged, unlocking label free imaging of protein fragments at the scaffold/pore interface. We will also show that lipid imaging is possible in this challenging material class, extracting information in 2 and 3D from the pores of lipid modified poly(2-hydroxyethyl methacrylate)-co-methacrylic acid scaffolds.

1 M. J. Taylor, H. Aitchison, M. J. Hawker, M. N. Mann, E. R. Fisher, D. J. Graham and L. J. Gamble, *Biointerphases*, 2018, **13**, 03B415.

9:00am **BI-MoM-4 NESAC/BIO IMPACT: Innovative Multivariate Programs Applied Carefully to ToF-SIMS**, ***Daniel Graham,*** *L Gamble, D Castner,* University of Washington

ToF-SIMS data is complicated. Even a single spectrum can contain hundreds if not thousands of peaks. Each peak corresponds to a unique element, fragment or molecule from the surface analyzed. The relative intensity of these peaks can encode information about the chemistry, structure and composition of the surface. With modern ToF-SIMS instrumentation it is straight forward to collect multiple spectra across multiple samples resulting in large, complex data sets. To further add to the scale of the data one can also produce 2D and 3D ToF-SIMS images which can consist of millions of spectra and fill gigabytes of storage space. Since 1992 NESAC/BIO has lead the way in developing innovative tools that enable digestion of this smorgasbord of ToF-SIMS data. This included some of the first papers published applying multivariate analysis (MVA) methods to ToF-SIMS data. This effort has lead to the creation of the NBToolbox which contains a set of advanced tools to process and display ToF-SIMS spectra and images. Though the ToF-SIMS community is relatively small, the NBToolbox has over 300 users across 39 countries on 6 continents. It is regularly used in research presented in publications and presentations around the world. In this presentation I will highlight the developments spearheaded through the years by NESAC/BIO in ToF-SIMS data processing from spectra to 3D imaging. Examples will be presented from the early beginnings of “simple” controlled systems to current work with complex tissue samples in 2D and 3D.

9:20am **BI-MoM-5 Challenges to Nanoparticle Preparation and Analysis: An Unexpected Phase Transformation of Ceria Nanoparticles**, ***Donald Baer,*** Pacific Northwest National Laboratory; *S Kuchibhatla,* Parisodhana Technologies Pvt. Ltd.; *A Karakoti,* Ahmedabad University; *S Seal,* University of Central Florida

Nanoparticles in a variety of forms continue to grow in importance for fundamental research, technological and medical applications, and environmental or toxicology studies. Physical and chemical attributes that lead to multiple types of particle instabilities complicate the ability to produce, appropriately characterize, and consistently deliver well-defined particles, frequently leading to inconsistencies, and conflicts in the published literature. In previous work examining 3-5 nm cerium oxide crystallites that had formed ~10 nm soft agglomerates in aqueous media we had observed chemical state changes (the ratio of Ce^{+3}/Ce^{+4}) and related optical absorption changes during particle formation and in response to environmental changes. The transformations have been further examined using micro-X-ray diffraction and Raman spectroscopy. We observed that in response to the environmental changes – adding H_2O_2 to the solution – these particles transformed from a ceria structure to an amorphous complex and returned to the crystalline phase upon solution aging. For comparison, 40 nm ceria nanoparticles were not observed to undergo this transformation and particles made up of crystallites of ~ 8 nm appeared to partially transform (or transform more slowly). We note that ceria nanoparticles of smaller size frequently have beneficial biological effects in comparison to the larger particles. The chemical state changes observed in ceria nanoparticles are usually assumed to be particle size dependent and to involve a change from cubic fluorite-type dioxide (CeO_2) to a hexagonal cerium sesquioxide (Ce_2O_3) with a continuous range of partially reduced CeO_{2-x} phases, where oxygen vacancies can be rapidly formed, arranged or eliminated. Our XRD and Raman data suggest that a much more complex transformation can occur for smaller ceria crystallites. Such changes were not readily identified by macroscopic *in situ* measurement such optical measurements or *ex situ* examination using TEM and XPS but were discovered by examination of ceria nanoparticles with molecularly and structurally sensitive methods with the particles in wet conditions (near *in situ*). Considering cerium oxide’s useful abilities to scavenge radicals, control the oxygen environment and provide regenerative oxidation state switching, it appears that the ease of ceria nanoparticles to transform between Ce^{4+} and Ce^{3+} rich phases is facilitated by small size, but is not constrained to be a transformation between defected and non-defected ceria phases.

9:40am **BI-MoM-6 A Calibration Procedure for a Traceable Contamination Analysis on Medical Devices by Combined X-ray Spectrometry and Ambient Spectroscopic Techniques**, ***Beatrix Pollakowski-Herrmann,*** *A Hornemann,* Physikalisch-Technische Bundesanstalt, Germany; *A Giovannozzi,* INRIM; *F Green,* National Physical Laboratory; *P Gunning,* Smith & Nephew; *C Portesi, A Rossi,* INRIM; *C Seim,* Physikalisch-Technische Bundesanstalt; *R Steven,* National Physical Laboratory; *B Tyler,* Westfälische Wilhelms-Universität Münster; *B Beckhoff,* Physikalisch-Technische Bundesanstalt

There is a strong need in the medical device industry to decrease failure rates of biomedical devices by reducing the incidence of defect structures and contaminants during the production process. The detection and identification of defect structures and contaminants is crucial for many industrial applications. The present study exploits reference-free X-ray fluorescence (XRF) analysis as an analytical tool for the traceable characterization of surface contaminants of medical devices, in particular

N,N’-ethylene-bis(stearamide), an ubiquitous compound used in many industrial applications as a release agent or friction reduction additive.

Reference-free XRF analysis as primary method has been proven to be capable of underpinning all other applied methods since it yields the absolute mass deposition of the selected N,N’-ethylene-bis (stearamide) contaminant whilst X-ray absorption fine structure analysis determines the chemical species. Ambient vibrational spectroscopy and mass spectroscopy methodologies such as Fourier transform infrared, Raman, and secondary ion mass spectroscopy have been used in this systematic procedure providing an extensive range of complementary analyses.

The calibration procedure was developed using specially designed and fabricated model systems varying in thickness and substrate material. Furthermore, typical real medical devices such as both a polyethylene hip liner and a silver-coated wound dressing have been contaminated and investigated by these diverse methods, enabling testing of this developed procedure. These well-characterized samples may be used as calibration standards for bench top instrumentation from the perspective of providing traceable analysis of biomaterials and surface treatments. These findings demonstrate the potential importance and usefulness of combining complementary methods for a better understanding of the relevant organic materials.

[1] B. Pollakowski-Herrmann, A. Hornemann, A. M. Giovannozzi, F. Green, P. Gunning, Ch. Portesi, A. Rossi, Ch. Seim, R. Steven, B. Tyler, B. Beckhoff, Journal of Pharmaceutical and Biomedical Analysis 150, 2018, 308–317.

10:20am **BI-MoM-8 Protein Catalysis of Minerals and Ice – A Molecular View*, Tobias Weidner,*** University of Arrhus, Denmark **INVITED**

Proteins can act as Nature’s engineers at interfaces and manipulate both hard and soft tissue – they can shape biominerals, manipulate cell membranes and control water. Despite the apparent importance for chemists working in the fields of biomineralization, surface engineering and drug delivery the molecular mechanisms behind interfacial protein action have largely remained elusive. We use static and time resolved sum frequency generation spectroscopy combined with computer simulations to determine the structure and the mode of action by which these proteins interact with and manipulate interfaces. Here, I discuss our recent advances in the study of protein driven nucleation.

Taking clues from Nature we aim at understanding biomineralization processes at the molecular level to develop design rules for biogenic nanophase materials. Especially the high fidelity control of nanostructured silica within diatoms has been the envy of material scientists for decades. Where diatoms can grow silica using proteins at cell interfaces under ambient conditions, we still need high pH and harsh conditions to structure silica. Despite the apparent importance for physicists and chemists working in the fields of biomineralization, surface engineering, drug delivery, or diagnostics, the molecular mechanisms behind interfacial silica protein action have remained largely elusive. Our goal is to probe the structure and structural dynamics of such active proteins – in action at the surface. As a first step we study the diatom silica peptide R5 when interacting with silica. We use methods based on theoretical and experimental sum frequency generation spectroscopy combined with computer simulations to determine the structure and the mode of action by which these proteins interact with and grow extended 2D silica interfaces.

A particularly fascinating example of protein driven nucleation and phase transitions are ice-nucleating proteins. These proteins are used by specific bacteria to attack plants and cause frost damage by growing ice crystals at temperatures that would otherwise not allow ice formation. A recent survey by the NASA found that biogenic ice nucleators in the troposphere may affect global precipitation patterns. We have followed the interaction of biogenic ice seeding proteins with surrounding water to gain a detailed picture of protein-driven ice nucleation.

11:00am **BI-MoM-10 Multi-Functional Polyampholyte Hydrogels with Covalently Attached SIBLING Proteins for Bone Tissue Engineering*, Matthew Bernards,*** *S Haag, E Mariner,* University of Idaho

In the ten years since leaving the NESAC/BIO, the Bernards group has focused on developing polyampholyte polymers for biomedical applications due to their unique multi-functional properties. Polyampholyte polymers resist nonspecific protein adsorption, while being able to covalently attach biomolecules. The physical properties (mechanical, degradation, etc.) of these polymers are also tunable by changing their underlying chemistry. Therefore, polyampholyte hydrogels represent a promising platform technology. In this presentation we will cover the development of these polymers for biomedical applications and present recent efforts to understand the degradation behavior of polyampholyte hydrogels as a function of chemistry, while also applying this platform technology for bone tissue engineering. Specifically a polyampholyte hydrogel composed of equimolar mixtures of [2-(acryloyloxy)ethyl] trimethylammonium chloride (TMA) and 2-carboxyethyl acrylate (CAA) is being pursued as a bone tissue scaffold. This hydrogel scaffold is being used as a delivery platform for individual members of the SIBLING (small integrin binding N-linked glycoprotein) family of proteins. SIBLING proteins are the primary non-collagenous proteins found in mineralized tissue and they all contain a cell binding RGD amino acid sequence, a collagen binding domain, and a hydroxyapatite binding domain. This family includes seven proteins or protein cleavage products. Following hydrogel synthesis, individual SIBLING proteins are conjugated to the hydrogel using EDC/NHS chemistry. The initial MC3T3-E1 osteoblast recruitment was investigated using 2-hour cell adhesion assays and the short-term response of the cells was investigated following 24 hours of culture. Hydrogels with conjugated osteopontin exhibited the highest cell recruitment after 2 hours, so polyampholyte hydrogels with conjugated OPN were also used in primary synoviocyte and primary bone marrow derived connective tissue progenitor cell studies. Characterizations with the primary cells include an evaluation of the initial stages of bone matrix production and cell differentiation. The results presented throughout this presentation demonstrate the promising potential for polyampholyte hydrogels in bone tissue engineering applications and beyond.

Nanomaterials
Room Naupaka Salon 5 - Session NM-MoM
Nanocharacterization

Moderator: Roya Maboudian, University of California at Berkeley

8:00am **NM-MoM-1 Identification of Point Defects in Transition Metal Dichalcogenides by Combining Atomic Resolution Force Microscopy, STM/STS and Density Functional Theory: Missing Vacancies in $MoSe_2$ and WS_2*, Frank Ogletree,*** Lawrence Berkeley National Laboratory*; S Barja,* UPV/EHU-CISC Ikerbasque, Spain*; S Refaely-Abramson,* University of California Berkeley*; B Schuler,* Lawrence Berkeley National Laboratory*; D Qiu,* University of California Berkeley*; S Wickenberg,* Lawrence Berkeley Laboratory*; J Neaton, A Weber-Bargioni,* Lawrence Berkeley National Laboratory

Point defects can strongly influence material properties of 2D materials including Transition Metal Dichalcogenides (TMDs), where they can modify optical and transport properties, catalytic activity, and act as single photon emitters. It has been difficult to directly correlate specific defects with macroscopic measurements of TMD optical and transport properties. Scanning transmission electron microscopy (STEM) investigations have provided significant structural information, but STEM cannot directly probe electronic structure . In addition radiation damage is a significant problem for TMDs, making it difficult to determine intrinsic defect concentrations [1].

Here we report on the first applications of atomic resolution AFM to TMD point defects [2,3]. Cryogenic AFM/STM/STS studies using a CO molecule tip, when combined with advanced density functional excited-state theory, provide sufficient information for detailed point defect characterization. The experimental methods can resolve:

- defect location through AFM, including local strain with ~ 30 pm lateral and 3 pm vertical resolution. This is difficult to do with STM alone due to the strong convolution of geometric and electronic structure [4]
- electronic structure, through scanning tunneling spectroscopy (STS), which identifies localized resonances and in-gap states, and STM spatial maps of localized states and orbitals
- charge state, through Kelvin-probe AFM and STS charging peaks
- radial and reflection symmetry breaking, for example defects in the chalcogen plane appear very different in AFM if located on the upper or lower TMD surface, while the STS maps and spectra are similar. Defects localized in the metal plane have one AFM signature for a given STS structure.

The detailed information from scanning probe studies strongly constrains geometric structural models for theoretical simulations, and the results of these simulations can be directly compared to STS maps and local spectra, allowing detailed understanding of defects.

We will report on studies on MBE-grown MoSe$_2$ and CVD-grown WS$_2$. Based on STEM studies, chalcogen vacancies have been identified as the most common point defects, and have been predicted to have in-gap states. While our AFM/STM studies show chalcogen site defects whose AFM contrast is consistent with Se or S vacancies, they do not show any electronic in-gap states. In combination with theory, we identify these sites as substituted oxygen, which has very low STEM contrast.

[1] Wang, Robertson, Warner, *Chem Soc Rev* 2018.

[2] Barja, Refaely-Abramson, Schuler, Qiu et al, submitted.

[3] Schuler, Kastl, Chen et al, submitted.

[4] Barja et al, *Nature Physics* 2015.

8:20am **NM-MoM-2 CO-tip AFM Identification and STM-induced Luminescence of Point Defects in Monolayer WS$_2$*, Bruno Schuler,*** Lawrence Berkeley National Laboratory*; D Qiu,* University of California Berkeley*; S Rafaely-Abramson, C Kastl, K Cochrane,* Lawrence Berkeley National Laboratory*; S Barja,* Lawrence Berkeley Lab, USA, Spain*; C Chen, N Borys, R Koch, F Ogletree, S Aloni, A Schwartzberg,* Lawrence Berkeley National Laboratory*; S Louie,* University of California Berkeley*; J Neaton, A Weber-Bargioni,* Lawrence Berkeley National Laboratory

The advent of transition metal dichalcogenides (TMDs) and other two-dimensional (2D) materials has attracted considerable attention due to unique material properties emerging from their reduced dimensionality. Because of this strong confinement, structural defects greatly modify such properties and have therefore become of increasing interest to the 2D materials community. Particularly the creation of in-gap defect states is decisive for their optoelectronic properties and catalytic activity.

Using low-temperature scanning probe microscopy with CO functionalized tips we identified and characterized common point defects in monolayer WS$_2$ (see Fig. 1).

Contrary to previous reports, we suggest that the most abundant defect is an O substitution at a S site, not a S vacancy, with a distinctively different electronic structure.

In contrast to O decorated S vacancies, a W substitutional defect and pristine S vacancies create distinct defect states within the band gap of WS$_2$. Interestingly, both types of point defects exhibit spin-orbit split defect states with a large splitting of 80 meV and 280 meV, respectively. Moreover, these defects exhibit electron-induced luminescence with a characteristic bias dependence. Spectrally integrated luminescence maps resemble the defect orbitals.

The same sample was also characterized with nano-ARPES and photoluminescence spectroscopy, which shows that thermally grown graphene on SiC constitutes a suitable platform for cross-correlation microscopy of TMD materials (and potentially other van der Waals materials) in both, UHV and ambient conditions.

The atomic-scale characterization allows an unprecedentedly detailed picture on the structure and functionality of point defects in 2D-TMDs.

8:40am **NM-MoM-3 Intermolecular and Molecule-Substrate Interactions in Surface-Supported Nanostructures Characterized by Ultrahigh Vacuum Tip-Enhanced Raman Spectroscopy***, J Schultz, P Whiteman, S Mahapatra,* ***Nan Jiang,*** University of Illinois at Chicago

In order to fully characterize molecular assemblies at the single molecular scale, advanced analytical surface techniques have to be employed. We carried out scanning tunneling microscopy (STM) experiments on two molecules (N-N'-bis(2,6-diisopropylphenyl)-perylene-3,4:9,10-bis(dicarboximide) (PDI) and subphthalocyanine (SubPc)), which are both self-assembled on noble metal substrates. The STM experiments were complemented by tip-enhanced Raman spectroscopy (TERS), surface-enhanced Raman spectroscopy (SERS) and density functional theory (DFT) calculations. In particular, we have interrogated the lifting of an accidental vibrational degeneracy of a mode of PDI on Ag(111) and Ag(100) surfaces, with the most strongly perturbed mode being that associated with the largest vibrational amplitude on the periphery of the molecule. In the other hand, the alignment between expeimental TERS of SubPc on surface and DFT calculated Raman spectrum of gas phase SubPc was quite good, which indicates that the interaction between SubPc molecules in the monlolayer is very weak. New two-dimensional molecular superstructures were discovered to consist of several distinct molecular binding configurations. Both TERS and SERS experiments of SubPc yielded nearly identical vibrational spectra for both binding configurations, consistent with their small adsorption energies (<0.2 eV) as calculated by DFT. Our results demonstrate the necessity of advanced Raman techniques such as TERS when precisely probing molecule-molecule and molecule-substrate interactions.

9:00am **NM-MoM-4 Quantifying the Thermodynamics of Ligand Binding to CsPbBr$_3$ Quantum Dots via Solution ^{1}H NMR Characterization***,* ***Sara Smock****, R Brutchey,* University of Southern California

The characterization of surface ligand binding to quantum dots is important to fully understand their behavior, such as photoluminescence quantum yield. One of the most promising recent classes of quantum dot materials is the CsPbX$_3$ halide perovskites (where X = Cl^-, Br^-, I^-) because of their growing applications in LEDs, X-ray detectors, and lasers. These CsPbX$_3$ quantum dots possess bright photoluminescence and narrow emission line widths over a wide color gamut. Using the hot-injection synthesis first reported by Protesescu et al. (*Nano Lett.***2015**, *15*, 3692), the ligand shell supporting the resulting CsPbBr$_3$ quantum dots has been reported to be highly dynamic and primarily comprised of oleylammonium bromide binding to the surface in an NC(X)$_2$ fashion without accompanying oleate X-type coordination. To date, however, the characterization of ligand binding has been qualitative in nature. Herein, we will report on quantifying the thermodynamics of *n*-alkyl carboxylic acid and amine ligand binding to CsPbBr$_3$ quantum dots via ^{1}H NMR spectroscopy. ^{1}H NMR is a powerful characterization tool for organic ligands on the surfaces of nanocrystals to observe ligand binding and gain insight into the thermodynamics of ligand exchange processes. In agreement with previous studies, we find the supporting ligands to be fluxional in nature; however, both ammonium and carboxylate binding to the purified nanocrystal surface is unequivocally observed. *n*-Alkyl carboxylic acids undergo an exergonic exchange equilibrium with bound oleate (K_{eq} = 1.97) at 25 ˚C, while *n*-alkyl phosphonic acids undergo an irreversible ligand exchange. *n*-Alkyl amines exergonically exchange with oleylamine (K_{eq} = 2.52) at 25 ˚C. Exchange occurs with carboxylic acids, phosphonic acids, and amines on CsPbBr$_3$ quantum dots without etching the nanocrystal surface; increases in steady-state PL intensities are correlated with more strongly bound conjugate base ligands.

9:20am **NM-MoM-5 Nanomaterials for Creating Sensitive and Selective Biosensing Interfaces***,* ***Leyla Soleymani,*** McMaster University, Canada **INVITED**

Biosensors bring together biorecognition and signal transduction to analyze biologically relevant targets. The performance metrics of biosensors, such as limit-of-detection and speed, are strongly influenced by their structure. Designing material architectures that increase the sensor sensitivity, decrease background signals, and reduce analysis time is critical for entering biosensors into clinical decision making and health monitoring. Through this work, we have developed strategies for creating three-dimensional electrodes, combining them with biorecognition and self-cleaning interfaces, and translating biorecognition into electrochemical signals.

Porous and wrinkled hierarchical electrodes are created through self-assembly, electroless deposition, and bulking enabled by shape memory polymer substrates. Biorecognition is achieved by combining functionalized electrodes with molecular machines created using DNA nanotechnology. Self-cleaning is achieved using strategies that transform electrodes to omniphobic surface. Signal transduction is performed by electrochemical and photoelectrochemical readout using photo-active electrodes.

Three-dimensional electrodes, biorecognition elements, and signal transduction components are integrated into microfluidic networks for sensing small molecules, nucleic acids, and proteins. This integrated biosensing platform is used for analyzing clinical samples, and a test with a clinically-relevant limit-of-detection is achieved for diagnosing endometriosis.

10:20am **NM-MoM-8 Effects of Defects on Band Structure and Excitons in WS2 Revealed by Nanoscale Photoemission Spectroscopy***,* ***Adam Schwartzberg****, C Kastl, S Aloni, A Weber-Bargioni, C Chen,* Lawrence Berkeley National Laboratory

Two-dimensional materials with engineered composition and structure will provide designer materials beyond conventional semiconductors. However, the potentials of defect engineering remain largely untapped, because it hinges on a precise understanding of electronic structure and excitonic properties, which are yet not predictable by theory alone. Here, we introduce correlative, nanoscale photoemission spectroscopy to visualize how the local introduction of defects modifies electronic and excitonic properties of two-dimensional materials at the nanoscale. As a model system, we study chemical vapor deposition grown monolayer WS2, a prototypical, direct gap, two-dimensional semiconductor. By cross-correlating nanoscale angle resolved photoemission spectroscopy, core level spectroscopy and photoluminescence, we unravel how local variations in defect density influence electronic structure, lateral band alignment and excitonic phenomena in synthetic WS2 monolayers. Our results not only provide a unified picture of nanoscale heterogeneity, but they also open up the possibility to precisely understand and tailor lateral heterointerfaces in such two-dimensional materials.

10:40am **NM-MoM-9 4D Nanocharacterization by Spectro-ptychography Tomography of Alumina Aerogels Coated with Zinc Oxide by Atomic Layer Deposition**, ***Adam Hitchcock***, *J Wu, X Zhu,* McMaster University, Canada; *D Shapiro,* Lawrence Berkeley National Laboratory; *J Lee, M Biener, S Gammon, T Li, T Baumann,* Lawrence Livermore National Laboratory

Highly porous materials with nanoscale functional coatings are of increasing technological interest in the areas of energy conversion and storage, catalysis, and sensing [1,2]. 3D nanocharacterization with explicit chemical speciation capability is important for their optimization. Here the new method of soft X-ray spectro-ptycho-tomography [3] is used to characterize Al_2O_3 aerogel samples coated with ZnO by atomic layer deposition (ALD). 4D imaging (chemical mapping in 3D by spectro-tomography) of an Al_2O_3 aerogel coated with ZnO by atomic layer deposition (ALD) was performed using both scanning transmission X-ray microscopy (STXM) and ptychography [4]. 2D and 3D spatial resolution was significantly increased by ptychography, relative to STXM. A 2D spatial resolution of 14 nm was achieved with ptychography while the spatial resolution of the 2D STXM maps was only 24 nm. The degree of ZnO coverage of the surface of the Al_2O_3 aerogel framework in 3 different samples was estimated and compared to the ALD targets. Quantitative analysis showed that the ZnO ALD coatings are non uniform. Comparisons are made to Electron microscopy imaging and X-ray fluorescence analysis results were performed, confirming the results. Other analyses of the 4D results, including 3D thickness distributions of each species and measurements of the degree of contact between Al_2O_3 and ZnO, were extracted from the reconstructed 3D data. Together the results provide useful feedback for optimization of the nanostructure of ALD coated alumina aerogels.

STXM performed using BL10ID1 at CLS and BL 5.3.2.2 at ALS . Ptychography performed using BL 11.0.2 and 5.3.2.1 at the ALS . Research supported by NSERC and the Department of Energy, Basic Energy Sciences under contracts DE-AC02-05CH11231 and DE-AC52-07NA27344. CLS is supported by the Canada Foundation for Innovation.

References

[1] J. Biener *et al.*, *Energy Environ. Sci.* **4** (2011) 656.

[2] M.M Biener *et al.*, *ACS Appl. Mater. Interfaces* **5** (2013) 13129.

[3] Y. Yu *et al.*, *Nature Communications* **9** (2018) 921.

[4] A.P. Hitchcock, *J. Electron Spectrosc. Rel. Phenom.* **200** (2015) 49.

Plenary Session
Room Naupaka Salons 4 - Session PL-MoM
Plenary Session I

Moderator: Alberto Herrera Gomez, CINVESTAV-Unidad Queretaro, Mexico

11:20am **PL-MoM-11 A Review of Defects in 2D Metal Dichalcogenides: Doping, Alloys, Interfaces, Vacancies and Their Effects in Catalysis & Optical Emission**, ***Mauricio Terrones***, Pennsylvania State University**INVITED**

Two-dimensional transition metal dichalcogenides (TMDs) such as MoS2 and WS2 hold great promise for many novel applications. Recent years have therefore witnessed tremendous efforts on large scale manufacturing of these 2D crystals. A long-standing puzzle in the field is the effect of different types of defects in their electronic, magnetic, catalytic and optical properties. In this presentation an overview of different defects in transmission metal di-chalcogenides (TMDs) will be presented [1,2]. We will first focus on: 1) defining the dimensionalities and atomic structures of defects; 2) pathways to generating structural defects during and after synthesis and, 3) the effects of having defects on the physico-chemical properties and applications. We will also emphasize doping and allowing monolayers of MoS2 and WS2, and their implications in electronic and thermal transport. We will also describe the catalytic effects of edges, vacancies and local strain observed in MoxW(1-x)S2 monolayers by correlating the hydrogen evolution reaction (HER) with aberration corrected scanning transmission electron microscopy (AC-HRSTEM) [3]. Our findings demonstrates that it is now possible to use chalcogenide layers for the fabrication of more effective catalytic substrates, however, defect control is required to tailor their performance. By studying photoluminescence spectra, atomic structure imaging, and band structure calculations, we also demonstrate that the most dominating synthetic defect—sulfur monovacancies in TMDs, is responsible for a new low temperature excitonic transition peak in photoluminescence 300 meV away from the neutral exciton emission [4]. We further show that these neutral excitons bind to sulfur mono-vacancies at low temperature, and the recombination of bound excitons provides a unique spectroscopic signature of sulfur mono-vacancies [4]. However, at room temperature, this unique spectroscopic signature completely disappears due to thermal dissociation of bound excitons [4]. Finally, hetero-interfaces in TMDs, will be studied and discussed by AC-HRSTEM and optical emission.

References:

[1] Z. Lin, M. Terrones, et al. “Defect engineering of two-dimensional transition metal dichalcogenides”. 2D Materials 3 (2016) 022002.

[2] R. Lv, M. Terrones, et al. "Two-dimensional transition metal dichalcogenides: Clusters, ribbons, sheets and more". Nano Today 10 (2015) 559-592.

[3] Y. Lei, M. Terrones, et al. "Low temperature synthesis of heterostructures of transition metal dichalcogenide alloys (WxMo1-xS2) and graphene with superior catalytic performance for hydrogen evolution". ACS Nano, 11 (2017), 5103-5112.

[4] V. Carozo, M. Terrones, et al. “Optical identification of sulfur vacancies: Bound excitons at the edges of monolayer tungsten disulfide”, Sci. Adv. 3 (2017), e1602813

Thin Films
Room Naupaka Salons 4 - Session TF-MoM
Nanostructured Surfaces and Thin Films: Synthesis and Characterization I

Moderator: Toshiyuki Taniuchi, The University of Tokyo

8:00am **TF-MoM-1 Characteristics of ZrO_2 Films Atomic-Layer-Deposited Using $Cp-Zr(NMe_2)_3$: Effects of Oxidant and Deposition Temperature**, ***Wan Oh***, *W Lee, S Choi, Y An, C Lee, S Wi, H Kim,* Sungkyunkwan University, Republic of Korea

The ZrO_2 thin films have been actively used as a dielectric material in various nanoelectronic devices, such as transistors and memories. In achieving excellent electrical performance, uniformity, and step coverage, atomic layer deposition (ALD) is the most perfect method. Consequently, development of the ALD ZrO_2 process itself as well as dielectric engineering (nanolaminating or alloying with other dielectrics) have been largely researched to lower the leakage current while taking advantage of its relatively high dielectric constant [1].

In this study, the ALD ZrO_2 thin films were deposited using $Cp-Zr(NMe_2)_3$ as a Zr precursor, and the effects of oxidant (H_2O, O_3) and deposition temperature (200-300°C) on their electrical properties were systematically studied. Metal-insulator-metal capacitors were fabricated and their electrical properties, such as capacitance and leakage current, were evaluated. In addition, the physical properties of the ZrO_2 thin films were compared by examining them using transmission electron microscopy, atomic force microscopy, and X-ray diffractometry. Lastly, the ALD ZrO_2 films were applied to a stacked structure of $ZrO_2/Al_2O_3/ZrO_2$, which has been popularly used in memory devices and their electrical properties were evaluated.

[1] D. Panda and T.-Y. Tseng, Thin Solid Films 531, 1 (2013).

8:20am **TF-MoM-2 Enantioselective Catalyst on Oxide Support: Study of the Chemical Nature of Tartaric Acid on Rutile $TiO_2(110)$ by XPS and HREELS**, ***Gregory Cabailh***, *E Meriggio,* Sorbonne Université, France; *R Lazzari,* CNRS, France; *C Méthivier,* Sorbonne Universitévier, France; *V Humblot, X Carrier,* Sorbonne Université, France

1. Objectives :

Chiral molecules play a vital role in the biochemistry of living organisms, justifying the essential challenge of controlling enantioselectivity in several fields such as the pharmaceutical and agrochemical industry. Heterogeneous asymmetric catalysis for the synthesis of enantiopure chiral compounds is a tool of choice for its many economic and ecological benefits. Several techniques have been developed, including the modification of a metal surface by an organic chiral inducer. Nevertheless, the number of systems developed successfully remains limited. Unlike monocrystalline metal surfaces, very little is known on the role of the oxide support in catalysts based on supported metallic nanoparticles. The control of the role of the oxide support and the chiral inducer is based on the knowledge of the interactions at the molecular level between the three parties involved in the reaction: the oxide, the metal nanoparticles and the chiral inducer, represented in this work by TiO_2 single crystals, nickel nanoparticles (NPs) and tartaric acid (TA). A model approach is used here, where TA molecules and NPs are deposited by evaporation in an ultra-vacuum environment and then characterized by surface analysis techniques.

2. Results :

The chemical state of TA is characterized by X-ray Photoemission Spectroscopy (XPS) and High Resolution Electron Energy Loss Spectroscopy (HREELS). TA is first deposited on single crystals of Cu (110) and Au (111), on which the chemical nature of TA is well known, in order to obtain reference XPS spectra. By analyzing the C 1s and O 1s spectra, the presence of monotartrate adsorbed species (COO- / COOH) is demonstrated on copper, while the molecules are in the bi-acid form (COOH / COOH) on gold. The comparison of these results with the data recorded on rutile TiO_2(110) (in particular the energy differences between the C1s peaks) and complementary HREELS measurements allow to conclude that TA is absorbed as monotartrate on TiO_2 in analogy with other carboxylic acids. In addition, the organization and the nucleation point on the surface can be observed by scanning tunneling microscopy (STM). TA is finally deposited on the Ni / TiO_2system at different coverage rates and studied by XPS and STM to characterize the interaction between the three parties of the system.

8:40am **TF-MoM-3 The Study on Flash Light Sintering Characteristics of Printed Copper Pattern Electrodes with Respect to their Width and Interval**, ***Yong-Rae Jang***, *H Kim, C Ryu, Y Hwang,* Hanyang University, Seoul, Korea

In this work, copper nano/micro-ink screen-printed on a polyimide (PI) substrate, were sintered by flash light irradiation. To find out the effects of the pattern width and interval between copper patterns on the flash light sintering characteristics, analytical thermal transfer simulation was conducted by finite difference method, where the temperature of the substrate and electrodes during the flash light irradiation could be predicted. The copper nano/micro-ink was printed with different widths and intervals and sintered via flash light. The flash white light irradiation conditions such as pulse duration, frequency, and number of pulses were optimized on each pattern sizes. To investigate the macrostructure of the copper pattern, optical microscope and alpha step were used. The microstructures of the copper pattern were observed using scanning electron microscope (SEM). Also, in-situ resistance monitoring was conducted to find the tendency of the sintering characteristics according to the Cu printed pattern. From the study, it was confirmed that the heat generated in the copper pattern by flash light irradiation, was dramatically increased as the pattern width becomes wider and the pattern interval becomes narrower. It is noticeable that the flash light irradiation condition should be designed considering the size of the pattern due to pattern dependent heat transfer phenomena.

9:00am **TF-MoM-4 High Throughput XPS Surface Analysis of Novel Materials Generated by a Combinatorial Approach**, *J Counsell, S Coultas,* Kratos Analytical Ltd., UK; ***David Surman***, *C Moffitt,* Kratos Analytical Inc.

Combinatorial approaches have been widely used to discover new material phases for many years, allowing rapid exploration of composition–structure properties in complex material systems[1]. The mapping of chemical properties such as oxidation state and alloying as a function of composition is an integral part of understanding the underlying physical and chemical properties. Here we apply combinatorial techniques for preparation of model systems to be characterised by X-ray photoelectron spectroscopy (XPS). Two diverse sample sets have been characterised by high throughput XPS - ternary alloy formation post thin-film deposition and polymer microarrays for biomaterial screening.

Ternary metal compounds are used in a wide range of applications; as high-performance alloy materials and electronic semiconductors. We have examined a range of thin-films of first-row transition metals co-deposited on Si wafers to form a matrix of ternary alloys. The surface composition was analysed with XPS to determine the stoichiometric mixing for different alloy compositions and the extent of oxidation and chemical bond formation during deposition. Further analysis of large datasets allows the user to determine areas of particular interest and performance for further investigation – leading to more detailed bulk/surface comparison studies by destructive and non-destructive depth profiling techniques.

Combinatorial methods are also exploited for screening of functional biomaterials. The surface composition of a series of printed polymer microarrays are analysed with XPS to correlate differences in surface chemistry with specific biological performance. This high throughput method allows for library databases to be created for parallel screening of a wide range of polymer blends.

Workflow and data-handling will be discussed for the two different systems. Data visualisation through XPS processing is also described for large datasets generated during these analyses.

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9:20am **TF-MoM-5 Semiconductor Nanowire Y-Junction Arrays Grown by MBE**, ***Esteban Cruz-Hernandez,*** CIACYT, Universidad Autonoma de San Luis Potosi, Mexico **INVITED**

Energetically unstable crystalline surfaces, among their uses, can be templates for the self-assembling of semiconductor structures at the nanometric level. Highly uniform structures such as quantum wires can now be fabricated from the self-assembly of nanometric facet arrays produced by using high-index substrates and epitaxial techniques such as Molecular Beam Epitaxy (MBE) [1]. However, the self-assembling of more complex nanostructures such as Y-junctions (produced by the union of two semiconductor nanowires) is a more complex problem. In MBE the growth process is carried out under non-equilibrium conditions, then the nonlinear evolution processes (such as step-bunching, meandering instabilities, and coarsening) that produce a very rich variety of surface morphologies have to be understood to precisely control the self-assembly of such complex nanostructures.

The control on the assembly of semiconductor Y-junctions could have great potential in technological applications (for example, in nanoelectronics as quantum logic gates) and one-dimensional physics exploration. Until very recently, related works on nanometric Y-junctions have been based on carbon nanotubes and graphene [2, 3], but not with semiconductor crystalline materials. In this contribution we report on the high-order and two-dimensional mechanisms in the MBE growth of GaAs on high-index GaAs substrates, which allow the formation of a regular alternating pattern of bifurcated nanowires [4] with suitable dimensions to form a Y-junction electron gas device.

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10:20am **TF-MoM-8 Controllable Bandgap Design in (2+1) D Colloidal Photonic Crystals**, ***Lijing Zhang,*** Dalian University of Technology, China

Photonic crystals (PCs) are artificial periodic dielectric materials with the characteristic of photonic bandgap (PBG), which can control the behavior of photons in a similar manner as what semiconductors do for electrons. (2+1) D photonic crystals, as a novel photonic crystal structure, possess unique advantages in both structural tenability (control in single layer level) and optical property (PBG broadening and deepening) compared with traditional 1D, 2D and 3D photonic crystals. However, the fabrication of high quality (2+1) D photonic crystals is still a big challenge, which greatly limit the systematic study on its optical property. Here we present a simple strategy to achieve (2+1) D photonic crystal with enhanced crystalline integrity by layer-by-layer deposition of annealed colloidal crystal monolayers. By simply manipulating the diameter of PS spheres, arrangement type and repetition period of the colloidal monolayers, flexible control in structure and stopband position of the (2+1) D photonic crystals (including superlattice and heterostructure) have been realized. The optical properties of the resulting (2+1) D PCs with different lattice constants were systematically studied and a universal photonic stopband variation rule was proposed, which makes it possible to program any kind of stopband structure as required. The superlattice structure exhibits fine control in PBG position and obvious PBG resonance enhancement. While dual- or multi-stopbands and ultra-wide stopband can be achieved by fabricating heterostructures. This work may afford new opportunities for delicate engineering photonic bandgap materials. Furthermore, we explored their fluorescence (FL) enhancement ability based on their special bandgap effect and demonstrate their application in heavy metal ion detection. A multiple heterostructure photonic crystal (MHPC) with super-wide stopband improved the limit of detection of Cr(VI) to 0.2ppb. and may find significant applications for augmenting FL intensity in chemical and biochemical sensing, imaging, disease diagnosis, and environmental monitoring.

10:40am **TF-MoM-9 Effects of Interface on Proton Ordering in Heteroepitaxially Grown Ice Films***, **Toshiki Sugimoto,*** Institute for Molecular Science, Japan **INVITED**

Materials with a strongly correlated and highly frustrated degree of freedom have potential for exhibiting dramatic and unusual responses to external stimuli. In the case of common water ice, p rotons in the hydrogen-bond network are strongly correlated and highly frustrated under th e Bernal-Fowler-Pauling ice rules. The ubiquity of water ice makes it essential to clarify the fundamental physicochemical properties of the strongly correlated many-body proton system. It is, however, extremely difficult to directly access the local configuration of protons and their ordering dynamics through traditional experimental approaches. Moreover, the strongly correlated protons inevitably lose ergodicity at low temperature. These problems prevent us from fully understanding cooperative thermodynamic and electric responses of the many-body protons to external stimuli at the low temperature.

To open up a new route to unveil hidden exotic properties of many-body protons in ice, we have investigated a possibility of interface - induced ferroelectric proton ordering by focusing on heteroepitaxially grown crystalline-ice films on metal substrates as model systems [1-3]. We have used recently developed phase-resolved sum-frequency generation (SFG) vibrational spectroscopy in an ultrahigh vacuum chamber [4]. The Im $\chi^{(2)}$ SFG vibrational spectra ($\chi^{(2)}$: the second-order nonlinear susceptibility) exhibits positive and negative sign for OH oscillators with H-up and H-down orientation, respectively. Thus, heterodyne-detected SFG has a great advantage to directly observing local configuration of protons that cannot be investigated by other traditional experimental methods.

Recently, we have demonstrated that the adsorbed first-layer water molecules prefer an net-H-down configuration on model platinum substrate: Pt(111) [1,3] . The coverage dependence of the Im $\chi^{(2)}$ SFG spectra in the hydrogen-bonded OH stretching region s clearly reveals that the H-down proton ordering in the first layer is significantly pinned by the Pt(111) substrate and is subsequently propagated to the overlayer during the multilayer film growth . Temperature dependent SFG measurement revealed that s uch a ferroelectric proton ordering is t hermodynamically stable and has a n extremely high critical temperature of ~ 1 75 K [1,3] , which is more than twice as large as that of ferroelectric bulk ice XI (T_c ~ 72 K). In addition to these results, I will discuss our recent challenges on the interface engineering for modulation of the ferroelectric proton ordering.

[1] *Nature Phys.***12**,1063(2016);[2,3] *Phys.Rev.B* **96**,115405(2017); **97**,075410 (2018); [4] *Phys.Rev.Lett.***117**,186101(2016).

Energy Harvesting & Storage
Room Naupaka Salon 6-7 - Session EH-MoE

Process

Moderator: Paul Dastoor, University of Newcastle, Australia

5:40pm **EH-MoE-1 Surface Engineered Smart Optical Nanostructures for Energy Saving and Thermal Control***, **Ludvik Martinu,*** Montreal Ecole Polytechnique, Canada **INVITED**

Optical coating (OC) applications represent a multibillion dollar market worldwide; they range from antireflective (AR) coatings found in most optical components and low emissivity windows in buildings and automobiles to narrowband optical interference filters used in telecommunications. As the range of applications of OCs continuously broadens and extremely attractive market opportunities arise, it is becoming increasingly important to develop new nanostructured thin film materials with specific multifunctional properties. Further progress in this fast evolving field is strongly stimulated by a simultaneous action of two forces: a) the "pulling force" represented by the economic, technological and societal needs, including sustainable development, and b) the "pushing force" related to the curiosity-driven nanotechnology combining new design concepts of materials and devices, fabrication processes and innovative characterization tools, where the only limitation frequently appears to be our imagination.

This presentation will describe a holistic approach to OCs based on a broad and in depth knowledge of the interplay between the design, material, process and performance with respect to specific applications and coating system durability. It will review the progress and future opportunities for the use of nanostructurally-controlled architectures, advanced deposition techniques including high power impulse magnetron sputtering (HiPIMS), atomic layer deposition (ALD), glancing angle deposition (GLAD) and tailored plasma- and ion-surface interactions, as well as complex systems implementing active (smart, tunable thermochromic and electrochromic) materials.

These trends will be illustrated by examples from the field of advanced glazings for energy saving using smart windows, and smart radiators with self-tuned emissivity for the thermal management in satellites

6:20pm **EH-MoE-3 Carbon Capture by Metal Oxides: Unleashing the Potential of the (111) Facet***, **Ryan Richards,*** Colorado School of Mines, USA*; S Shulda,* National Renewable Energy Laboratory, USA*; G Mutch,* Newcastle University*; J Anderson, D Vega-Maza,* University of Aberdeen

Carbon capture, utilisation and storage is a portfolio of processes to combat climate change. The capacity of sorbents proposed for low temperature carbon capture is entirely limited to surface interaction, resulting in a race to produce ever increasing surface areas - exemplified by metal-organic frameworks.

Metal oxides have a diverse range of electronic and physical properties that make them useful for a variety of applications such as semiconductors in diodes, electro- and thermo-chromics, catalysis and Li ion batteries --to name a few. One of the simplest structures of metal oxides is the rock-salt structure that are face-centered cubic crystals with the metal ion surrounded by six nearest-neighbor oxygen ions and vice versa. Amongst the rock-salt metal oxides, MgO is the most widely studied and is the second most abundant compound in the Earth's crust at 35% (behind silica which is 42%). [1] Due to surface area reduction by sintering, solid metal oxides generally exhibit reduced adsorption capacity for carbon capture following high temperature exposure.

The preponderance of literature studies involving the properties of metal oxides has been conducted on the (100) surface because this surface is the most readily obtained and most thermodynamically stable form for most rock-salt metal oxides. The (100) surface is a checkerboard of alternating metal cations and oxygen anions. While most methods produce materials dominated by (100) surfaces, decomposition of metal hydroxides such as $Mg(OH)_2$can initially yield materials with hydroxylated (111) surfaces via topotactic dehydration. [1-3] Following the development of techniques that allow for the deliberate preparation of materials with primarily (110) and (111) surfaces, came interest in potentially new properties of these surfaces. [4, 5]

The (111) facet of MgO however, exhibits a high concentration of low coordinate sites. [4, 5] In recent work, MgO(111) nanosheets displayed high capacity for CO_2, as well as a ≈ 65% increase in capacity despite a ≈ 30% reduction in surface area following sintering (0.77 mmol g^{-1}@ 227 m^2g^{-1}vs 1.28 mmol g^{-1}@ 154 m^2g^{-1}). [6] These results, unique to MgO(111) suggest intrinsic differences in the effects of sintering on basic site retention. Spectroscopic and computational investigations provided a new structure-activity insight; the importance of high temperature activation to unleash the capacity of the polar (111) facet of MgO. In summary, we present the first example of a faceted sorbent for carbon capture and challenge the assumption that sintering is necessarily a negative process; here we leverage high temperature conditions for facet-dependent surface activation.

6:40pm **EH-MoE-4 Graphene Oxide-cellulose Nanocrystal Sponge as a Tunable Platform for Contaminant and Pathogen Removal from Water***, **Nathalie Tufenkji,** N Yousefi, R Allgayer, A Filina,* McGill University, Canada

Graphene oxide (GO) sponges are a new class of sorbents for removal of a diverse range of contaminants from water. The immobilization of GO in a solid porous macrostructure eliminates the requirement for removal of the otherwise stable colloidal GO from the treated water. Unlike colloidal GO, solid macrostructures can be easily stored, transported and manipulated. Although much progress has been made on forming high surface area and multifunctional GO sponges, synthesizing mechanically robust multifunctional sponges, especially in wet state, is a challenge. We report the preparation of an ultrastrong GO-based sponge strengthened with cellulose nanocrystal (CNCs) – natural nanorods isolated from wood pulp – using a green synthesis method with the aid of excess vitamin C (VC). VC acts as a natural reducing agent, whereas CNCs provide a scaffold that links the reduced GO (rGO) nanosheets together, resulting in an exceptionally stiff nanocomposite. During sponge synthesis, undissolved excess VC grains act as soft templates, yielding nanocomposites with hierarchical pore architecture, even in the core of large sponges as confirmed by micro and nano X-ray tomography. The use of ultra-large GO nanosheets, as well as the interconnected hierarchical pore structure translate into sponges with a high specific surface area and large removal capacity for a wide range of contaminants such as dyes, heavy metals, and pharmaceuticals. The GO-CNC sponges exhibit excellent contaminant removal from single and multicomponent waters, in batch and continuous removal modes. Additionally, we show that the sponges of this study can be readily functionalized with antimicrobial peptides and biopolymers to enhance removal and inactivation of bacteria from contaminated water supplies.

7:00pm **EH-MoE-5 Surface Science Approach For Alumina Supported Hydrodesulphurisation Catalysts***, **Anne-Félicie Lamic-Humblot,*** Sorbonne Université, France*; C Bara,* Solvay*; R Garcia de Castro,* Sorbonne Université, France*; E Devers, G Pirngruber, M Digne,* IFPEN*; X Carrier,* Sorbonne Université, France

Since 2009, the sulphur content need to be reduced to 10 ppm in gasoline. In order to achieve this goal, hydrodesulphurisation process is efficient for now, using sulfided molybdenum (doped or not by cobalt) deposited on alumina.

In order to optimize this process, a molecular-scale understanding of the adsorption of the active phase (metal ions) is of fundamental importance. However, this objective is difficult because of the high surface area developed by the support (g-alumina) and the large number of exposed sites. One way to simplify the system is to use oriented single crystals of alumina presenting a lower number of sorption sites and well defined surface sites. As single crystals of g-alumina do not exist, we use some of a-alumina commercial wafers in order to mimic the g-alumina exposed surfaces.

Ammonium heptamolybdate complexes were deposited on the surface using conventional aqueous routes ("equilibrium" adsorption and impregnation). The samples were then calcined and sulphided. The samples were characterised (XPS, AFM) after each thermal treatment.

The sulphurisation degree was determined with sulphurisation temperature, and a correlation between the exposed sites and molybdenum sulphide is discussed. GI-EXAFS allowed us to show that the exposed surface induce in some case a certain orientation of MoS_2slabs on the surface.

Hence it is possible to conclude that the control of the industrial support morphology constitutes a way to tune the genesis of the hydrotreating catalysts sulfide phase.

7:40pm **EH-MoE-7 Direct 3D Printing of Reactive Agitating Impellers for the Convenient Treatment of Various Pollutants in Water***, **Xueyan Sun,*** Dalian University of Technology, China

Mass transfer plays a key role in the diffusion-controlled heterogeneous reactions. Varied efforts have been made to design the structure of catalysts and reactors to optimize the diffusion process. Herein, a facile strategy is reported to construct highly reactive agitating impeller (denoted as AI) by employing 3D printing and a facile surface activation treatment. On the one hand, experimental results and numerical simulation analysis reveal that the 3D printing AI with appropriate structure can not only effectively eliminate external diffusion but also conveniently be separated from heterogeneous reaction systems. On the other hand, surface activation helps to significantly promote the chemical reactivity of AI for Fenton and galvanic replacement reaction, which are used to treat organic and inorganic pollutants in water, respectively. Benefiting from these cooperative merits, the integrated catalytic AI delivers a catalytic performance toward Fenton reactions as high as a homogeneous catalyst, and the removal rate for heavy metal ions is nearly 100% through galvanic replacement. This 3D printing with surface engineering strategy should also be extended to other applications, and provide new field for preparing efficient and durable heterogeneous catalysts in a more economical way.

8:00pm **EH-MoE-8 BN Films for Hydrogen Permeation Barrier*, Motonori Tamura,*** The University of Electro-Communications (UEC-Tokyo), Tokyo, Japan

Cubic boron nitride (c-BN) has attracted much attention because of its outstanding physical and electrical properties. However, there are limited research data on hydrogen permeation of BN thin films that can be applied to components of hydrogen fuel cells. Several techniques such as sputtering, laser ablation, ion-beam deposition, and plasma-enhanced chemical vapor deposition are used to synthesize c-BN films. To realize a stable c-BN structure and film stoichiometry, precise control of the plasma parameters is necessary. In this study, a magnetically enhanced plasma-ion-plating system was successfully designed and applied to produce stable c-BN films.

Hydrogen-permeation tests of BN-, SiC-, and TiN-coated Type 316L stainless steels were performed. A diffusion-limited permeation regime was confirmed on the coated samples at 573-773 K. The permeability depended on the test temperature, where high values of permeability data were obtained at high temperature. The hydrogen permeability data of SUS316L stainless steel in the temperature range of 573-773 K correlated well with results of a previous study. Our results indicate that the 1.5-micrometers-thick films of SiC, TiN, and BN were all effective in reducing the hydrogen permeability. In comparison with TiN and SiC coatings, the c-BN (cubic boron nitride) coating was most effective to reduce the rate of hydrogen permeation through stainless steel.

Nanomaterials
Room Naupaka Salon 5 - Session NM-MoE
NanoCatalysis

Moderator: Fumitaro Ishikawa, Ehime University

5:40pm **NM-MoE-1 Strong Interactions Between the Admetal and Molybdenum Carbide Substrates for Catalyzing H2 Related Reactions*, Chuan Shi,*** Dalian University of Technology, China **INVITED**

Transition metal carbides (TMCs) are known to display catalytic properties similar with those of noble metals. The high activity of TMCs compared with their parent metals originates from a modification of the electronic properties from the addition of carbon, which in turn affects the binding strength and the reactivity of adsorbates. In the present talk, special interest will be focused on employing TMCs as a substrate to load another metal and the strong interactions between the admetal and the carbide. Several reactions involved will be discussed, including dry reforming of methane, water gas shift and reverse water gas shift reactions [1,2], as well as liquid phase reforming of methanol for H_2 production [3].

References:

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6:20pm **NM-MoE-3 Nanostructured MoO_3/Al_2O_3 Powders and Films for Chemical-Looping Oxidative Dehydrogenation of Ethane*, H. Henry Lamb,*** *P Novotný, S Yusuf, F Li,* North Carolina State University

Ethylene, a major petrochemical building block, is produced industrially by endothermic steam cracking of ethane and petroleum naphtha at 800-850°C. Catalytic oxidative dehydrogenation (ODH) of ethane offers huge potential for reductions in energy consumption and greenhouse gas emissions; however, ethane ODH using co-fed O_2 also requires costly cryogenic air separation [1]. As an alternative, we are investigating redox catalysts that operate in a cyclic mode (chemical looping, CL) and utilize lattice oxygen (O^{2-}) as the sole oxidant [2-3]. One monolayer (1 ML) equivalent MoO_3/Al_2O_3 catalysts prepared by conventional impregnation and calcination methods contain highly dispersed supported molybdate species and exhibit high ethylene selectivity (>95%) in CL-ODH at 500-550°C. In contrast, at higher MoO_3 loadings the $Al_2(MoO_4)_3$ bulk phase predominates, as evidenced by Raman spectroscopy and x-ray diffraction (XRD); these catalysts have somewhat higher activity albeit 10–12% lower ethylene selectivity under equivalent conditions. X-ray photoelectron spectroscopy (XPS) studies indicate that high ethylene selectivity correlates with reduction of Mo^{+VI} to Mo^{+V}. The presence of Mo in lower oxidation states (+V, +IV) triggers H_2 and CH_4 generation resulting in selectivity loss. Interaction of molybdate species with the Al_2O_3 support appears to decrease reducibility and enhance ethylene selectivity in CL-ODH. Even after extended reduction in ethane at 550°C, the monolayer catalyst retained about 25% Mo^{+VI}. In contrast, for 3 ML equivalent catalysts, surface Mo^{+VI} is rapidly consumed, and its concentration eventually approaches zero. To better elucidate the nature of the catalytically active sites, model catalysts consisting of nanostructured MoO_3 films on c-plane sapphire were deposited at 580°C by molecular beam epitaxy using a conventional Knudsen cell. The sapphire substrate after annealing at 700°C in UHV exhibited a streaky reflection high-energy electron diffraction (RHEED) pattern. Films deposited at short times (<1 min) were polycrystalline with relatively smooth surfaces (1.1 nm RMS roughness by atomic force microscopy). XPS revealed that MoO_3 films deposited *in vacuo* were oxygen-deficient. Surface asperities grew with deposition time and with annealing at 700°C in UHV. The catalytic properties of the films are currently under investigation using molecular beam methods.

References:

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3. P. Novotný, S. Yusuf, F. Li, and H.H. Lamb, *Catal. Today* (2018) in press.

6:40pm **NM-MoE-4 Fabrication of Visible Light Active Nanostructured TiO_2/Cu_2O Heterojunction Thin Films*, Anna Patricia Cristobal,*** *M Ramos, A Montallana,* University of the Philippines, Philippines*; L Zhang, J Chu,* National Taiwan University of Science and Technology, Taiwan, Republic of China*; M Vasquez,* University of the Philippines, Philippines

Designing multiphase or multicomponent semiconductor heterojunctions is a promising strategy to enhance the performance of photocatalytic materials. Titanium dioxide (TiO_2) is a material of interest as a photocatalytic material because of its availability, stability, and cost-effectiveness. However, one major drawback of TiO_2 is its wide band gap resulting to photocatalytic activity in the UV region only. Through heterojunction coupling of TiO_2 with a lower band gap semiconductor such as cuprous oxide (Cu_2O) with a direct band gap of 2.17 eV, visible light active photocatalytic activity can be achieved. TiO_2/Cu_2O heterojunction thin films were assembled in a configuration wherein the junction of the coupled semiconductors is exposed to light irradiation for photocatalysis. This design ensures that photocatalytic reaction can occur in both semiconductors since they are exposed to the light source. A layer of TiO_2 thin film was deposited on (100) silicon (Si) substrate via reactive RF magnetron sputtering coupled with post deposition thermal annealing at 500°C. To form the heterojunction, ordered Cu clusters were patterned on top of the TiO_2 layer through a mask. The deposited Cu were transformed into Cu_2O by thermal oxidation at 200°C in air atmosphere followed by slow cooling at a rate of 0.48°C/min. The TiO_2/Cu_2O heterojunction films were characterized using XRD and FE-SEM with EDS mapping. Photocatalytic performance was evaluated by visible light photodegradation of methylene blue dye as the test analyte. The XRD pattern of the TiO_2/Cu_2O heterojunction film indicated the existence of rutile and anatase phases of

TiO_2 as well as the existence of mostly Cu_2O phase. SEM image of the TiO_2/Cu_2O showed a patterned thin film design composed of a TiO_2 thin film layer decorated with grain-like Cu_2O clusters that are approximately 500 µm in diameter. At higher magnification, the TiO_2 thin film exhibited a porous columnar structure while the Cu_2O is characterized by terraced grain-like structures. Using an effective thin film surface area of 1.0 cm x 2.5 cm, around 50% removal rate of methylene blue was observed in 6 h of visible light irradiation. This promising approach of designing immobilized heterojunction thin films offers a potential for wastewater treatment applications using visible light irradiation.

7:00pm **NM-MoE-5 Enhanced Photocatalytic Activity of Plasma-modified Electrospun PVA/TiO_2 Nanocomposites***, **Arantxa Danielle Montallana**, A Cristobal,* University of the Philippines, Philippines*; B Lai, J Chu,* National Taiwan University of Science and Technology, Taiwan, Republic of China*; M Vasquez,* University of the Philippines, Philippines

Poly(vinyl alcohol)/titanium oxide **(**PVA/TiO_2) nanocomposites were successfully synthesized using the electrospinning method. 1% (w/v) <25 nm TiO_2 nanoparticles (NP) were dispersed in 12% (w/v) PVA solution and was electrospun using the following parameters: V = 15 kV, tip-to-collector distance = 15 cm, and flow rate = 0.5 mL/hr. The nanofibers were collected on an aluminum foil mounted to a 3 in diameter grounded electrode rotating at ~850 rpm. Scanning electron microscopy images revealed a smooth and continuous fiber morphology with average fiber diameter of 281.84 ± 53.47 nm. Energy dispersive x-ray spectroscopy maps showed the dispersion of TiO_2 NPs in the nanofiber mats (NFMs). Raman spectral analysis showed TiO_2 peaks at 142.76, 394.64, 515.42, and 639.07 cm^{-1} confirming the integration of the NPs in the NFM. No changes were observed in the PVA peak at 2911.7 cm^{-1} after TiO_2 NP loading, implying that the addition of TiO_2 NPs did not alter the chemical composition of PVA and TiO_2. The NFMs were irradiated with a 13.56 MHz radio frequency plasma system using oxygen gas for 1 min exposure time. Plasma exposure allowed the controlled etching of the nanofiber to expose the TiO_2 NP on the surface. Using a 3 x 3 cm^2 NFM, photodegradation of methylene blue (MB) as the test analyte under UV irradiation was conducted. UV-vis spectral analysis was used to monitor the change in concentration of MB. After 9 hr irradiation, pristine samples showed 83% removal of the dye while plasma-treated samples showed 90% removal rate. Using only TiO_2 NP, 95% removal efficiency was achieved after 4 hr UV irradiation. However, use of NPs only for photodegradation is not advisable since it becomes difficult to collect and reuse the NPs. Thus, immobilizing the TiO_2 NPs would allow reusability of the photocatalytic nanocomposites.

7:40pm **NM-MoE-7 Large Scale Production of Nanoparticle Catalysts for Biomass Conversion Processes***, E Roberts, L Wang,* University of Southern California*; F Baddour, D Ruddy, S Habas,* National Renewable Energy Laboratory, USA*; N Malmstadt, **Richard Brutchey**,* University of Southern California

In order to realize more sustainable routes for the conversion of biomass into useful liquid fuels, the use of lower-cost and more Earth-abundant catalysts is required. This necessitates the development of advanced catalysts that promote the desired transformations (e.g., hydrogenation, deoxygenation), while resisting deactivation, and that can be produced cost-effectively at relevant scales. Advances in the controlled synthesis of colloidal nanoparticle catalysts have resulted in the demonstration of promising catalytic performance for these materials, with Earth-abundant transition metal and transition metal carbide nanoparticles representing two such examples. Research by our team has focused on developing chemistry that enables precise control over nanoparticle catalyst phase and/or morphology. This presentation will focus on recent developments regarding the translation of these chemistries to continuous flow reactors for nanoparticle catalyst scale up. A key metric for scale up is ensuring that the resulting nanoparticles synthesized in flow are functionally equivalent to those produced in small (mL) batch reactors. The catalytic performance of these nanoparticles will be compared between those produced in batch and continuous flow, and further compared to their "bulk" material equivalents, for key transformations of model biomass compounds.

8:00pm **NM-MoE-8 Influence of a Tailored Nanoparticle Composite Cathode on Electrochemical Properties of Anode-Supported Solid Oxide Fuel Cells***, **Jong-Eun Hong**, H Ishfaq, T Lim,* Korea Institute of Energy Research (KIER), South Korea*; S Lee,* Korea Institute of Energy Research (KIER),South Korea, South Korea*; K Lee,* DGIST, South Korea*; R Song,* Korea Institute of Energy Research (KIER), South Korea

Application of nanocatalysts to a solid oxide fuel cells cathode is expected to increase triple phase boundary (TPB) density and electrocatalytic reactivity to oxygen reduction reaction, resulting in performance improvement. Thus a conventional Sr- and Fe-doped $LaCoO_3$ (LSCF) based composite cathode was tailored with nanoparticles of a multi doped ceria that has an enhanced ionic conductivity and evaluated for electrochemical properties. In this study, Sm- and Nd-doped ceria (SNDC) nanoparticles were successfully prepared on the composite cathode via an in situ sol–gel process, which was confirmed by field emission scanning electron microscopy analysis. The tailored nanoparticle cathode indicated an increase in power density for a reduction of polarization resistance in anode supported SOFCs. It was attributed that more conductive nanoparticles led to enlarge the specific surface area and promote the reactivity for the cathode reaction.

Thin Films

Room Naupaka Salons 4 - Session TF-MoE

Nanostructured Surfaces and Thin Films: Synthesis and Characterization II

5:40pm **TF-MoE-1 Synthesis and Characterization of Novel Nitride Semiconductor Thin Films***, S Bauers, A Holder, S Lany, **Andriy Zakutayev**,* National Renewable Energy Laboratory

Nitride thin films have proven to be an invaluable class of materials with a broad range of uses. Examples include transition metal (TM) nitride rocksalts used as hard-wearing industrial and decorative coatings, and semiconducting III-N wurtzites with exceptional optoelectronic properties. We used high-throughput experimental and computations tools to investigate new inorganic ternary nitrides that have previously received very little attention. Specifically, we focused on heterovalent II-IV-N analogues to well-known III-N binary nitrides, most of which had not been reported in crystallographic databases.

Thin films of Mg-TM-N (TM=Ti, Zr, Hf, Nb, Mo) have been made by combinatorial sputtering, which has allowed for rapid investigation of how film stoichiometry and growth conditions affect properties. Most of the Mg-based ternary compounds form as rocksalt derived structure, with the transition metal in the high valence state. In each case, the heterovalent ternary space provides for tunable properties, characterized by composition-dependent metallic to semiconducting transition. When grown Mg-rich, the materials exhibit semiconducting visible-range optical absorption onsets and mobilities near 1 cm2/Vs – quite high as for nanocrystalline thin films. The calculated indirect bandgaps are in the visible - near IR range (0.9-2.4 eV), and the calculated static dielectric constants are large (30-80).

Finally, the lattice parameters fall within the range of existing nitrides, suggesting compatibility with established growth techniques and possibility for epitaxial integration of these materials into functional nitride devices. This structural compatibility, along with the tunable properties, make these new nitrides promising materials for various electronic applications

6:00pm **TF-MoE-2 Rheology Behavior and Flash Light Sintering Characteristics of Cu/Ag hybrid-ink for Multi-layered Flexible Printed Circuit Board (FPCB) Application in Printed Electronics***, **Ji-Hyeon Chu**, S Joo, H Kim,* Hanyang University, Seoul, Korea

For decades, global printed circuit board (PCB) market has been continuously expanded due to increasing demand of smart devices. Also, PCB became smaller and thinner than before, which resulted in multi-layered flexible printed circuit board (FPCB). Conventionally, multi-layered FPCB was manufactured through a photolithography method. However, the photolithography method has serious drawbacks, such as long tact time, use of toxic chemicals, and high cost. Therefore, a printed electronics technique was considered as an alternative technique, which consists of three simple processes: printing, sintering, and inspection. This technique enables fabrication of electronic devices with short process time, low cost, and environmentally friendliness. Once this technique is combined with a flash light sintering method, it can be a powerful process for the fabrication of multi-layered FPCB. The flash light sintering method uses xenon lamp that irradiates intensive white light, various nano/micro materials can be sintered in a few milliseconds under room temperature and ambient condition. However, there is no study considering printabillity and sinterbility of inks in multi-layered PCB with via-holes. Therefore, in this work, rheological property and flash light sintering characteristics of Cu/Ag hybrid-ink were simultaneously investigated for multi-layered FPCB application. Cu/Ag hybrid-inks were fabricated with various epoxy content, then the fabricated inks were printed on via-hole formed in polyimide substrate to analyze printing characteristics according to the rheology of ink. The printed Cu/Ag hybrid-ink was subsequently sintered by using flash light sintering method with various irradiation conditions including irradiation energy, pulse number, and pulse duration. The sintered Cu/Ag hybrid-inks were characterized using a scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). From these results, it was found that the Cu/Ag hybrid-ink with optimal ratio of epoxy binder content showed high printability, and the optimized multi-pulse flash light irradiation condition (irradiation energy: 7 J/cm^2, and pulse duration: 1 ms, off-time: 9 ms and pulse number: 20) exhibited high conductivity (pattern: 9.52 μΩž cm, via-hole: 12.69 μΩž cm) and high adhesion strength (5B) with well-sintered morphology.

6:20pm **TF-MoE-3 Synthesis and Characterization of Pt-Ag Alloyed Thin Films Deposited using Inverted Cylindrical Magnetron Sputtering with a Configurable Target Assembly*,*** ***Saxon Tint,*** Johnson Matthey Inc.*; G Taylor,* Rowan University*; E Burkholder,* Johnson Matthey Inc.*; J Hettinger,* Rowan University*; S Amini,* Johnson Matthey Inc.

Cylindrical magnetron sputtering cathodes, which sputter from the surface of cylindrical targets, were first described by Penfold and Thornton in the mid 1970's. They described cathodes that can be built in either post (sputtering outwards) or inverted (sputtering inwards) geometries. Inverted cylindrical magnetrons (ICM) can be used to efficiently and uniformly coat wires, extended objects, and complex geometries for a variety of industrial and medical applications. ICM targets are typically manufactured by roll-forming a flat sheet of a metal or an alloy into a cylinder. However, the mechanical characteristics of some materials preclude this method. An example of this is observed in platinum (Pt) - silver (Ag) alloys that are too brittle to roll-form, thus an alternative target assembly must be used. This work will focus on a systematic study using a configurable target assembly to deposit Pt-Ag alloyed thin films by inward sputtering from an inverted cylindrical cathode for their use as antibacterial/antimicrobial coatings on orthopedic and dental implants. The target assembly comprised of hollow Pt and Ag rings which were stacked in various configurations in order to vary the composition of the final Pt-Ag films. Additionally, varying chamber pressure and cathode power were used to study their effect on film composition and film stress. Finally, film compositional uniformity was investigated throughout the height of the target assembly, which is of particular interest considering the large variation in the size of orthopedic and dental implants ranging from around one to several centimeters in length.

6:40pm **TF-MoE-4 Surface and Interface Imaging by Ultrahigh Resolution Laser-based Photoemission Electron Microscopy*,*** ***Toshiyuki Taniuchi,*** The University of Tokyo, Japan*; S Shin,* The University of Tokyo, AIST-UTokyo OPERANDO-OIL, Japan **INVITED**

Photoemission electron microscopy (PEEM) is an imaging method based on a cathode objective lens, which enables non-scanning and relatively high-resolution imaging of photoelectrons emitted from sample surfaces. With ultraviolet light sources, PEEM is one of the suitable techniques for chemical and magnetic nano structures because threshold photoemission yields are very sensitive to chemical and magnetic properties. However the spatial resolution of PEEM is limited by space charge effect in use of pulsed photon sources as well as aberrations in the electron optics. We have developed the Laser-PEEM system with combination of the continuous wave (CW) laser and the aberration-corrected PEEM instrument to achieve the spatial resolution better than 3 nm. In this talk , we first show that the use of continuous wave laser has a capability to overcome such a limit due to the space charge effect. Using this technique, we have demonstrated structural and magnetic imaging using the Laser-PEEM with circular and linear dichroism . As another use case, we also show carrier-selective imaging on two-dimensional electron gases (2DEGs) at oxide surfaces and interfaces. Since threshold photoemission gives selective detection of their surface carriers, we successfully observed the imaging of 2DEGs at the oxygen-deficient surfaces and interfaces of $SrTiO_3$. By using magnetic circular dichroism, we have found that the 2DEGs of $SrTiO_3$ surfaces show room-temperature ferromagnetism. Besides threshold photoemission using ultraviolet light sources is expected to have very large probing depth due to less electron scattering in materials. Using this technique we have also succeeded in visualization of chemical states of buried nanostructures. Since this technique enables us to observe changes in chemical and magnetic structures during operations without removing capping layer or top electrodes, We expect that it can be applied not only to non-destructive observations but also *operando* measurements.

7:40pm **TF-MoE-7 All Photonic Annealing of Solution based Indium-Gallium-Zinc-Oxide Thin Film Transistor with Printed Ag Electrode via Flash White Light combined with Deep-UV Light*,*** ***Chang-Jin Moon,*** *H Kim,* Hanyang University, Seoul, Korea

Recently, Indium-Gallium-Zinc-Oxide (IGZO)-based thin film transistor (TFT) has received significant attention due to high electrical mobility, optical transparency and flexibility in next generation display field. Despite of these benefits, IGZO-based TFTs have disadvantage that the film is formed on the substrate through expensive vacuum deposition process. To solve this problem, solution-process of IGZO semiconductor were attempted at room temperature. However, high temperature annealing process was indispensably required. Using light annealing system such as deep-UV, laser and flash light irradiation, the process temperature applied to the annealing of IGZO could be significantly reduced. However, the manufacturing process of the IGZO-based TFT still involves deposition process under vacuum condition because metal-based electrode (source, drain) on the IGZO layer is fabricated by a deposition process.

In this study, all photonic annealing process of IGZO-based TFT was conducted via flash white light combined with deep-UV irradiation method for high performance TFT. Through solution-process using IGZO precursor solution and Ag ink, the TFT was made on heavily-doped Silicon wafer covered with thermally grown silicon dioxide. The IGZO semiconductor layer was coated on silicon dioxide using spin coating system and Ag electrode was printed on phonic-annealed IGZO layer by screen printing method. In order to optimize the flash light irradiation condition for annealing process, flash light irradiation energy was varied from 70 J/cm^2 to 130 J/cm^2 for IGZO, from 40 J/cm^2 to 60 J/cm^2 for Ag electrodes, respectively. The electron transfer property and several performances such as field effect mobility on saturation region, threshold voltage, subthreshold swing and on-off ratio of all photonic-annealed TFT were measured and calculated using parameter analyzer. Based on various channel lengths of Ag electrode, the contact resistance between IGZO and Ag was derived through transmission line model (TLM). The cross-sectional microstructure of interface on TFT was observed using scanning electron microscope. As a comparative case, the TFT structure was annealed by conventional thermal process. Finally, it was found that the flash light annealed IGZO with Ag electrodes shows similar performance compared to that fabricated by thermal process. The photonic annealing process of solution based IGZO TFT with printed Ag electrode using flash light combined with deep-UV light is expected to open a new path in the IGZO TFT field.

8:00pm **TF-MoE-8 Carbon-nanotube Dispersed Ga_2O_3Films for UV Transparent Electrodes Fabricated by Molecular Precursor Method*,*** ***Tohru Honda,*** *Y Takahashi, R Yoshida, C Mochizuki, H Nagai, T Onuma, T Yamaguchi, M Sato,* Kogakuin University, Japan

Light extraction is a crucial issue for UV LEDs. For realization of their high efficiencies, absorption in electrode should be reduced. Transparent conductive oxide (TCO) is one of the candidates. In this case, very wide bandgap (VWBG) oxides are required for its realization. Generally, VWBG oxides are known as "insulator." Thus, these materials selection is limited. On the other hand, carbon nanotube (CNT) has a good electric conductivity and its diameter is several nanometers. This means that a transparency in CNTs depend on Rayleigh scattering and a high light transparency will be expected for CNT dispersed VWBG oxides. In this paper, the fabrication of CNT dispersed Ga_2O_3films by molecular precursor method [1], which is one of the chemical solution methods, is reported. Their transparent properties and conductive properties are also discussed.

The Ga_2O_3precursor solution was prepared as follows [1]. The 3.65 g (12.5 mmol) of ethylenediamine-N, N, N′, N′-tetraacetic acid (EDTA) and 5.00 g (12.5 mmol) of $Ga(NO_3)_3 \cdot nH_2O$ (n = 7–9) [calculated as $Ga(NO_3)_3 \cdot 8H_2O$] were added to 30 mL of pure water at 80°C, and the solution was stirred for 1 hour, and then cooled to room temperature (RT). The white powder (abbreviated as Ga-edta complex) precipitated from the solution was collected on a paper filter under reduced pressure and air-dried. The precursor solution was prepared by a reaction of 1.34 g (3.55 mmol) of Ga-edta complex with 0.51 g (3.91 mmol) of dibutylamine in 10 g of ethanol. The solution was refluxed for 0.5 h, and then cooled to RT. The Ga concentration for the precursor solution was adjusted to 0.3 mmol g^{-1}. CNT solution of ethanol solvent (CNT; 0.0583 mmol g^{-1}). The solutions were then mixed with the CNT solution. The 100 mL of solution was coated on quartz glass substrate by spin-coating method, and the films were dried in air at RT for 10 min and were then thermally treated using a tubular furnace in an Ar gas flow of 1.0 L min^{-1}at 600°C for 30 min. Thickness of the resultant CNT doped Ga_2O_3films were about 100 nm.

The transparencies of the films are over 80% in UV spectral regions longer than a wavelength of 300 nm. The typical resistivity of a CNT-dispersed Ga_2O_3film is 2 x $10^{-2}\Omega\cdot$cm. The results indicate that the CNT-dispersed VWBG oxides have a potential for the application of UV transparent oxides.

[1] H. Nagai and M. Sato, in *Heat Treatment— Conventional and Novel Applications, Heat Treatment in Molecular Precursor Method for Fabricating Metal Oxide Thin Films*, ed. Dr. F. Czerwinski (InTech, Rijeka, 2012).

Biomaterial Surfaces & Interfaces
Room Naupaka Salon 6-7 - Session BI-TuM

Bioimaging and Bionanotechnology

Moderator: Lara Gamble, University of Washington

8:00am **BI-TuM-1 Exosomes and Extracellular Vesicles: Small Particles with a Big Impact**, ***Renee Goreham,*** Victoria University of Wellington, New Zealand **INVITED**

Extracellular vesicles (EVs), such as exosomes are membrane-bound vesicles released by most living cells and play a vital role in cell function and cell-cell communication. EVs have shown massive potential as biomarkers for a wide range of diseases and are found in most bodily fluids, including blood, saliva, breastmilk and urine. Detection and measuring cell specific EVs in complex solutions can lead to more sensitive detection of diseases, such as cancer. We have synthesised water soluble InP/ZnS (core/shell) quantum dots using optimised ligand exchange methods. Subsequently, the water-dispersible quantum dots were conjugated to EV-specific antibodies or aptamers. The quantum dot-antibody conjugates and their EV binding, were characterised using a suite of techniques to confirm the size, morphology and surface chemistry. The use of non-cadmium-based quantum dots implies that these conjugates would be more viable for use in a clinical setting. The same strategy has also been applied to bacteria cells (i.e. A*cinetobacter baumannii*) and bacteria derived EVs. Combined with custom designed platforms for surface plasmons resonance or spectroscopy detection, we aim to develop novel methods for EV detection.

8:40am **BI-TuM-3 Protein Corona Shield Particles of Drug-loaded Nanocarriers Enhances in vivo Therapeutic Efficacy**, ***Ja-Hyoung Ryu,*** Ulsan National Institute of Science and TechnologySchool of Natural Science, Republic of Korea

Nanoscopic delivery vehicles capable of encapsulating drug molecules and releasing them in response to external stimuli are of great interest due to implications in therapeutic applications. Polymeric micellar assemblies are promising scaffolds to overcome many of the problems faced with traditional chemotherapies because of their capacity for non-covalent, hydrophobic guest molecule binding. However, the stability of encapsulation with such self-assembled systems is limited during blood circulation because of a requisite concentration for assembly formation. Thus, deliberate molecular design for stable encapsulation, targeting and triggered release is required. For this purpose, we have developed a facile synthetic method for highly stable, polymeric nanogels or polymer-caged hollow nanoparticles using a simple intra/inter-chain crosslinking reaction. We show a simple method for the preparation of biocompatible nanovehicles that provides the ability to encapsulate hydrophobic or hydrophilic drug molecules. We can control the size of the nano-carriers and release kinetics depending on crosslinking in responsive to stimuli. Nano-carriers showed great stability to encapsulate drug molecules and drugs were only released inside cell. In addition, we can use surface modified nano-carriers for target delivery system. Hence, the stimuli responsive nano-carrier formation using self-crosslinking polymers and the corresponding method of surface modification are a promising platform for creating polymer nanogels for a range of biomedical applications, from drug delivery to biosensing.

9:00am **BI-TuM-4 The Role of Lipid Surfaces in Molecular Mechanism of Alzheimer's Disease**, *E Drolle, M Robinson, B Lee, C Filice, S Turnbull, N Mei,* ***Zoya Leonenko,*** University of Waterloo, Canada

Alzheimer's disease (AD) is a neurodegenerative disease characterized by dementia and memory loss for which no cure or prevention is available. Amyloid toxicity is a result of the non-specific interaction of toxic amyloid oligomers with the surface of plasma membrane. We studied amyloid aggregation and interaction of amyloid beta (1-42) peptide with lipid model membranes using atomic force microscopy (AFM), Kelvin probe force microscopy (KPFM) and surface Plasmon resonance (SPR). Using AFM-based atomic force spectroscopy (AFS) we measured the binging forces between two single amyloid peptide molecules. Using AFM imaging we showed that amyloid binding and aggregation are affected by charge and polarity of the surfaces (we studied chemically modified inorganic surfaces, phospholipid monolayers and bilayers (membranes)). Furthermore, we demonstrated that lipid membrane surfaces play an active role in amyloid binding and toxicity and thus in molecular mechanism of AD: changes in membrane composition and properties increase amyloid binding to the membrane and membrane damage. Effect of lipid composition, the presence of cholesterol and melatonin are discussed. We discovered that membrane cholesterol creates nanoscale electrostatic domains which induce preferential binding of amyloid peptide, while membrane melatonin reduces amyloid-membrane interactions, protecting the membrane from amyloid attack. These findings contribute to better understanding molecular mechanisms of Alzheimer's disease and aid to the developments of novel strategies for cure and prevention of AD.

References

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9:20am **BI-TuM-5 An PEEM and Imaging XPS study of Neutrophil Extracellular Traps Caputuring Nanoparticles**, *A Skallberg, K Bunnfors, C Brommesson,* ***Kajsa Uvdal,*** Linköping University, Sweden

Photoelectron Emission Microscopy (PEEM) and Imaging X-ray Photoelectron Spectroscopy (XPS) have the potential to deliver element specific imaging useful for biomedical visualization. This may increase the understanding of biological processes on the cellular level, contributing with element specific information and data on topographical morphology combined. The technique is based on chemical composition, chemical states and work-function shifts.

This is hereby demonstrated by combined PEEM and Imaging XPS investigation of neutrophils and their activation processes. Neutrophils are vital components in the human defense system, with the fundamental role to fight invading pathogens. Neutrophils are also able to release nuclear DNA done by formation of extracellular web-like structures called neutrophil extracellular traps (NETs) to capture and occasionally kill intruding microbes.

Here we reportneutrophils externally triggered by in this case nanoparticle (NPs). The neutrophils and NETs formation are imagined in presence of NPs and we report elemental composition of single-cells and structure of NETs. Active cellular uptake of nanoparticles is imaged both before and after NETs release. Element specific imaging of this novel capability for mass transport. This shows the potential for element specific bio-related cell studies on surfaces and nanoparticle tracking on the cellular level.

9:40am **BI-TuM-6 Chemical Imaging of Aggressive Basal Cell Carcinoma using ToF-SIMS**, *M Munem, K Dimovska Nilsson,* University of Gothenburg, Göteborg, Sweden*; O Zaar, N Neittaanmäki, J Paoli,* Sahlgrenska University Hospital, Gothenburg*;* ***John Fletcher,*** University of Gothenburg, Göteborg, Sweden

Time-of-fight secondary ion mass spectrometry (ToF-SIMS) is starting to be of increasing value to clinicians and has been used on different tissue samples to successfully identify and localise chemical components to various areas of the tissue and answer disease related questions [1]. Compared to other methods, the main advantage of ToF-SIMS is the label free detection of a large number of different molecules within one experiment on the same tissue section. ToF-SIMS is successfully used for analysing lipids behaviour in biological samples like breast cancer tissue [2]. Basal cell carcinoma (BCC) is one of the most increasing cancers worldwide and it is the most common malignancy in white people. Although the mortality is low as BCC rarely metastasises, this malignancy causes considerable morbidity and places a huge burden on healthcare services worldwide. Furthermore, people who have this condition are at high risk of developing further BCC and other malignancies [3].

Samples were collected from patients with BCC, by Mohs surgery. The tissue was sectioned for ToF-SIMS analysis and H&E staining of consecutive tissue slices was performed. ToF-SIMS was performed using an Ionoptika J105 instrument using a 40 keV $(CO_2)_{6000}^+$ ion beam. The analysis provided detailed chemical information about the individual lipid species and the spatial distribution of these within the tissue. It was possible to observe differences between the layers of the skin as well as between healthy and cancerous tissue (see figure). ToF-SIMS data was correlated with H&E stained images to understand and confirm, from which structures or regions of the tissue that the individual signals originated.

10:20am **BI-TuM-8 Combining the Benefits of GCIB-ToF-SIMS, MALDI-FTICR-MS and LC-MS/MS for Location specific Lipid Identification in Planarian Flatworm Tissue Sections***, **Tina Angerer**,* University of Washington, USA*; D Velickovic, J Kyle, C Nicora, C Anderton,* Pacific Northwest National Laboratory, USA*; D Graham, L Gamble,* University of Washington, USA

Phagocata gracilis are planarian, non-parasitic flatworms. Planarians are best known for their fascinating regenerative abilities, requiring a complex interplay of a wide range of molecules. The regeneration process and the molecules involved are still poorly understood. Most notably there is a lack of lipid and fatty acid data, a diverse group of molecules fulfilling numerous functions such as energy storage and cell signaling.

To gain a better understanding of the lipidomic landscape in planarians we analyzed positive and negative ions from longitudinal sections of *P. gracialis* with MALDI-FTICR-MS and ToF-SIMS along with homogenized whole worm extracts with LC-MS/MS.

Imaging MALDI-FTICR-MS (15T, Bruker Solarix) provides location specific (50 µm/pixel), ultra-high mass resolution (R≈250,000 @m/z=400) and ultra-high accuracy (<1ppm) lipid data capable of distinguishing intact lipid species of similar exact mass and showing their distribution in the tissue. The drawbacks for this technique are that the spatial resolution is too low to clearly identify features within the worm and its low fragmentation rate. While beneficial for molecular peak intensities, the lack of fragments does not allow for specific lipid assignments with structural information (e.g. lipid headgroup and both fatty acid chains identified).

Imaging GCIB-ToF-SIMS (J105, Ionoptika) generates high mass accuracy (< 5ppm), cell/organ-specific data (3 µm/pixel) consisting of intact lipids, lipid fragments and fatty acids. The moderate mass resolution (R≈10,000@m/z=700) is sufficient to resolve most lipid species. Mass peaks consisting of more than one species are indicated by broad and/or asymmetric peaks with poor mass accuracy. However co-localizing fragments can add confidence for the assignment of overlapping species, provide us with structural information and allow for unambiguous identification of resolved peaks.

LC-MS/MS (Thermo Velos Pro Orbitrap) separates different lipid species prior to fragmentation so, in contrast to SIMS, the observed lipid fragments are guaranteed to stem from the analyzed species. The drawback with this technique is that it provides no location specific information. Similar to SIMS, lipids with similar mass are not separated leading to mixed fragments in the MS/MS data. Comparing LC-MS/MS to SIMS data shows that the same lipid fragment species are present in both spectra.

This work demonstrates that only by correlating all 3 techniques can we get highly accurate, high mass, high spatial resolution, structural and location specific lipid information. Together this data provides detailed information about all major structures and organs within planarians.

10:40am **BI-TuM-9 Hybrid SIMS: A New SIMS Instrument for High Resolution Organic Imaging with Highest Mass-resolving Power and MS/MS***, **Nathan Havercroft**,* ION-TOF USA, Inc.*; A Pirkl,* IONTOF GmbH, Germany*; D Scurr, N Starr,* University of Nottingham*; R Moellers, H Arlinghaus, E Niehuis,* IONTOF GmbH, Germany

Introduction

Secondary ion mass spectrometry (SIMS) offers the possibility to acquire chemical information from submicron regions on inorganic and organic samples. This capability has been especially intriguing for researchers with life science applications. In recent years, the vision to image and unambiguously identify molecules on a sub-cellular level has been driving instrumental and application development. While new ion sources expanded the usability of SIMS instruments for biological applications, SIMS analyzers lacked the required mass resolution, mass accuracy and MS/MS capabilities required for the thorough investigation of these materials.

Methods

To specifically address the imaging requirements in the life science field a powerful new Hybrid SIMS instrument [1] was developed in a research project by IONTOF and Thermo Fisher Scientific™, following Prof. Ian S. Gilmore's original idea, in close cooperation with the National Centre of Excellence in Mass Spectrometry Imaging (NiCE-MSI), GlaxoSmithKline, and the School of Pharmacy of the University of Nottingham. The instrument combines an Orbitrap™-based Thermo Scientific™ Q Exactive™ HF mass analyzer with a high-end ToF-SIMS system (IONTOF GmbH). The instrument provides highest mass resolution (> 240,000) and highest mass accuracy (< 1 ppm) with high lateral resolution cluster SIMS imaging.

Preliminary data

Secondary ions, generated by primary ion bombardment from liquid metal ion clusters or large gas clusters can be analyzed in either of the mass analyzers. Fast switching between the mass analyzers is achieved by pulsing of a hemispherical electrode. This even allows combined measurement modes using the TOF for very fast imaging and the Orbitrap mass analyzer during intermediate sputtering cycles for generation of spectra with high mass resolution and mass accuracy from the same sample area in a single experiment.

First application data including high resolution SIMS spectrometry, MS/MS analyses, high resolution imaging of tissues and depth profiles of biological samples with this new instrument will be presented. For example, single beam depth profiling data were collected, from porcine skin samples, that clearly exhibited different molecular ion signals for different skin layers. This method potentially allows one to measure the permeation of skin for various compounds, e.g. drug molecules.

[1] The 3D OrbiSIMS – Label-Free Metabolic Imaging with Sub-cellular Lateral Resolution and High Mass Resolving Power, Passarelli et al., Nature Methods, 2017, 14(12):1175-1183, DOI 10.1038/nmeth.4504

11:00am **BI-TuM-10 Latest Developments in Cluster Beam Technology for ToF SIMS: Towards Greater Spatial Resolution, Improved Ion Yields, and Faster Etch Rates!***, **Paul Blenkinsopp**,* Ionoptika Ltd, UK

The emergence of Gas Cluster Ion Beams (GCIB) for SIMS has significantly extended the available mass range of the technique, and in so doing has also widened the scope of its applications. The low-damage nature of GCIB sputtering greatly improves yields of higher mass molecular species, however spatial resolution remains a challenge. Of particular interest is the ability to detect and image intact bio-molecules in tissue and cells at spatial resolutions below 1 micron. Here, we present on the latest advancements in gas cluster beam technology for ToF SIMS, demonstrating significant progress towards these goals.

We report on the results of our latest innovation – a 70kV Gas Cluster Ion Beam, the GCIB SM. Most current GCIB sources operate at energies between 10 and 40kV, however there are several theoretical benefits to extending the energy range beyond this, including improved focusing and greater secondary ion yields. With the GCIB SM, we demonstrate both a reduction in spot size – improving the resolving power by a factor of 3 – as well as an increase in total current – which has benefits for both speed of analysis, as well as for greater depth profiling capabilities.

We also present on methods to increase ion yields of high-mass species by utilizing alternative source gases to argon. We demonstrate that by choosing an appropriate source gas, yield enhancements greater than 10 times can be achieved. As analysis volumes decrease with greater resolving power, techniques such as this are expected to play a vital role in obtaining the highest quality imaging SIMS data. These latest developments are now enabling SIMS imaging of species such as lipids and gangliosides in tissue at resolutions greater than 2 microns.

11:20am **BI-TuM-11 SIMS with Higher Resolution and Higher Signal: 40keV Water Cluster Primary Ion Beam and Prospective Orbital Ion Trapping***, J Hood, **Peter Cumpson**, I Fletcher,* Newcastle University, UK*; S Sheraz,* Ionoptika Ltd, UK

Increasing the secondary ion yield from organic and biological molecules has been a key pursuit in the development of secondary ion mass spectrometry (SIMS) since the inception of the technique, with novel primary ion sources a promising avenue of research. The development of a water cluster primary ion beam has offered improvement in this regard, with ion yield enhancements of the order of 100 to 1000 times observed for beams with water cluster size 7,000, relative to argon cluster beams of size 2,000 [1] [2].

We demonstrate that exploiting larger cluster sizes, in excess of $(H_2O)_{10,000}^+$, with higher beam energy of 40 keV, offers further enhancement of the secondary ion yield, including for large fragments.

To complement the increased secondary ion yield of higher mass fragments, higher mass resolution is desirable. One way to achieve this is through the coupling of a high resolution Fourier transform mass spectrometer (FT-MS) to a SIMS instrument. One form of such hybrid instrumentation utilizes an orbital trapping mass analyser [3] [4], which we have designed and fabricated for our J105 SIMS instrument [3]. However, as with ion cyclotron resonance (FT-ICR MS) techniques, orbital trapping analysers operate at a much slower repetition rate than time-of-flight (ToF) variants, with acquisition dwell times per pixel of the order of 100ms to several seconds, as opposed to as little as 10µs for modern ToFSIMS instruments such as the Ionoptika J105[5].

In FT-MS the field which governs ion motion can potentially be manipulated by applying different voltages to the component electrodes, a process known in ICR-MS as Stored Waveform Inverse Fourier Transform (SWIFT)[6]. The time-domain excitation waveform is formed from the inverse Fourier transform of the appropriate frequency-domain excitation spectrum, which is chosen to excite the resonance frequencies of selected ions. The application of a SWIFT signal to the orbital ion trap improves the speed of acquisition, making high mass resolution SIMS practical.

The combination of a water cluster primary ion beam with high mass resolution orbital ion trapping offers considerable potential for analyzing the molecular chemistry in organic and biological systems.

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11:40am **BI-TuM-12 In-Situ TEM Studies of Biomineralization*, Tolou Shokuhfar*,** *R Shahbazian-Yassar,* University of Illinois at Chicago

This talk will provide an overview of the PIs' efforts to understand the dynamics of biomineralization via in-situ transmission electron microscopy. First we demonstrate how to utilize graphene sheets to build a liquid-cell nanoreactor that fits the chamber of high-resolution TEM. Graphene is impermeable to liquids such as aqueous solutions and therefore can be used to seal liquid solutions from leaking to the high vacuum of TEM environment. In addition, the excellent electrical conductivity of graphene and its ability to scavenge the radicals produced by the interaction of electron beam and liquid solutions provide an excellent platform to perform imaging of biological or hydrated specimens. We then demonstrate our success to observe the biomineralization of calcium oxalate crystals that are the primary constituent of kidney stones. We show that the addition of citrate and other molecular inhibitors can affect the crystallization pathway of these minerals. In addition, we will showcase example of biomineralization of iron oxide core in ferritin proteins and demonstrate the ability to monitor the biomineralization of these crystals using graphene liquid cells in TEM. We will show that the ratio of L and H subunits in the ferritin protein shells can affect the nucleation and growth of iron oxide cores. We also will present our latest results on the biomineralization of magnetosomes in magnetotactic bacteria grown in iron-rich media using in situ GLC-TEM studies.

Nanomaterials
Room Naupaka Salon 5 - Session NM-TuM
Nanofabrication and Nanodevices

Moderator: Adam Hitchcock, McMaster University

8:00am **NM-TuM-1 High-throughput, Continuous Flow Synthesis of Colloidal Nanoparticles as a Safe and Sustainable Nanofabrication Method*, Emily Roberts*,** *R Brutchey,* University of Southern California

In the past two decades, flow chemistry methodologies have been recognized as a step towards more green and sustainable chemical and material production. As an industrial demand for colloidal nanoparticles increases, there will be an increasing need to scale up and process intensify typical small-scale bench-top reactions. In respect to nanofabrication, continuous flow reactors have efficient heat and mass transport, excellent control of local mixing conditions, improved safety, decreased solvent waste, and are automatable. These advantages address green chemistry values by decreasing or preventing waste, improving the atom economy by increasing production yields, offering less hazardous synthetic methods, increasing throughput, and enhanced energy efficiency.

We will present our recent results on the development of high-throughput, continuous flow reactors for the synthesis of various colloidal nanoparticles. Reactor designs for a wide range of temperatures (150-320 ˚C), using various heating methods (conventional oven, microwave heating, and sand bath), reusable solvents, and one- and two-phase flow will be discussed. The differences between resulting products in terms of yield, morphology, and functionality will also be evaluated. Lastly, the continuous flow methods will be compared to analogous batch reactions to assess the viability of continuous flow nanofabrication methods.

8:20am **NM-TuM-2 Nanoporous Oxide Memristive System & Artificial Synapses for Next Generation Electronic Device Application*, Gunuk Wang*,** Korea University, Republic of Korea

The two-terminal oxide-based memristive switch is garnering enormous interest for the development of next-generation nonvolatile memory beyond current Si-based memory technology and is concurrently considered as an artificial synapse candidate for the neuromorphic computing hardware. In this talk, I will introduce a breakthrough and attractive approach, that is utilized a nanoporous oxide structure as a switching medium, for fabricating simple and cost-efficient high-density memory arrays with acceptable switching performances, low power consumption, and low electroforming voltage (or forming-free). I will talk a topic about the single nanopore (SNP)-based SiOx memories that enable unipolar switching through its internal vertical nanogap, which outperforms the switching ability of any other unipolar memory [1-3]. As a second part, I will briefly introduce our recent approaches and achievements for the neuromorphic device technology using two-terminal self-rectifying memristor synapse employing a Pt/Ta_2O_{5-y}/nanoporous (NP) Ta_2O_{5-x}/Ta layers [4,5].

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8:40am **NM-TuM-3 Synaptic Plasticity and Learning Behaviors Mimicked in Electromigrated Au Nanogaps*, Keita Sakai*,** *K Minami, S Tani, T Sato, M Ito,* Tokyo University of Agriculture & Technology, Japan*; M Yagi,* National Institute of Technology, Ichinoseki College, Japan*; J Shirakashi,* Tokyo University of Agriculture & Technology, Japan

For many years, neuromorphic devices that can mimic functions of biological brains have been studied in the field of neuromorphic engineering. The synaptic functionality of neuromorphic hardwares originates in a gradually modified resistance. Previously, we have investigated simple methods for controlling the tunnel resistance of the nanogaps called activation. In this technique, electromigration is induced between nanogap electrodes by a field emission current, resulting in the reduction of the gap width. The tunnel resistance of the nanogaps also decreases after activation. In this study, we apply the activation procedure for Au nanogaps and demonstrate the experimental implementation of synaptic functions in Au nanogaps. First, Au nanogaps were fabricated by electron-beam lithography and lift-off process. Then, a fixed width and height voltage pulse was loaded to Au nanogaps periodically. After the applied pulse was removed, current decayed rapidly at the beginning of the time followed by a gradual fading to a stable level. By increasing the number of stimulations, the relaxation time increased, implying a slow fade in forgetting process time. Meanwhile, it was observed that current level was clearly elevated, showing a potentiation of synaptic weight. These phenomena confirm the STP-to-LTP transition in our device. These results indicate that inorganic synapses are successfully achieved using Au nanogaps controlled by the activation.

9:00am **NM-TuM-4 Preparation and Corrosion Properties of Bulk Nanocrystalline Two-phase Ag-25Cu Alloys*, Zhongqiu Cao*,** *X Yin, Q Tian, Y Wang, K Zhang, J Lu,* Shenyang Normal University, China

In this paper, two bulk nanocrystalline LPRAg-25Cu and MAAg-25Cu (at.%) alloys were prepared by liquid phase reduction and mechanical alloying methods, respectively, and afterwards hot pressing process. Fig. 1 depicts the X-ray diffraction (XRD) pattern (a) and the transmission electron microscopy (TEM) photograph (b) of LPRAg-25Cu alloyed powders. These alloyed powders have no impurities with about 10 nm average grain sizes.

The densities of two bulk nanocrystalline Ag-25Cu alloys exceed 99%. The average grain size measured by XRD is about 13 nm after liquid phase reduction and about 27 nm after hot pressing, about 8 nm after mechanical alloying and about 19 nm after hot pressing.

Fig. 2 depicts the microstructures of two nanocrystalline alloys and a coarse grained counterpart (PMAg-25Cu). They all are composed of two phases. One is α phase rich in Ag, the other is β phase rich in Cu. The microstructure of coarse grained PMAg-25Cu alloy is extremely inhomogeneous. The microstructure of nanocrystalline LPR or MAAg-25Cu alloys is more homogeneous than that of coarse grained PMAg-25Cu alloy, while the microstructure of nanocrystalline LPRAg-25Cu alloy is most homogeneous.

Fig. 3 depicts Open Circuit potential (a), polarization (b), EIS (c), and Mott-Schottky (d) curves of three Ag-25Cu alloys. Corrosion rates of three Ag-25Cu alloys increase in the range of PMAg-25Cu, MAAg-25Cu and LPRAg-25Cu alloys. The corrosion rate of nanocrystalline alloy is faster than that of corresponding coarse grained alloy. The faster corrosion rates are attributed to the different microstructures of three Ag-25Cu alloys prepared by the different processes including the grain size as well as phase distribution and compositions. EIS plot of coarse grained PMAg-25Cu alloy is composed of a single capacitive loop. The corrosion process is controlled by electrochemical reactions. EIS plots of nanocrystalline MAg-25Cu and LPRAg-25Cu alloy are composed of a single capacitive loop with diffusion tail. The corrosion processes of two nanocrystalline Ag-25Cu alloys are controlled by diffusion. The passive films formed on three Ag-25Cu alloy surface exhibit n-type semiconducting properties. The passive current density of LPRAg-25Cu alloy is lower than that of PMAg-25Cu alloy, but higher that of MAAg-25Cu alloy. Thus, the chemical stability of passive films on MAAg-25Cu alloy surface is highest.

Acknowledgements

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9:20am **NM-TuM-5 Nanomaterials-enabled Advances in Microfabricated Sensors for Environmental and Health Monitoring*, Roya Maboudian,*** University of California at Berkeley **INVITED**

Accurate detection of toxic and flammable gases is critical to public health and the environment, and to the safe operation of many industrial processes. This presentation will discuss our efforts in low-power gas sensing for health, environmental and process monitoring. The core technology is a suspended polycrystalline silicon microheater functionalized with a number of nanotechnology-based sensing materials, targeting various analytes. Our microheater platform will be described and the latest results in sensitive, selective, and stable detection of several target gas molecules (including H_2, propane, CO and NO_2) will be presented. The talk will end with plans for future directions.

10:20am **NM-TuM-8 Nature-Inspired Approaches to Nanotechnologies*, Jong-Souk Yeo,*** Yonsei University, Republic of Korea

Biomimetics, Biomimicry, Nature-Inspired, or Biologically Inspired technologies are all referring to the emerging fields where innovations are strongly influenced by the wisdom from nature or biological systems. Biomimetics is the scientific approach of learning new principles and processes based on systematic study of living organisms, plants, or animals in order to develop novel engineering systems through the convergence of biology, materials science, cognitive science, robotics, and nanotechnology. Especially, the multi-functionality offered by nature can enable various applications with the help of nanotechnology. Multiple levels of approaches are feasible from nature-inspiration – adaptation of how nature works, adoption of what nature provides, or replication of natural processes and functionalities for eco-friendly, sustainable, and highly efficient technologies. In this talk, nature-inspired approaches to nanotechnology will be introduced for next generation technologies in omniphobic surfaces, color reflective displays, neuromorphic semiconductors, stretchable electronics, biomaterials and biosensors enabled by biomimetic surface, optical, electronic, or bio functionalities.

This research was supported by the MIST (Ministry of Science and ICT), Korea, under the “ICT Consilience Creative Program” (IITP-2018-2017-0-01015) supervised by the IITP (Institute for Information & communications Technology Promotion) and also under the “Mid-career Researcher Program” (NRF-2016R1A2B2014612) supervised by the NRF (National Research Foundation) and by the MOTIE (Ministry of Trade, Industry & Energy (project number 10080625) and KSRC (Korea Semiconductor Research Consortium) support program for the development of the future semiconductor device.

10:40am **NM-TuM-9 A Reproducible Assay for Versatile Biosensing by Surface-enhanced Raman Scattering***, M Al Mamun, N Cole, S Juodkazis,* ***Paul Stoddart,*** Swinburne University of Technology, Australia

Over the forty years since its discovery, surface-enhanced Raman scattering (SERS) has attracted significant attention as a sensitive technique for surface analysis. The high sensitivity of SERS and compatibility with microfluidic techniques makes it an attractive option for point-of-care sensing applications. However, we are not aware of any routine analytical applications of SERS that have emerged to date. In particular, SERS substrates are subject to variability due to high sensitivity to nanometre scale structure, complex surface interactions in real-world samples, susceptibility to environmental contamination, and a limited substrate shelf life. Here we report a versatile biosensing technique, where the target analyte is labelled with biotin, and is in turn reliably captured by a streptavidin-coated substrate. Subsequent exposure to an excess of biotin saturates the remaining binding sites and provides an internal intensity reference to assist quantification. Once the analyte has been immobilized via the biotin-streptavidin interaction, a photochemical reduction process is used to deposit silver nanoparticles over the surface. This generates a SERS substrate on demand, with high sensitivity and high reproducibility, while protecting the surface from environmental contamination. Using atto-488 as a model analyte, it has been shown that the process can deliver nanomolar sensitivity. The fluorescent emission of the atto-488 was used to confirm the surface immobilization, but is quenched by the presence of the metal coating in the SERS measurements. With appropriate extensions to an integrated microfluidic platform, the developed technique has the potential to be used to detect a wide range of small molecule targets of interest in body fluids .

11:20am **NM-TuM-11 Molecular Dynamics Investigation for Chemical Effects of Nanobubble Collapse on Precision Polishing*, Yoshimasa Aoyama,*** *N Miyazaki, Y Ootani, N Ozawa, M Kubo,* Tohoku University, Japan

For manufacturing high-performance semiconductor devices, the fabrication of a highly-planar surface is important. As the planarization method, chemical mechanical polishing (CMP) is used for efficient processing. The efficient process leads cost-savings. Therefore, the design of more efficient and more precise CMP process is required. Then, Aida et al. have recently reported that the nanobubble contributes to CMP process[1]. In this polishing process, the water hammer shock is regarded as the elemental process, which brings the jet stream when the nanobubble collapses[2]. From their study, effects of the jet would depend on the solvents around the nanobubble and the inner gaseous species of the nanobubble. However, the details of chemical relationship among CMP process, solvents, and gaseous species are unclear. Therefore, understanding the atomistic CMP mechanism with nanobubble and the chemical effects of solvents and gaseous species in nanobubble collapse phenomenon are required to establish more efficient CMP process. In this study, we performed nanobubble collapse simulation by molecular dynamics method using reactive force field, which is possible to simulate the formation and dissociation of chemical bonds.

First, we prepared the simulation model with vacuum nanobubble in the water solvent and the simulation model without nanobubble. A vacuum nanobubble is modeled by removing the water molecules as the spherical shape. Then, we performed nanobubble collapse simulation and applied a shock for the substrate surface by using “momentum mirror”[3]. From these simulations, we found that the jet was generated in the model with a nanobubble, and this jet brought larger plastic deformation on the substrate, indicating that the nanobubble increased the efficiency of CMP process. Second, in order to investigate the effects of gaseous species in the nanobubble, we prepared nanobubble models with various gaseous species. By determining the density of gas molecules in the nanobubble to satisfy the Young-Laplace law, we succeeded in creating oxygen and nitrogen nanobubble stably. By this procedure, we got to be able to fabricate various gaseous nanobubbles stably and simulate nanobubble collapse process under various solvents and gaseous species. In the conference, we are going to report the atomistic CMP mechanism and chemical effects of solvents and gaseous species in nanobubble collapse simulation.

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11:40am **NM-TuM-12 Determination of Anisotropic Diffusion Ratio on Si(110)-16×2***, **Masahiro Yano**, T Terasawa, S Yasuda, S Machida, H Asaoka,* Japan Atomic Energy Agency, Japan

Establishing bottom-up nanofabrication-techniques are required to develop electronic devises and create novel functional devices because further miniaturization using top-down techniques is becoming hard due to fundamental physical and technological limitation. The anisotropic material-diffusion, which dominates the formation of the nanostructures, should be clarified to control the nanofabrication using template surface more precisely. Si(110)-16×2 reconstructed structure has been used as a template for fabricating several types of nanowires and nanodots due to the one-dimensional structure in which the one-atomic-layer steps are arranged at a period of 2.5 nm. However, the influence of the anisotropic material-diffusion on the Si(110)-16×2 surface has not been clarified because of difficulty determining the anisotropic material diffusion ratio on the reconstructed structure.

In this study, we focused on a nano-hole, called as "void", formed during the thermal decomposition of oxide layer on Si, where the pure Si was exposed due to the desorption of the oxide layer to determine the anisotropic Si diffusion rate ratio on the Si(110)-16×2. The void is grown by the Si atoms which was created and diffused on the void bottom decomposed the oxide layer following the reaction, $Si + SiO_2 \rightarrow 2SiO\uparrow$. The voids were observed by scanning tunneling microscope (STM) at room temperature because the oxide layer is decomposed by STM at high temperatures.

The void sidewall exposed the (17, 15, 1) plane, meaning that the void is surrounded by crystallographically equivalent planes. This indicated that the anisotropic void growth rate ratio depends on only the density ratio of diffusing Si supplied to oxides between the void edges because the reaction and desorption rate of oxide were uniform around the void. The length of the voids along to the step rows of the 16×2 reconstructed structure was longer than that of perpendicular to the step rows. We found that the anisotropy of the void shape decreased as the void became deeper, indicating the reduction of the Si density ratio during the diffusion on the sidewall. Taking the migration of diffusing Si atoms between the adjacent sidewalls and the creation of diffusing Si atoms on sidewalls into account, we determined that the diffusion parallel the step rows of the reconstructed structure at the void bottom was 7 times faster than that perpendicular to the step rows. This diffusing ratio will help to realize the precise control of the nanodots and nanowires formation on the Si(110)-16×2 reconstructed structure.

Thin Films

Room Naupaka Salons 4 - Session TF-TuM

Innovations in the Development of Multifunctional Thin Films

Moderator: Jolanta Klemberg-Sapieha, Polytechnique Montréal

8:00am **TF-TuM-1 Anion Interactions with Vapour Deposited Conducting Polymers***, **Drew Evans**,* University of South Australia, Australia

Conducting polymers offer several key advantages over their inorganic counterparts, such as mechanical flexibility, transparency, and material abundance, which can enable low-cost fabrication and novel applications such as printed and flexible electronics. The conducting polymer poly(3,4-ethylenedioxythiophene), PEDOT, is one material which displays (among others) high electrical conductivity [1], enhanced thermal conductivity [2], good electrocatalytic performance [3], as well as thermoelectric behaviour [4]. Enhancing the properties of PEDOT has been achieved through Vapour Phase Polymerisation (VPP), an oxidative polymerization process under vacuum conditions. We report that VPP PEDOT shows interesting interactions with anions, in some examples almost specific ion effects [5]. For example, the uptake of anions from an aqueous solution into electrochemically reduce PEDOT is highly dependent on the anion itself. More interestingly is nitrate is specifically absorbed by PEDOT when present in a mixed electrolyte solution [6]. This selective absorption is hypothesised to originate from anion-π interactions, in part validated by MD simulations [5]. Such interactions, relating to both chemistry and structure, lead to interesting opportunities in energy storage as well as (agricultural) sensing.

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8:20am **TF-TuM-2 Decorative Electro-magnetic Transparent Metal-semiconductor Thin-films for Consumer Electronics***, **Bastian Stoehr**, E Charrault, D Evans,* University of South Australia, Australia*; F Lacroix,* ENSCBP - Bordeaux INP, France*; J Parks,* University of Bath, United Kingdom*; P Murphy, C Hall,* University of South Australia, Australia

Electro-magnetic (EM) transparent decorative coatings with a metallic appearance are highly desirable for military, automotive and communication applications. More specifically, they are advantageous as decorative coatings for consumer electronics. Such coatings will enable device to device communication with minimal attenuation of the signal. This will allow devices to save energy and result in increased battery life.

Inherently, a metallic thin-film, e.g. aluminium, interferes with EM radiation rendering it unsuitable for these applications. Hence, to create multifunctionality, aluminium was alloyed with semiconductors in order to manipulate its EM transparency, whilst maintaining the decorative properties of the metal thin film. One challenge for these coatings is to maintain their desired properties during thermal events, either during manufacturing into a final device or as a result of environment conditions during use.

Metal-semiconductor thin films have the inherent advantage that the optical and electrical properties of the thin film can be manipulated in multiple ways.[1] The properties of the thin films can be controlled not only by changing the alloy composition (type and amount of semiconductor), but also by varying the deposition parameters. We report the influence of deposition parameters and thin film composition on the EM transparency, as well as the optical properties of these coatings.

We also report on their response to thermal stress. The optical and electrical properties of these thin films have been studied for relevant process temperatures of up to 240 °C. Their properties were analyzed and compared post processing. It was revealed that after processing the thin films at relevant temperatures, the properties changed. Interestingly, the magnitude and direction of change was dependent on the type of semi-conductor used. Possible mechanisms include oxidation, phase changes, grain formation, grain size changes and changes along grain boundaries. This information will be used to select composition and process properties so that aluminium-semiconductor alloys can be used in a number of applications.

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8:40am **TF-TuM-3 Applications of Polarized Neutron Scattering for Development of Novel Functional Heterostructures***, **Valeria Lauter**,* Oak Ridge National Laboratory, USA

New functionality often arises at the mesoscale where defects, interfaces, and non-equilibrium structures are formed [1]. Probing the internal structure morphology and spin structure in thin films and nanostructured materials via Polarized Neutron Reflectometry (PNR) is a type of experiments addressing not only a kind of "surface visualization" or integration over the whole sample size. PNR is a tool providing depth resolved information and establishes a direct and precise correlation between local interfacial characteristics and global physical properties and delivers the most exhaustive and detailed information on the 3-dimensional structure of thin films and hidden interfaces on enormous length scale [2]. In this talk I will present a spectrum of experiments performed at the Magnetism Reflectometer at the Spallation Neutron Source, that covers multiple scientific areas, e.g. new generation of heterostructures based on integrating topological insulators (TIs) with conventional materials to induce ferromagnetic interactions with symmetry breaking at the interface [3], tunnel barriers in hybrid organic/metallic spin-valve structures, asymmetric block-copolymer/nanoparticle composite structures. The specific details will be presented.

Research at Oak Ridge National Laboratory's Spallation Neutron Source was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, and the US Department of Energy, by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory.

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9:00am **TF-TuM-4 Oxygen-Free Palladium/Titanium Coating, a Novel Non-Evaporable Getter Coating with an Activation Temperature of 133 °C***, T Miyazawa,* SOKENDAI, Japan*; M Kurihara, S Ohno,* Yokohama National University, Japan*; N Terashima, Y Natsui, H Kato,* Hirosaki University, Japan*; Y Kato,* Irie Koken Co., Ltd., Japan*; A Hashimoto,* National Institute for Materials Science, Japan*; T Kikuchi, **Kazuhiko Mase**,* KEK, Japan

We developed a novel non-evaporable getter (NEG) coating with an activation temperature as low as 133 °C, that is, a palladium/titanium coating with extremely low oxygen concentration (oxygen-free Pd/Ti coating) (Fig. 1) [1]. The substrate was coated with Ti, and then overcoated with Pd using sublimation under ultra-high vacuum conditions. The morphology and surface elemental composition of the Pd/Ti thin film were investigated with electron microscopes and X-ray photoelectron spectroscopy, respectively. The thicknesses of Ti and Pd films were approximately 1.3 µm and 50 nm, and the Ti film was completely overcoated by the Pd film. Ti and oxygen were found to be negligible on the oxygen-free Pd/Ti surface. The oxygen-free Pd/Ti coating was applied to formed bellows. The bellows was successively baked at 133 °C for 12 h, 176 °C for 3.5 h, and 200 °C for 3.5 h. After sealing off a turbomolecular pump from the vacuum system containing the bellows, the pressure reached values of 4.6×10^{-6} Pa, 1.7×10^{-7} Pa, and 6.1×10^{-8} Pa, respectively (Fig. 2). The pumping speeds of the bellows were estimated to be 0.028, 0.23, and 0.23 L s^{-1}, respectively. These results demonstrate that oxygen-free-Pd/Ti deposition can be used as a new NEG coating for vacuum systems with a baking temperature of 133 °C or higher. Oxygen-free Pd/Ti coating was applied for a NEG pump that can be activated by baking at 150 °C for 12 h [2].

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9:20am **TF-TuM-5 Droplet assisted Growth and Shaping (DAGS): A Broadly Applicable Method for Chemical *in situ* Shaping of Complex Polymeric Nano and Microstructures***, **Stefan Seeger**, G Artus, N Saddiqi,* University of Zurich, Switzerland

The synthesis of nano and microstructures is an emerging field in chemistry and materials science. They can be made from a large variety of materials, for example metals, semi-metals, or polymeric substances. Usually, these particles exhibit a simple shape.

Some years ago, we have presented the synthesis of silicone nano filaments in particular for surface coatings. Now, we have shown a mechanism, called **Droplet assisted Growth and Shaping (DAGS)** explaining how these one-dimensional growths can be explained. Based on this synthesis scheme we are able to synthesize silicone nanoparticles of different shapes depending on the reaction conditions at room temperature from gas phase and liquid phase. Some of these structures exhibit a shape complexity which goes clearly beyond wires and filaments. Very recently, we could show that the mechanism of this synthesis is applicable not only to silicone structures but also to other chemical compounds. For example we have synthesized Germanium oxide and Aluminumoxide nanostructures. For these structures we have used Germaniumchloride and Tributyl-Aluminum. The procedure for all of them is identical, does not require high temperature, pressure or other cost invcreasing conditions.The shape of the structures depend on the grade of humidity in the gas phase during the reaction.

In this presentation, we will give an overview about the synthesis and process reaction conditions allowing the directed growth of of nano and microstructures of complex shape.

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9:40am **TF-TuM-6 Low Temperature Nitridation of Hafnia with Low Density of N-O Bonds***, J Torres-Ochoa, O Cortazar-Martinez, M Mayorga-Garay, A De Luna Bugallo, Y Chipatecua-Godoy, O Ceballos-Sanchez, D Silva-Cabrales, F Corona-Davila, J Raboño-Borbolla,* CINVESTAV-Unidad Queretaro, Mexico*; **Alberto Herrera-Gomez**,* CINVESTAV-Unidad Queretaro, Mexico, México

The nitridation of hafnia is attractive because it improves its dielectric properties and minimize its crystallization. The thermal budget employed might be large when nitridation is carried out through rapid thermal annealing [1]. Ultraviolet-assisted nitridation might be carried out at lower temperatures; however, N-O species dominates the N 1s spectrum [2], affecting the dielectric quality. These species are also present when the nitridation is carried out through decoupled-plasma processing [3] and can only be removed through high-temperature annealing.

We have developed a low-temperature nitridation process that minimize the formation of N-O species. It also minimizes the formation of a hafnium silicate interface layer in hafnia/Si structures [4]. It is based on remote-plasma employing a gas-mixture. The structure of the multilayer films was characterized through ARXPS, and the effect on the dielectric properties through I-V and C-V curves.

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10:20am **TF-TuM-8 Fundamental Properties of Transition-metal Nitrides: Materials Design Strategies for Extreme Properties***, **Joe Greene**,* Linköping University, Sweden, University of Illinois at Urbana-Champaign **INVITED**

Transition-metal (TM) nitrides exhibit an enormous range of properties and offer a smorgasbord of opportunities for materials scientists. Cubic TM nitrides have wide single-phase compound fields that can be exploited. We show results for vacancy hardening in 3d Group-IV TiN_x(001) and Group-V VN_x(001); the hardness H (and resistivity ρ) of epitaxial layers increases, while the elastic modulus E and the relaxed lattice constant decreases linearly, as x is decreased from 1.0 to 0.67 and 0.80, respectively. In contrast, H(x), E(x), and ρ(x) for 5d Group-V TaN_x(001) remain constant due primarily to the presence of isoelectronic antisites. Strong electron/phonon coupling in VN_x results in thermal conductivity at room temperature and above being dominated by electronic contributions.

All Group-IV TM nitrides, TiN, ZrN, and HfN, are very good metallic conductors with room-temperature resistivities of 12-14 μΩ-cm. 3d Group-III ScN(001) is a transparent semiconductor with an indirect Γ-X gap of 1.3 eV. Reflectivity measurements from $Sc_{1-x}Ti_xN$(001) layers show TiN is strongly reflecting up to the reflectance edge at $\hbar\omega_e = 2.3$ eV, while ScN is transparent, and $\omega_e \propto x^{0.5}$ for the alloy. ZrN is intermediate with $\hbar\omega_e = 3.04$ eV. Thus, hard decorative coatings can be obtained with a wide palette of colors.

Superconducting transitions T_c for the Group-IV TM nitrides range from 10.4 K for ZrN to 9.18 K for HfN to 5.35 K for TiN. For comparison, superconductivity is not observed for the Group-IV rare-earth (RE) nitride CeN. These results are consistent with electron/phonon coupling parameters of 1.11 (ZrN), 0.82 (HfN), 0.73 (TiN), and 0.44 (CeN). The acoustic phonon modes soften monotonically with increasing cation mass; optical mode energies remain approximately constant for the TM nitrides, but are significantly lower for the RE nitride due a lower interatomic force constant.

The extreme range of materials properties available in TM nitrides and related systems can be enhanced through the formation of self-organized superhard nanostructures consisting of commensurate nanolamellae, nanocolumns, nanospheres, and nanopipes.

An issue with hard ceramic films, however, is that they are typically brittle, leading to failure by crack formation and propagation. We show several approaches to obtaining TM nitride layers that are both hard *and* ductile (i.e., tough). IV-VI and V-VI alloys, e.g. $Ti_{1-x}W_xN$ and $V_{1-x}Mo_xN$, exhibit dramatic delocalization of electron density leading to a more ductile response to shear stress while exhibiting increased hardness under tensile and compressive loading. Vacancy-induced toughening is also observed in under-stoichiometric $(V,Mo)N_x$ alloys.

11:00am **TF-TuM-10 Surface Reactions of Metal and Metal Oxides on Hybrid Perovskite Materials for Optoelectronics Applications***, J Cazares-Montañez, M Martínez-Puente, R Garza-Hernández, E Martínez-Guerra,* CIMAV-Monterrey, Mexico*; M Quevedo-Lopez,* University of Texas at Dallas*; **Francisco Aguirre-Tostado**,* CIMAV-Monterrey, Mexico

Hybrid perovskites (HPV) have recently emerged as highly efficient optoelectronic materials and are currently being intensively investigated as alternative active layer materials for photodetectors, light-emitting diodes, laser devices, sensors and X-ray detectors, among others. Since HPV are direct band gap materials with high optical absorption coefficients (~ 10^5cm^{-1}) the majority of publications have been dedicated to hybrid organic-inorganic solar cells with certified efficiencies over 20%. However the realization of a long-lasting device implies the understanding of chemical and structural stability of HPV materials and their interface with electron and hole transport layers (ETL and HTL, respectively). This presentation will show detailed XPS analyses of the the chemical stability of the transition metal and transition metal oxides with ABX3 hybrid perovskites for A=MethylAmmonium (MA), B=Pb, and X=Cl, I, and Br. HTL/HPV interface is not trivial as the reactivity of halogen group elements forms an unstable high resistance interlayer at the charge transport layer interface compromising the optimum operation of the device. The electrical characterization and work function measurements will be discussed and correlated to the chemistry and cristallyne structure of the materials of interest.

11:20am **TF-TuM-11 Thin-Film Alchemy: Engineering Oxide Films to Unleash their Hidden Properties***, **Darrell G. Schlom**,* Cornell University **INVITED**

Guided by theory, unparalleled properties—those of hidden ground states—are being unleashed by engineering oxides at the atomic level. This engineering includes strain engineering, dimensional confinement, and defect engineering. Using these thin-film tricks, materials that are not ferroelectric or ferromagnetic in their unstrained state can be transmuted into ferroelectrics, ferromagnets, or materials that are both at the same time. Similarly, new tunable dielectrics with unparalleled performance have been created. Our studies reveal details about the microscopic growth mechanism of these phases, which are relevant to preparing multicomponent oxide heterostructures with atomic precision. A new era for engineering functional oxide thin films for electronics is upon us: oxides by design. This work was performed in collaboration with the coauthors listed in the references below.

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Biomaterial Surfaces & Interfaces
Room Naupaka Salon 1-3 - Session BI-TuP

Biomaterial Interfaces Poster Session

Moderator: David Castner, University of Washington

BI-TuP-1 Inhibiting Upstream Motility of *Pseudomonas Aeruginosa via* Nanopillared Surface Structuring*, Rachel Rosenzweig*, *V Ly, K Perinbam, A Siryaporn, A Yee,* University of California, Irvine

Bacteria often populate environments where fluid flow is present such as the lungs of mammals, vasculatures of plants, industrial transportation fuel lines, and medical devices. *Pseudomonas aeruginosa* is an opportunistic biofilm forming bacterium that exhibits the ability to twitch upstream when surface attached. The upstream movement is facilitated by the retraction and extension of their type iv pili mechanosensor ATPase motors, pilT and pilU, when encountering shear stress. Such motility modalities of *P. aeruginosa* lead to bacterial surface adherence, colonization, and infectious biofilm formation. Here, upstream motility inhibition and surface detachment of *P. aeruginosa* were accomplished on polymeric biomaterial structures with arrays of nanopillared geometries.

Nanopillared surface structures were fabricated using thermal nanoimprint lithography on a synthetic polymer, poly(methyl methacrylate) (PMMA), commonly used in medical devices. The arrays of nanopillars range in periodicities from 200nm, 300nm, 500nm to 600 nm. Upstream motility direction, displacement, velocity, and detachment of wild-type *P. aeruginosa* expressing GFP were monitored in microfluidic flow channels with flat or nanopillared bottom surfaces and quantified using fluorescence microscopy. The cell motility inhibition and detachment under shear stress were observed to have a nanopillar surface area dependence most likely due to decrease in surface mechanosensing capabilities of the type iv pili. This bacteria-nanostructured surface interface phenomenon allows us to tailor surfaces with specific nanopillared geometries for structurally controlling cell motility and detachment under fluid flow. The disruption of surface attached biofilm forming bacterial upstream movement is crucial in preventing harmful infection from contaminated medical devices such as catheters and has broad application in industrial fuel line dependent transportation.

BI-TuP-2 Effect of Preheating Treatments on Interfacial Reaction between Dental Porcelain and Low Magnetic Susceptibility Zr–14Nb Alloy*, Atsushi Takaichi,* Tokyo Medical and Dental University, Japan*; Y Kajima,* Tohoku University, Japan*; H Doi, T Hanawa, N Wakabayashi,* Tokyo Medical and Dental University, Japan

[Objective]

In this study, we focus on using the Zr-14Nb alloy for porcelain-fused-to-metal (PFM) restoration in dental prosthetics, owing to their good mechanical properties and biocompatibility, as well as the low magnetic susceptibility. The interface between the alloy and the porcelain is of critical value in ensuring the long-term integrity of the PFM restoration, thus we investigated the changes at the ceramo-metal interface induced by preheating treatments.

[Methods]

Cylindrical cast specimens of the Zr–14Nb alloy were prepared. After sandblasting with Al_2O_3, the Zr–14Nb samples were subjected to a preheat treatment at 700 °C for 5, 10, or 20 min and those without treatment were taken as control samples. Dental porcelain was veneered on them; then, their bond strength (MPa) was evaluated by performing shear bond tests ($n = 8$/group) and the results were analyzed using ANOVA and Tukey's tests ($p = 0.05$). The surface characteristics of the preheated Zr–14Nb specimens were evaluated by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS), laser microscope, and X-ray diffractometry (XRD). The elemental distribution on the interface between the Zr–14Nb alloy and the porcelain was determined by SEM-EDS. MR images were obtained using 3.0 T MR scanners (MAGNETOM Spectra 3T), and artifacts volume from the specimens were quantified by constructing 3D image.

[Results and Discussion]

The samples subjected to the heat treatment for 5 min showed the highest mean bond strength (43.7±5.9 MPa). On the preheated sample groups, white oxide layers, which were predominantly composed of monoclinic zirconia, were formed, exhibiting a greater roughness than control samples; besides, on the interface of the metal–ceramics, a greater diffusion range of Nb was observed than that found on the control samples, which could contribute to increase the bond strength between porcelain and Zr-Nb alloy. On the other hand, the bond strengths of the samples subjected to 20 min preheating treatment were the lowest (33.6±3.2 MPa), which may be ascribed to the formation of a brittle thick oxide layer under excessive heat treatment.

[Conclusion]

The suitable preheat treatment performed on the Zr–14Nb substrates contributed to the increase in the surface roughness and the diffusion of Nb, which enhanced the micro-retention and chemical bonding and improved the bond strength of Zr–14Nb and porcelain. The Zr-14Nb alloy is a promising candidate for fixed dental prosthesis, as long as the appropriate treatment conditions are adopted.

BI-TuP-3 Surface Characteristics and Corrosion Behavior of CoCrMo Alloys Fabricated by Selective Laser Melting after Various Heat Treatments*, Yuka Kajima,* Tohoku University, Japan*; A Takaichi, T Oishi, N Kittikundecha, Y Tsutsumi,* Tokyo Medical and Dental University, Japan*; N Nomura,* Tohoku University, Japan*; N Wakabayashi, T Hanawa,* Tokyo Medical and Dental University, Japan*; A Kawasaki,* Tohoku University, Japan

[Objective] Selective laser melting (SLM) has attracted significant attention as an advanced method for fabricating biomedical devices. SLM-manufactured parts easily accumulate large amounts of residual stress due to rapid heating and cooling. Thus, they require a post-fabrication heat treatment to relieve the residual stress. However, the heating process inevitably changes the microstructure of the alloys, which may affect their corrosion behavior. The objective of this study was to assess the morphological characteristics and corrosion properties of SLMed CoCrMo alloys following various heat treatments.

[Methods] Block specimens were prepared using an SLM machine equipped with a fiber laser (EOSINT M280) and commercially available CoCrMo alloy powders (MP1). Specimens were heated to 750 or 1150 °C and held at this temperature for 1 or 6 h in a furnace in an Ar atmosphere. Specific section cuts of XY and YZ planes were used for analyzing microstructures and corrosion resistance. Microstructures were investigated via scanning electron microscopy (SEM), field-emission transmission electron microscopy (FE-TEM), field-emission electron probe microanalysis (FE-EPMA), electron backscattered diffraction (EBSD), and X-ray diffraction (XRD). Additionally, anodic polarization was performed with a potentiostat (HABF-501A) with a function generator (HB-111).

[Results and Discussion] The SEM images showed that fine precipitates were formed within the grains and at the grain boundaries in the specimens heated to 750 °C. On the other hand, after heating to 1150 °C, coarse precipitates, identified as $M_{23}C_6$ by TEM and EPMA analysis, grew along the grain boundaries. Both γ and ε phases formed in all heat-treated specimens, and the volume fraction of the ε phase decreased with increasing heat-treatment temperature and time. In the samples heated to 750 °C, the microstructures exhibit the epitaxial growth of columnar grains with a < 001 > fiber texture along the build direction as well as the as-built state. In samples heated to 1150 °C, defect-free equiaxed grains with random orientations were found, indicating that recrystallization occurred. Considering the anodic polarization curves, the heat treatment process did not greatly affect the corrosion resistance of the SLMed specimens; resistances of all heated samples were comparable to traditional cast samples, with those heated to 750 °C exhibiting the highest corrosion potential. The enhanced corrosion resistance of SLMed CoCrMo alloys provides further support for their use in medical applications.

BI-TuP-4 Analysis of Drug Coated Polymer Stents Studied by XPS and Ar_n^+ Sputter Profiling*, David Surman,* Kratos Analytical Inc.*; J Counsell,* Kratos Analytical Ltd., UK

Cardiovascular interventional therapy with stents has emerged as one of the most effective treatment methods for coronary heart disease, however, thrombosis and hyperplasia are the usual pathological responses to the implantation of foreign devices into the body. Originally stents were made of steel although these have now been superseded by polymer based materials. Recent developments have introduced a new range of stents made from bio-resorbable polymers, however problems such as thrombosis and hyperplasia still remain. To suppress this immune response and that of overgrowth and subsequent restenosis anti-inflammatory drugs are now loaded onto the surface of stent implants.

In this presentation we investigate the surface of drug loaded polymer stents using X-ray photoelectron spectroscopy (XPS) and sputter depth profiling using Ar_n^+ clusters. The stents studied are made of polylactic acid (PLA) dosed with an anti-inflammatory drug with a molecular structure of $C_{51}H_xNO_{13}$. XPS yields quantitative information regarding drug distribution which is shown to be higher on the abluminal (outer) than the luminal (inner) surfaces of the stent. Combining Argon cluster sputtering with XPS enables the distribution of the drug into the stent structure to also characterised.

Conventional methods to study the effects of aging and drug mobility in stents involve immersion in a buffer solution for varying periods of time. Subsequent analysis of the solution with HPLC determines the extent of drug dissolution from the stent. Although this approach is accurate in determining the amount of drug dissolved, it is still unknown how much drug remains and how it is distributed. This is addressed in this study where the drug distribution for stents immersed in PBS buffer solution for 1-3 months was determined by Ar_n^+ cluster depth profiling of the stents themselves. These results were used to determine the effects on simulated ageing and the propensity for the drug to migrate into the solution with time.

BI-TuP-5 Anchored Protease-Activatable Polymersomes for Molecular Diagnostics of Cancer Cells*, **Jong-Woo Lim,*** Yonsei University, Republic of Korea*; H Kim,* Korea University, Republic of Korea*; J Choi,* Yonsei University, Republic of Korea*; H Lee,* Korea Basic Science Institue, Republic of Korea*; H Son, J Kim, G Park, H Chun,* Yonsei University, Republic of Korea*; D Song,* Korea University, Republic of Korea*; Y Huh, S Haam,* Yonsei University, Republic of Korea

Real-time quantitative and qualitative analyses of metastasis-associated proteases are critical for precise diagnosis and novel therapeutic treatment of advanced cancers. However, conventional methods based on DNA, peptides, and proteins require sophisticated chemistry and additional processes to expose detection moieties, and they lack elements of temporal control, which limit their applicability. We designed unique protease-activatable polymersomes (PeptiSomes) for high sensitivity, in situ quantitative analysis of activating membrane-type 1 matrix metalloproteinases (MT1-MMP, MMP14). To do this, we first synthesized an amphiphilic block polymer–peptide and a copolypeptide based on mPEG -b-pLeu and MT1-peptide-b-pLeu, respectively. Amphiphilic self-assembled PeptiSomes in water were capable of disassembling and releasing the encapsulated self-quenched fluorescence dye (calcein) via enzymatic activation by MT1-MMP. Our PeptiSome system may potentially prevent the initiation and progression of cancer metastasis. Furthermore, the PeptiSome approach described here is likely to facilitate the development of rapid protease assay techniques and further extend the role of proteases as metastasis indicators and therapeutic targets.

BI-TuP-6 Study on Meta-material Structure in Oil Repellent Bile Duct Stent*, **Tomoki Nishino,*** Ritsumeikan University, Japan*; H Tanigawa,* The Research Organization of Science and Technology, Japan*; A Sekiguchi,* Litho Tech Japan Corporation, Japan*; K Aikawa,* Saitama Medical University, Japan

The bile duct is a tubular pathway that drains the bile made in the liver into the duodenum. In bile duct cancer, biliary atresia or the like, the bile duct narrows, the flow of bile is inhibited and it becomes difficult for the duodenum to flow from gall bladder to the duodenum. For this reason, bile flows back to the liver, causing a disorder that causes jaundice. Natural progression will result in liver failure, possibly leading to death. As a treatment method, in order to open the obstruction of the bile duct, the endoscope is used to indwell the stent in the bile duct to ensure discharge of the bile into the duodenum. By placing the stent with a metal tube or a resin tube having a mesh-like structure, a path through which bile normally flows is secured.

However, since bile is a viscous liquid containing oil, it is known that the tube clogs by adhesion or gelling in the bile duct stent. Currently, no effective technology has been studied for this problem. When the tube is clogged, there is only a countermeasure therapy to replace the biliary stent by reoperation. If it is possible to reduce clogging of the stent, it is possible to reduce the number of reoperation, which not only reduces the burden on the patient but also leads to a reduction in the burden on the medical field including doctors.

This study is a technology development to reduce clogging of the biliary stent. We introduce a biliary stent combining metamaterial technology that realizes oil repellency and antifouling property which is not realized on the surface of the material prepared. When considering the oil repellency function for oil containing fluid such as bile, we considered the snail shell structure with nano hydrophilic effect to be effective. On the shell surface of the snail, there is a concavo-convex structure of 200 nm to 400 nm, and it is running a dirt by making a thin water film. The film having a metamaterial structure was produced by a semiconductor fine processing technique. When the produced film was evaluated for oil repellency, it was confirmed that good oil repellency in water was obtained. Therefore, in order to evaluate a bile duct stent with a metamaterial structure, bile ducts were placed in pigs for 7 days. The inner surface of the usual bile duct tube resulted in bile sticking and a lot of contamination, but the bile duct tube of the meta-material structure was a result that the bile was repelled and there was no stain. We present that bile duct with oil repellency and antifouling property is effective as new metamaterial technology.

BI-TuP-7 The Blood Cell-nanoparticle Interface: Functional Cellular Responses, Mechanisms of Interaction and Signaling pathways*, C Brommesson, N Abrikossova, P Eriksson, Z Hu, K Uvdal, **Andreas Skallberg,*** Linköping University, Sweden

The use of nanomaterials in biomedical applications create a large need for studies elucidating potential harmful effects of the materials in living systems. Nanomaterials specifically aimed for *in vivo* applications are sure to encounter all components of blood, directly or indirectly, and increased knowledge of underlying mechanisms at the blood cell-nano interface will be valuable in the further development of these materials.

We have specifically investigated blood platelet and neutrophil granulocyte interaction with several types on nanoparticles. These blood cells are rapidly responding, and potent cells involved the immune response and following inflammatory processes. Using well-defined and characterized NPs we have focused on clarifying the induced functional cellular responses, interaction mechanisms and involved signaling pathways. Our results demonstrate uptake of polymeric (Pdots) and Cerium/Gadolinium based NPs in neutrophils and show that both active and passive uptake processes contribute to the internalization of these particles. In connection, cellular mechanisms underlying our previously described antioxidative properties of cerium containing NPs[1] are further investigated and identified. Nanoparticle induced platelet aggregation and release of inflammatory mediators is also shown herein to be valuable for evaluating NP- blood compatibility.

[1] *P. Eriksson el al. Cerium oxide nanoparticles with antioxidant capabilities and gadolinium integration for MRI contrast enhancement. Scientific Reports 2018; 8:6999*

BI-TuP-8 Developing a pH Responsive Hydrogel as an Alternative for Colonoscopy Preparation*, **Phuong Nguyen,*** University of New Mexico*; S Mounho,* University of Texas at Austin, USA*; D Cuylear, H Canavan,* University of New Mexico

Colorectal cancer (CRC) is the second leading cause of cancer-related deaths in the United States. The most reliable screening method of CRC is a colonoscopy which requires a 4-Liter poly(ethylene glycol) electrolyte lavage solution (PEG-ELS) for preparation. ~40% of patients are non-compliant to their colonoscopy schedules, with many patients who abstain reporting refusal due to significant discomfort associated with this preparation. Furthermore, there are distinct gender differences in the tolerance of PEG-ELS in male and female populations. We hypothesize the differences in clinic are a result of cytotoxicity effects of PEG. PEG is approved by the FDA for use in medical devices, and has been recognized for many years as a biocompatible/bioinert polymer but few studies have truly studied the short-term and long-term effects of high concentrations of PEG on multiple cell lines. We have developed a pH responsive hydrogel to control the release of PEG – reducing adverse effects associated with colonoscopy preparations. The hydrogels have been characterized using NMR, and XPS to ensure chemical identity, rheometry to assess the stiffness/robustness of the hydrogels in varying environments, and SEM and other techniques to confirm uniformity of size. Biocompatibility testing of exposure to increasing PEG concentrations over a period of 3 hours, 6 hours, 12 hours, 24 hours, and 48 hours shows PEG is biocompatible to intestinal human cell lines in short intervals and low concentrations. Furthermore, at low concentrations PEG increases cell growth and viability as seen in previous studies. At higher concentrations, however, PEG is cytotoxic to cells. Although it would be difficult to get to toxic levels of PEG in the body in a single dose, current uses of PEG in which large, non-uniform, quantities are ingested in a short time frame should be re-evaluated due to possible adverse cumulative effects due to the cytotoxicity effects seen *in vitro.* Further directions of this work will evaluate the pH responsiveness of our hydrogel formulation to deliver PEG *in vitro* and *in vivo,* and assessment of the cellular response to the hydrogels using mammalian cells specific to the gastrointestinal system of humans, as well as imaging analysis to envision their penetration.

BI-TuP-9 Atmospheric Pressure Mass Spectrometric Imaging of Live Tissue Specimen using Electrospray assisted CW Laser Desorption and Ionization Source*, **Jae Young Kim**,* Daegu Gyeongbuk Institute of Science & Technology*; S Lee, M Shin,* Daegu Gyeongbuk Institute of Science & Technology, Korea*; D Moon,* Daegu Gyeongbuk Institute of Science & Technology, Republic of Korea

Although atmospheric pressure mass spectrometry (AP-MS) is a promising analytic technique for biological samples because of its ambient analytic process and no or minimal sample pretreatment, still many challenges must be overcome to acquire MS data from them. Because mass spectrometry is a quantitative technique for the measurement of the masses of the charged molecules that comprise a sample of material, small but actual parts should be severed from the sample. Thus, desorption and ionization methods for small spot sampling to the biological sample are the most important technique to minimize the sample damage and to obtain high resolution MS imaging. Currently many ambient desorption/ionization sources except lasers are working in ionized gaseous state or spray state of charged droplet, reducing the size of source devices is limited.

We use electrospray ionization source and visible continuous wave (CW) lasers as AP-sampling/ionization sources and develop/combine these electrospray and lasers for the purpose of mass spectrometry applications. The energetic light generated by CW lasers focuses on a very small spot of the sample through the objective lens. At same time, the electrospray device forms the charged droplet particles on the sample. Regarding desorption and ionization procedures in open air, CW lasers mainly desorb actual parts from the sample and electrospays mainly ionize these small substances.

An inverted optical microscope was used as a sampling stage and the additional pumping system including ion transfer tubing, chamber, and dry pump known as air flow assisted ion transfer equipment was installed with the MS inlet. Therefore an AP-MS system is developed and preliminary MS data are achieved with a help of gold nanoparticles. With an addition of the two-dimensional programmed scanning stage to this ambient MS system, many bio-molecular mass spectrometric imaging were obtained from the mouse hippocampal tissues. High spatial resolution MS imaging with a pixel size of four micrometer can be secured at a sample moving velocity of 30 µm /s. MS imaging of bio-molecules including monoacylglycerols, cholesterols, fragments of sphingolipids and glycerophospholipids has been obtained from mouse hippocampal tissues.

BI-TuP-10 Improvement of Cell Imaging by Graphene Encapsulation in ToF-SIMS Method*, **Sun Young Lee**,* Daegu Gyeongbuk Institute of Science & Technology, Korea*; H Lim, J Kim,* Daegu Gyeongbuk Institute of Science & Technology*; D Moon,* Daegu Gyeongbuk Institute of Science & Technology, Republic of Korea

For last decades, ToF-SIMS has been in use in bio sample imaging and has resulted in some important bio issue discoveries. SIMS analysis requires ultrahigh vacuum environment and analysis in atmospheric not allowed. Its ultra-high vacuum based operation necessitates proper sample preparations ranging from simple ones like washing and drying to relatively sophisticated as frozen hydration.[1] Therefore, any of them can neither represent the biologically native state nor preserve membrane integrity. So we have developed a new sample preparation using wet cells covered by single layer graphene for hydrated and native state bio sample.

Graphene acts as a gas impermeable honeycomb mesh on cells preventing solution evaporation and keeping cells wet even under ultra-high vacuum. Besides, the high electrical conductivity of graphene compensates the charging effects during analysis. ToF-SIMS images in this study were obtained using ToF-SIMS 5 (ION-TOF GmbH) equipped with liquid metal ion gun (LMIG) [2,3] and analyzed both positive and negative ion modes and about 1000 specimen-related spectra were obtained from A549 lung carcinoma cell. Thus, we obtain various lipid SIMS images from cell membrane through a graphene layer without cracking.

Major limitations of applying mass spectrometry imaging techniques such as SIMS to biomedical researches are due to harsh bio-sample preparation including freezing, matrix addition and drying. The possibility that secondary molecular ions can be sputtered through a single layer graphene from wet cells will open innovative applications of mass spectrometry imaging of wet cells to various biomedical research areas.

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BI-TuP-11 Behavior of Shewanella Oneidensis MR-1 in a Sulfur and Zinc-Rich Medium and its Applications for Biosensing and Biomaterials*, **James Rees**, S Sawyer, Y Gorby,* Rensselaer Polytechnic Institute

An increasing focus of current microbiology research is the fact that some strains of bacteria, called dissimilatory metal-reducing bacteria (DMRB), are capable of utilizing certain metallic ions as terminal electron acceptors in their metabolic processes. One strain in particular, Shewanella oneidensis MR-1, can reduce ions of iron, lead, arsenic, and uranium, among others. Under anaerobic conditions it has also been shown to reduce sulfur compounds, nitrates, and chromates. The cultivation of DMRB under controlled conditions therefore has significant implications for the low-energy, room-temperature synthesis of metal sulfide and/or metal oxide semiconductors. Furthermore, Shewanella and other DMRB can form biofilms that interact electronically with solid-phase minerals in their environment. For this reason there exists a potential to grow DMRB directly into porous substrates in order to create biosensors that are capable of producing electrical signals that provide information about metal ion concentration in water as well as a range of other water quality variables.

I will highlight my recent work exploring the behavior of Shewanella oneidensis MR-1, in a medium rich in both zinc and thiosulfate ions. I have grown Shewanella bacteria in a three-electrode system and used a potentiostat to hold the system at a fixed DC voltage during cultivation while also measuring current output. After completing the cultivation step, I have used cyclic voltammetry and electrochemical impedance spectroscopy to characterize the DC and AC current-voltage dynamics of the system, which can reveal the reduction-oxidation activity of key bacterial proteins. In the second experiment, I have grown Shewanella bacteria under both aerobic and anaerobic conditions in media rich in zinc and thiosulfate ions and used scanning electron microscopy and energy dispersive microscopy to characterize the minerals that precipitate within the batches. I compare results from a minimal medium containing only the zinc and thiosulfate sources to a more traditional Shewanella medium containing various vitamins, minerals and other nutrients to support growth. I also compare the inoculated batches to sterile control batches containing no bacteria in order to infer the effect that the bacteria have on mineralization in their environment. Finally, I use confocal microscopy to explore the fluorescence behavior of the precipitates generated in both inoculated and sterile batches.

Energy Harvesting & Storage
Room Naupaka Salon 1-3 - Session EH-TuP

Energy Harvesting and Storage Poster Session

Moderator: Satoshi Ishii, National Institute for Materials Science

EH-TuP-1 Oxygen Vacancies Boost δ-Bi_2O_3 as High-Performance Electrode for Rechargeable Aqueous Batteries*, **TingTing Qin**, W Zhang,* State Key Laboratory of Automotive Simulation and Control, and School of Materials Science & Engineering, and Electron Microscopy Center, and International Center of Future Science, Jilin University, Changchun 130012, China

Metal oxides as electrode materials are of great potential for rechargeable aqueous batteries. However, they suffer from inferior cycle stability and rate capability because of poor electronic and ionic conductivities. Herein, taking vertically-orientated Bi_2O_3 nanoflakes on Ti substrates as examples, we found that δ-Bi_2O_3 electrode with plenty of intrinsic positively-charged oxygen defects have shown remarkably higher specific capacity (264 mAh g^{-1}) and far superior rate capability than that of α -Bi_2O_3 with less oxygen vacancies . Through pinpointing the existence form and the role of oxygen vacancies within the electrochemical processes, we demonstrate that oxygen vacancies in δ-Bi_2O_3 serve as central entrepots collecting OH^- groups *via* electrostatic force effect, which has boosted the oxidation reaction and enhanced the electrochemical properties. Besides, oxygen vacancies can largely facilitate electronic conductivity. Our work merited an excellent Bi_2O_3 negative electrode material via giving full play to the role of oxygen vacancies in electrochemical energy storage.

EH-TuP-3 Novel Cathode Nanomaterials and Electrolytes for Al-ion Batteries*, **Nicolò Canever,*** Victoria University of Wellington, New Zealand*; N Bertrand,* Ecole Nationale Supérieure de Chimie de Clermont-Ferrand, SIGMA Clermont, Aubière,France*; T Nann,* Victoria University of Wellington, New Zealand

Battery-based energy storage could be a useful tool for transitioning to a fully renewable-based energy economy. Current battery technologies, however, often lack the cost-effectiveness [1] and safety [2] requirements necessary for large-scale grid energy storage applications. Aluminium-ion batteries (AIBs) are a very promising alternative to Lithium-based systems, thanks to the low cost, non-flammability, and three-electron redox chemistry of aluminium. [3] AIBs could, in principle, offer better cost-effectiveness, energy density [4] and safety, [5] than currently available energy storage technologies. This poster deals with the investigation of new electrode nanomaterials and electrolyte systems for Al-ion batteries, with the aim of improving the performance and cost-effectiveness of AIBs, and facilitate their commercial feasibility.

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EH-TuP-4 Study of Charge Transfer across C_{60}/BCP and BCP/Ag Interfaces Using Core-Hole Clock Spectroscopy*, **Tetsuya Miyazawa,*** SOKENDAI, Japan*; K Ozawa,* Tokyo Institute of Technology, Japan*; K Kanai,* Tokyo University of Science, Japan*; T Sakurai,* Tsukuba University, Japan*; K Mase,* KEK, Japan

Electronic properties at organic/metal and organic/organic interfaces affect the efficiencies of organic electronic devices such as organic solar cells, perovskite solar cells, and organic field effect transistors. Peuman *et al.* have found that the conversion efficiency of the organic solar cell is improved when bathocuproine (BCP) is inserted as buffer layer between the organic molecule of acceptor and negative electrode [P. Peuman *et al.*, Appl. Phys. Lett. **76**, 2650 (2000).]. In order to reveal the role of buffer layers, we investigated C_{60}/BCP and BCP/Ag layered systems by resonant photoelectron spectroscopy and X-ray absorption spectroscopy. A core-hole clock analysis was carried out to examine transfer times of an electron from C_{60} to BCP and that from BCP to Ag. The sample was prepared by the procedure that monolayer of BCP was deposited on Ag thin film and then monolayer of C_{60} was deposited on the BCP. The charge transfer times from LUMO+1 of BCP to Ag and C_{60} to BCP were calculated to be 2.5 fs and less than 60 fs, respectively. In the photoelectric conversion of organic solar cells, electrons generated by exciton separation transfer from organic molecule of acceptor to negative electrode. These results suggest that ultrafast charge transfers across C_{60} to BCP and BCP to Ag are one of the role of buffer layers to improve conversion efficiency of organic solar cells.

EH-TuP-6 Structure and Optical Properties of HfO_2-based Thermal Emitter Films for Thermophotovoltaic Energy Conversion Devices*, **Gregory Abadias**, Y Metayrek, A Michel, J Drevillon,* Institut Pprime, CNRS-Université de Poitiers, France

One of the key points for designing high-efficiency thermophotovoltaic (TPV) systems is to match the spectral emission of the radiator with the spectral range where photons are converted into electron-hole pairs inside the photovoltaic device. Recent studies have shown the potential offered by photonic crystals made of metal/dielectric stack of layers acting as Fabry-Pérot cavity, ensuring spectral selectivity to the emitter. Another material requirement is thermal stability in order to keep the same spectral emission at the operating temperature of the radiator. The Mo/HfO_2 system is a promising candidate material in this respect, as recently reported by Blandre *et al*. [1].

In this work we investigate the synthesis by magnetron sputtering of W/HfO_2 four-layer films for TPV applications. The individual layer thicknesses were optimized based on fluctuational electrodynamics calculations of thermal emissivity of one-dimensional layered media. Prior to the fabrication of the multilayer stack, the structure and optical properties of the transparent HfO_2 layer were investigating as a function of process parameters: substrate temperature T_s and O_2 flow rate. Films were characterized by X-ray reflectivity, X-ray diffraction and wavelength dispersive spectroscopy. The optical indices (*n* and *k*) were measured experimentally from variable angle spectroscopic ellipsometry in the visible and mid-infrared (MIR) range (up to 35 µm). Results show that dense, crystalline HfO_2 layers with monoclinic structure can be formed by reactive magnetron sputtering at room temperature with optical index *n* close to 2.1 at 550 nm; however, crystallinity was improved by increasing T_s up to 500°C, with little variation on *n* and *k*. In the MIR, the optical properties of HfO2 were consistent with the data reported by Bright *et al*. [2].The optical reflectance of the W/HfO_2 stack was measured using spectrophotometer and a good agreement with theoretical predictions was found, attesting of the potential of this system for TPV emitters.

EH-TuP-7 Bimetallic Cobalt-Iron Hydroxide Encapsulated in Organic Ligand Derived Carbon Layers as an Efficient Electrocatalyst for Oxygen Evolution Reaction*, **Jian Du**, F Li,* Dalian University of Technology, China

Water electrolysis as one of the prospective approach to produce hydrogen is limited by the anodic oxygen evolution reaction (OER) due to its sluggish kinetics. Considering the practical application, the development of highly efficient non-noble OER catalysts is essential. Among the reported low-cost electrocatalysts, CoFe-based oxides or hydroxides are intriguing owing to the rich redox chemistry. However, the severe aggregation and intrinsically poor electronic conductivity hinder their electrocatalytic performance. Hybridizing cobalt-iron oxides or hydroxides with carbon materials can not only enhance the conductivity of the catalyst, but also facilitate the uniform distribution of metal species within carbon matrix, thus improving the electrochemical performance towards OER. In view of this, we report here the bimetallic cobalt-iron hydroxide encapsulated in carbon layers derivedfrom organic ligand (Schiff base) via hydrothermal carbonization. In alkaline media, Co Fe/C loaded on GC electrode delivers a current density of 10 mA cm^{-2} at an overpotential of 260 mV and exhibits a low Tafel slope of 45.2 mV dec^{-1} as well as excellent durability. The remarkable OER performance outperforms those of CoFe-based electrocatalyst in the literature.

Keywords: Oxygen evolution reaction, cobalt-iron hydroxide, organic ligand, electrocatalyst

Results

As shown in Figure 1, the $Co_{1.2}Fe/C$ delivers a current density of 10 mA cm^{-2} at an overpotential of 260 mV and exhibits a low Tafel slope of 45.2 mV dec^{-1} as well as excellent durability in 1M KOH solution.

Figure 1 (a) LSV curves of GC, $Co_{1.2}Fe$ and $Co_{1.2}Fe/C$; (b) Tafel plots of $Co_{1.2}Fe$ and $Co_{1.2}Fe/C$; © Chronopotentiometric measurement of $Co_{1.2}Fe/C$ at 10 mA cm^{-2}. All tests were carried out in 1 M KOH.

Conclusions

The $Co_{1.2}Fe/C$ exhibits excellent OER performance in alkaline media, which can be ascribed to the following factors: 1) the homogenous distribution of metal hydroxide within carbon matrix inhibits the aggregation of the active nanoparticles; 2) the excellent electronic conductivity enables fast electron transport during the OER process; 3) the synergetic effect between the $Co_{1.2}Fe$ hydroxide and carbon species also contributes to the improvement of the electrochemical performance.

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EH-TuP-8 Anchoring Water Oxidation Catalysts on a DS-PEC via Pyridine Group for Light-Driven Water Splitting*, **Yong Zhu**, F Li,* Dalian University of Technology, China*; L Sun,* KTH Royal Institute of Technology, Sweden

Dye-sensitized photoelectrochemical cell (DS-PEC) water splitting into hydrogen and oxygen is a potential approach to realize the conversion solar energy to chemical energy efficiently. Ru(bda) (bda is 2,2`-bipyridine-6,6`-dicarboxylate) is one of the most efficient water oxidation catalysts in DS-PEC. Traditionally, Ru(bda) have been anchored onto the dye-sensitized photoanode by modifying phosphoric acid or carboxylic acid groups. These complexes can reduce the overpotentials of water oxidation and exhibit highest turnover. However, the efficiency of the entire system is inhibited due to the strong recombination effect of electrons injected into theTiO_2 bulk on the photosensitizer and catalyst in the oxidized state. Herein, we have replaced the anchor group of the water oxidation catalysts Ru(bda) (bda is 2,2′bipyridine-6,6′-dicarboxylate) from phosphoric acid to pyridine. Time-resolved transient absorption spectroscopy demonstrates that the pyridine anchor group have effect of inhibiting electron recombination. The photocurrent densities of 1.5-1.8 mA/cm^2 were achieved and produced an incident photon to current efficiency (IPCE) of 25.5% at 450 nm. Under pH=5.8 under 100mW/cm^2 (>400nm) illumination.

EH-TuP-9 On the Thermal Characterization of Heptane-Isooctane Mixtures*, Adrian Bedoya*, *E Marin, S Alvarado,* Cicata Legaria, Mexico

The thermal transport properties of heptane-isooctane mixtures in the liquid phase at room temperature and atmospheric pressure were measured and calculated. The thermal conductivity, k, was measured using the transient hot-wire (HW) method, and the thermal effusivity, e, was determined by the front photopyroelectric (FPPE) technique. Then, the thermal diffusivity, α, and the volume specific heat capacity (heat capacity per unit volume), C, were calculated using the well-known relationships $\alpha = (k/e)^2$ and $C = e^2/k$, respectively. We show that a correlation between these parameters and octane number exists, and that the obtained thermal parameters proved to be sensitive to detect molecular associations in binary hydrocarbon liquid mixtures. We also report about the thermal conductivity of mixtures of n-alkanes vapors and air showing that almost similar values are obtained for heptane and isooctane, so that octane number rating using the well-established binary mixtures of these substances becomes impossible with thermal properties measurements in the gas phase.

EH-TuP-10 A steady-state thermoreflectance method to measure thermal conductivity*, Jeffrey Braun*, *D Olson, J Gaskins, P Hopkins,* University of Virginia

We demonstrate a steady-state thermoreflectance based optical pump-probe technique to measure the thermal conductivity of materials using a continuous wave laser heat source. The technique works in principle on leaving a pump laser on long enough to induce a steady-state temperature rise in a material. A probe beam is then used to detect the resulting change in reflectance, which is proportional to the change in temperature of the sample. Varying the power of the pump beam to induce larger temperature rises, Fourier's law is used to determine the thermal conductivity. We show that this technique is capable of measuring the thermal conductivity of a wide range of materials having thermal conductivities ranging from 1 to > 2000 W m−1K−1, in excellent agreement to literature values. With a measurement length scale capable of reaching <10 microns, this techniques is capable of measuring both bulk material and films.

Nanomaterials
Room Naupaka Salon 1-3 - Session NM-TuP

Nanomaterials Poster Session I

Moderator: Shintaro Fujii, Tokyo Institute of Technology

NM-TuP-1 alginate based Nanocomposite for Microencapsulation of Probiotic: Effect of Cellulose Nanocrystal (CNC) and Lecithin*, Monique Lacroix,* INRS-Institut Armand-Frappier, Canada

Lactobacillus rhamnosus ATCC 9595 were encapsulated in alginate-CNC-lecithin microbeads for the production of nutraceutical microcapsules. The concentration of CNC and lecithin in alginate microbeads was optimized by monitoring the viability of *L. rhamnosus* after stabilization of the microbeads by freeze-drying. Results showed that alginate microbeads (AC-0) reduced by 0.95 log CFU/g whereas addition of 13 wt% CNC in alginate microbeads (AC-3) reduced ($P > 0.05$) by 0.01 log CFU/g of bacterial viability after freeze drying. Incorporation of 2 wt% lecithin in alginate-CNC microbeads (ACL-1) also revealed a protective effect during free drying same as alginate-CNC microbeads (AC-3). The compression strength of the freeze-dried ACL-1 microbeads improved 40% compared to alginate microbead alone. Swelling studies revealed that addition of CNC and lecithin in alginate microbead decreased (around 47%) the gastric fluid absorption but increased the dissolution time by 20 min compared to alginate microbeads (A-0). During complete transition through the gastric passage, the viability of *L. rhamnosus* in dried ACL-1 microbeads was 52% higher as compared to *L. rhamnosus* encapsulated in A-0 based beads. The viability of *L. rhamnosus* was also evaluated during storage at 25 and 4˚C. It was found that at 25 and 4˚C storage conditions, the viability of *L. rhamnosus* encapsulated in ACL-1 microbeads decreased by 1.23 and 1.08 log respectively, whereas the encapsulation with A-0 microbeads exhibited a 3.17 and 1.93 log reduction respectively.

NM-TuP-2 In-situ Low Energy Electron Microscopy at Near Ambient Pressures*, Thomas Schulmeyer,* SPECS-TII, Inc.

Low-energy electron microscopy (LEEM) is a spectromicroscopy technique, which allows the study of dynamic processes at surfaces and interfaces, such as thin-film growth, surface reactions, and phase transitions. With the FE-LEEM P90 from SPECS, which is based on the instrument design by Rudolf Tromp from IBM, lateral and energy resolution of below 5 nm and 250 meV, respectively, can be achieved. Depending on the excitation source and the settings on the instrument a variety of different imaging modes are possible: mirror electron microscopy, low energy electron diffraction (LEED), phase contrast imaging, reflectivity contrast, dark field imaging and bright field imaging, as well as photoelectron emission microscopy and spectroscopy. As a new development the technical capabilities of LEEM and PEEM have been extended towards near ambient conditions by developing a special objective lens concept and sample chamber geometry. This enables the analysis of materials and devices under near ambient conditions and even in situ during operation. For this a Laser heater allows for sample temperatures up to 800°C during the measurements. The technical realization will be presented in detail. Furthermore experimental results will be shown on Graphene, Silicon under Nitrogen atmosphere. First results from real surface reactions will be discussed.

NM-TuP-4 High-performance Nanofibrous $LaCoO_3$ Perovskitecathode for Solid Oxide Fuel Cells Fabricated via Chemically assisted Electrodeposition*, Seung-Bok Lee,* Korea Institute of Energy Research (KIER), South Korea*; S Rehman,* Korea Institute of Energy Research (KIER),South Korea, South Korea*; T Lim, J Hong, R Song,* Korea Institute of Energy Research (KIER), South Korea

In this study, a new method is developed for the fabrication of nanofibrous $LaCoO_3$ (LCO) perovskites as cathodes (oxygen electrodes) for solid oxide fuel cells (SOFCs). The proposed method involves chemically assisted electrodeposition (CAED) of mixed metal hydroxide onto a carbon nanotube (CNT) template, followed by a low-temperature heat-treatment process. The CNT template is first fabricated on porous zirconia-based ion-conducting scaffolds (ICS) by catalytic chemical vapor deposition (CCVD) of C_2H_4. Perovskite-type LCO is then fabricated on the CNT template by CAED process of mixed La–Co hydroxide combined with thermal conversion of hydroxide to perovskite oxide. The method proposed here allows for the fabrication of LCO perovskites with a unique nanofibrous structure at reduced temperatures (900 C), while avoiding the formation of pyrochlore phases (e.g., $La_2Zr_2O_7$), which are typically observed during conventional high-temperature sintering processes of $LaCoO_3$ with zirconia-based electrolytes. The new method also provides the precise control needed to achieve desired oxide loadings without the need for repeated deposition-annealing processes. The anode-supported SOFCs with nanofibrous LCO cathodes on zirconia and ceria scaffolds show high and stable electrochemical performance of 0.95 and 1.27 W cm^2, respectively, at 800 C. In addition to the absence of insulating pyrochlore phases, the unique nanostructure of the LCO cathode is believed to play a beneficial role in improving the electrochemical properties by providing a large number of active reaction sites and by facilitating mass transport through the porous nanofibrous structure.

NM-TuP-5 Analysis Insitu of Diffusion-nucleation in Multilayer InAs/GaAs Quantum Dots*, Christian Mercado-Ornelas,* *A Belio-Manzano, L Espinosa-Vega,* Center for the Innovation and Application of Science and Technology, Universidad Autónoma de San Luis Potosí, Mexico*; V Mendez-Garcia,* Center for the Innovation and Application of Science and Technology, Universidad Autónoma de San Luis Potosí, México

In(Ga)As semiconductor quantum dots (QDs) as low dimensional materials have been continuously studied due their interest in their optical and optoelectronic properties, from which have improved significantly the performance in nano-devices.[1] However, there are still some challenges to be overcome in order to reach the successful implementation of the QDs structures in common devices, that is the case of the vertical alignment in multilayer . In the present work, it is shown samples InAs/GaAs self-assembled QDs samples grown by MBE. The method implemented to synthesize self-assembled QDs is defined as Stransky-Krastanov growth mode, which is well-known that is based on the lattice mismatch between two different materials, recalling for the heterostructure of InAs/GaAs mismatch which is about 7%, this propitiates an increase of strain energy at the interface given as a result the formation of nanoislands. Therefore it is established that this mechanism is completely governed by strain.[2] A fist set of QDs heterostructures proposed in this work were grown on GaAs (100). Growing firstly a 150 nm thick buffer layer, continuing from three up to five multilayers of InAs QDs capped each layer with 10 nm of GaAs at low temperature. Finally, the structures were ended with 200 nm of GaAs. During each one of the growth stages were monitored by RHEED, taking a main importance in the QDs layers.

The transition curves from a 2D surface to the 3D nanoislands were monitored taking the RHEED 002 diffraction spot intensity during the InAs nucleation. Thus, it was performed a mathematical model to analyze the growth procedure in the multilayers of QDs where it was found that the critical thickness (H_c) decreases as the number of deposited QDs layers increased, such results are explained due to the accumulated strain for successive layers. On the other hand, in the same model proposes an estimation in the adatoms diffusion length, results that remained almost constant, suggesting a similar QDs density in each layer. The vertical alignment of the QDs is a well-known process, associated to the creation of low-strain nucleation centers above each one of the capped dots. Therefore, the similarities in the QDs density in the stacked layers should be expected, which explains the non-variation of adatoms diffusion length.

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NM-TuP-6 Analytical Model Proposal for the 2D-3D Growth Mode Transition in the Synthesis of InAs/GaAs Quantum Dots

Christian Mercado-Ornelas*, L Espinosa-Vega, E Eugenio-Lopez, I Cortes-Mestizo,* Center for the Innovation and Application of Science and Technology, Universidad Autónoma de San Luis Potosí, Mexico*; V Mendez-Garcia,* Center for the Innovation and Application of Science and Technology, Universidad Autónoma de San Luis Potosí, México

The synthesis and properties of low dimensional materials have been studied to improve significantly the performance in nano-devices. This is the case of semiconductor quantum dots (QDs), which have become a topic of interest due to their application in new electronic and optoelectronic devices. Thus, the development of analytical tools that could assist in describing the QDs growth becomes of crucial importance. In the present work, an analytical model to study the diffusion of the adatoms related with the nucleation of the QDs is reported.

As a starting point, it is schemed that along the 2D-3D transition the QDs self-assembling process is controlled with adatoms diffusion mechanisms, and so the surface density *r* of diffusing species evolves according to $\partial\rho/\partial t=D\nabla^2\rho$, where *D* is the diffusion coefficient. Considering an in-plane isotropic media the equation can be solved in cylindrical coordinates, and ρcan be expressed as $\rho(r,\ \phi,\ t)=\sum X_j(r,\ \varphi)e^{-K_m t}$, where $X_j(r,\ \varphi)$ is the 2D diffusion coordinate and K_m is termed as the rate constant which is proportional to *D*.

In order to analyze the QDs nucleation, the RHEED 002 diffraction spot was experimentally monitored in order to get for 2D-3D transition curves of the strained system InAs/GaAs. This RHEED spot intensity in particular accounts for the scattered intensity related to the islands nucleation. According to the kinematics theory, the intensity can be written as:

$$I(t)\propto|A(q)|^2\,|(1-e^{i\mathbf{q}d})^{-1}+\sum\theta_j(t)e^{-ij\mathbf{q}d}|^2$$

Here ***q*** is the scattering vector, *d* is the layer spacing, *q*(*t*) is the time-dependent coverage of the nth layer and *A*(*q*) is the scattering amplitude. These terms are related to ρ(r, ϕ, t). Considering the first order of scattered intensity equation as a solution for the adatoms diffusion, reaching an equilibrium 2D state *I*(*t*) can be expressed as $I(t)=|(1-e^{-K_m t})|$. Since the QDs nucleation process takes place not before the critical thickness H_c has been reached, *I*(*t*) must be rewritten as follows:

$$I(t)=|1-e^{-K_m(t-H_c)}|$$

This model was proven during the MBE growth of InAs QDs on GaAs (100) substrates. By fitting *I*(*t*) to the RHEED experimental intensity curves it was found that H_c did not present a significant dependence on the buffer layer growth temperature, T_{BL}. However, the K_m parameter decreased from 6.01 to 5.35 as T_{BL} increased. Since K_m is proportional to the surface adatoms diffusion, it means that QDs density increased as T_{BL} increased. Atomic force microscopy (AFM) measurements corroborated such information and consequently validated our theoretical model.

NM-TuP-7 Fano Resonances at Interference of Electron Waves in Geometrically Inhomogeneous Semiconductor 2D Nanostructures

Victor Petrov*,* Institute of Radio Engineering and Electronics RAS, Russian Federation

Fano resonances (FRs) in a semiconductor 2D nanostructure (NS) geometrically inhomogeneous along the propagation of the electron wave (EW) (the x-axis) are theoretically investigated. As is known, FRs [1] arise from interference of EWs propagating along two channels:one of them in the continuous energy spectrum, and the other - a quasistationary state against the background of this spectrum. The considered symmetric along the z-axis NS consisted of three sequentially arranged rectangular quantum wells (QWs) in which the motion of the particle was limited along the z-axis:QW_1 of width L_1 at x < - a, QW_2 of width L_2 at - a < x < a and QW_3 of width L_1 at x > a. It was assumed that $L_1 < L_2$. In this case, the potential along the x-axis abruptly changed at the points x = - a and x = a, and in each QW a series of quantum-size subbands (QSSs) was formed. Thus the energy QSSs $E_{(1),n}$ in QW_1 and $E_{(3),n}$ in QW_3 was the same for the same width of this QWs. In a wide QW_2 the distance between QSSs $E_{(2),m}$ was less than the distance similar number of QSSs in QW_1 and QW_3 (figures 1,2,3 in round brackets indicate the number of the QW, and n and m – number of QSSs, respectively, in QW_1, QW_3 and QW_2). Therefore, in QW_2 formed longitudinal rectangular QW along the x- axis of width 2a, due to the different energy position of the QSSs in QW_1, QW_3 and QW_2. These QWs also formed QSSs $E_{x(2),t}$ due to the restriction of motion in them along the x-axis. These QSSs were the quasistationary states providing the formation of FRs in the considered NS. We calculated the dependence of the NS transmission coefficient $|T(Ex)|^2$ for the electron wave of the unit amplitude propagating from the QW_1 along the lower QSS $E_{(1),1}$,on its longitudinal energy E_x in the range $E_{(1),1}< E_x< E_{(1),2}$. The widths of the QWs L_1 and L_2 in the symmetric on the z-axis NS were chosen so that in this range of variation of E_x in QW_2 there exist at least two longitudinal QWs of different depths with quasistationary states: $QW_{x,1}$, formed by the QSSs $E_{(1),2}$, $E_{(2),2}$ and $E_{(3),2}$, and lying higher in energy $QW_{x,2}$, formed by the QSSs $E_{(1),2}$, $E_{(3),2}$ and $E_{(3),2}$. In this case, the wave propagation to QW_2 was possible only through this overlying QSS, since the transition from the QSS $E_{(1),1}$ in QW_1 to the $E_{(2),2}$ QSS in QW_2 was forbidden by the symmetry of the NS. At the same time, the wave propagation in the channel in the continuous spectrum and in the quasistationary state with the corresponding energy was possible in QW_2. Further, the interfering waves propagated in QW_3 also along one lower QSS with energy $E_{(3),1} = E_{(1),1}$.Thus, when changing E_x, depending on $|T(Ex)|^2$, FRs appeared.

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NM-TuP-8 Surface Nanostructures Composed of Thiolated Cyclodextrin/Au and Fe Species: Gas- and Liquid-Phase Preparation

S Kotorova, Institute of Nuclear and Physical Engineering, FEI STU, Slovakia*;* ***Monika Jerigova****,* Comenius University, Bratislava, Slovakia*; D Lorenc,* International laser center, Bratislava, Slovakia*; M Prochazka,* Polymer Institute, Slovak Academy of Sciences, Bratislava, Slovakia*; D Velic,* Comenius University, Bratislava, Slovakia

Supramolecular surface nanostructures have application potential as functional devices. Studied system consists of a host molecule of monothiolated β-cyclodextrin chemically adsorbed on an Au surface through a S–Au bond (assigned as Au-S-CD) and of Fe species incorporated as the guest. Secondary-ion mass spectrometry (SIMS) is used to study the formation and composition of these surface supramolecular nanostructures.

The Fe species were prepared by pulsed laser ablation in water and thermal effusion in vacuum. Using laser ablation in water, the solution of Fe species was dropped on Au-S-CD. The relevant mass peaks were observed at 1227 m/z, 1243 m/z and 1260 m/z and were assigned to $C_{42}H_{68}O_{34}SNa\text{-}Fe^+$, $C_{42}H_{68}O_{34}SKFe^+$, $C_{42}H_{68}O_{34}SNa\text{-}FeO^+$ and $C_{42}H_{68}O_{34}SK\text{-}FeO^+$, which can be interpreted as supramolecular complexes with Fe as $C_{42}H_{68}O_{34}SNa\text{-}Fe$ and $C_{42}H_{68}O_{34}SK\text{-}Fe$ or adducts with FeO as $C_{42}H_{68}O_{34}SNa\text{-}FeO$ and $C_{42}H_{68}O_{34}SK\text{-}FeO$, respectively.The comparison of isotope distributions with the experimental data supported the presence of a supramolecular host–guest complex between Au-S-CD and the Fe species and an adduct between Au-S-CD and FeO. The Fe species were presumably the first product of the ablation, so the formation of a supramolecular CD-Fe complex was preferential. Presumably, the second product of the ablation were the FeO species. Thermal effusion, even with a cooled surface, was negative with respect to the complex observation, no mass peaks corresponding to supramolecular complexes were observed. Nevertheless, a glucopyranose unit of the CD-S molecule and a variety of molecular fragments corresponding to CD-S associated with Fe and FeO were observed. One can assume that supramolecular complex formation is in this case also dependent on the surface diffusion of the Fe species. Since the surface diffusion of the Fe species at this low temperature might be minimized, the probability of complex formation might be close to zero.

This work was supported by VEGA 1/0400/16 .

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NM-TuP-9 Controlled Pore Arrangement of Silicon Nanoparticles Having Mesoporous Structure*, **Taisuke Kuga, K Sato,* Tokyo Denki University, Japan

In recent years, semiconductor nanoparticles (NPs) having mesopores have been applied in a wide range of environment, energy and medicine fields, such as sensors, rechargeable batteries and drug delivery systems. The NPs can produce inexpensively by using electrochemical etching. However, they are confronting some serious problems, such as complicated preparation techniques and low production yield of mesopores. Therefore, it is necessary to develop new synthesis approaches for realization of facile preparation of the NPs with mesopore structures and large-scale production of the mesopores. We have prepared silicon nanoparticles (SiNPs) with mesopore structures using an inexpensive chemical route with good productivity. In this presentation, we propose a new way to fabricate SiNPs with mesopore structures by simplified procedures based on a chemical approach, and investigate the size distribution, depth and density of the mesopores by scanning electron microscopy (SEM). The features of our synthesis technologies are to adopt the simplified synthesis system in which only commercially available SiNPs with mean diameter of approximately 100 nm and redox agent were used. The size, depth and density of the mesopores on the SiNP surfaces strongly depends on the redox reaction time. When the redox reaction time was 1 min, the shallow mesopores with mean size of approximately 24 nm were formed on the SiNP surfaces. As the redox reaction time increased from 1 min to 5 min, the depth of the mesopores deepened without change of mean size. SEM images of SiNPs with mesopores obtained by redox reaction time for 10 min were shown in Figure 1. The mesopores with mean size of approximately 29 nm were densely formed on the SiNP surfaces, and also their depths became increasingly deeper. Therefore, our suggested synthesis technologies can provide a new chemical route for high production yield of mesopores.

NM-TuP-10 Nanobiosensor Comprising Conductive Polymer Enclosed with Polymer Vesicles for Selective Detection of Influenza A Virus*, **Geunseon Park,* Yonsei University, Republic of Korea*; H Kim,* Korea University, Republic of Korea*; J Lim, C Park, S Haam,* Yonsei University, Republic of Korea

Nanobiosensor has been selected as a method for detecting wide range of pathogens to prevent pandemic emergence. As one of promising platform, conductive polymer based nanobiosensor has a distinct advantage in the way that its ability to sensitive and rapid detection. In this study, we designed a detection system which is conductive poly aniline based on polymersome conjugated with peptide for specific recognition of influenza A virus. We synthesized poly aniline polymerized within a polymersome consisting of methoxy polyethylene glycol-block- polyphenylalanin co-polymer (mPEG-b-pPhe). Then we conjugated the polymersome with peptide binding to hemagglutinin located on the surface of influenza virus. In the presence of Influenza virus, the nanoparitlce aggregated with the virus, exposing absorption wave length change. These results indicate that this nanobiosensor could be a potential candidate in terms of detecting influenza virus.

NM-TuP-11 Efficient Antiviral Delivery Polymersomes by Optimization of Surface Density of Cell-targeting Groups for Virus Treatment*, **Chaewon Park, H Chun,* Yonsei University, Republic of Korea*; M Yeom, H Kim,* Korea University, Republic of Korea*; J Lim,* Yonsei University, Republic of Korea*; W Na,* Korea University, Republic of Korea*; G Park,* Yonsei University, Republic of Korea*; A Kang,* Korea University, Republic of Korea*; D Yun,* Yonsei University, Republic of Korea*; J Kim,* Yonsei University, Republic of Korea, Republic of Korea*; D Song,* Korea University, Republic of Korea*; S Haam,* Yonsei University, Republic of Korea, Republic of Korea

Influenza A virus (IAV), which causes one of the most contagious diseases is a global health concern, and is responsible for seasonal epidemics and pandemics. Despite laudable advances in antiviral agents and drugs, the vast majority of them have shown limited efficacy due to non-specificity and low viability in physiological or endosomal environment, especially in the case of intracellular drug. A nano platform, consisting of phenylboronic acid (PBA) pendant group polymer which has sialic acid-targeting property, gained greater access to the intracellular space transporting antivirals within the host cell. Amphiphilic copolymers made of pPhe-b-mPEG-PBA formed polymersomes which encapsulated hydrophilic antiviral agents in the core and hydrophobic drugs in the exterior layer. Combination of antiviral drug delivery using amphiphilic nanocarrier and cell-targeting functional group gives a better chance to improve transfection and intracellular distribution efficiency of therapeutic substances.

NM-TuP-12 Photovoltaic Performance of Inorganic/Organic Hybrid Solar Cells using Boron-doped Silicon Nanoparticles*, **Kuniaki Furuya, K Sato,* Tokyo Denki University, Japan

Solar cells using silicon nanoparticles (SiNPs) have attracted attention as one of highly-efficient cells because they not only widen the absorption bands of solar light but also enable the light harvesting via excitonic energy transfer [1]. In order to enhance the transfer efficiency of photogenerated charge carriers between the SiNPs region, we have fabricated boron (B)-doped p-type SiNPs of single nanometer in size by combining thermal diffusion at high temperature with redox reaction of the surface regions of the Si powders (100 nm in size) in etchant containing hydrofluoric acid/nitric acid. Additionally, we have also prepared the inorganic/organic hybrid solar cells consisting of the B-doped p-type SiNPs and poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) so as to reduce the production cost. In such hybrid solar cells, the arrangement of the B-doped p-type SiNPs and PEDOT:PSS in the active layer is critical to improve the power conversion efficiency (PCE). In this presentation, we focus on the position of the B-doped p-type SiNPs, such as the stacking structures consisting of n-type Si substrate/blend layer of B-doped p-type SiNPs and PEDOT:PSS and the stacking structures consisting of n-type Si substrate/B-doped p-type SiNPs/PEDOT:PSS, and discuss the photovoltaic performance of these inorganic/organic hybrid solar cells. The *J-V* characteristics of the hybrid solar cells consisting of n-type Si substrate/blend layer of B-doped p-type SiNPs/PEDOT:PSS (cell 1) and n-type Si substrate/B-doped p-type SiNPs/PEDOT:PSS (cell 2) were shown in Figure 1. The photovoltaic performance of these hybrid solar cells strongly depends on the arrangement of the stacking structures. The cell 1 constructed from the blend layer of B-doped p-type SiNPs/PEDOT:PSS obtained PCE of 3.85% with open circuit voltage (V_{oc}) of 0.36 V, short circuit current density (J_{sc}) of 26.5 mA/cm^2 and fill factor (FF) of 0.40. The value of the PCE increased to 5.27% for the cell 2 stacked individually the B-doped p-type SiNPs and the PEDOT:PSS, showing the V_{oc} of 0.34 V, J_{sc} of 29.6 mA/cm^2 and FF of 0.52. This result demonstrates that the control of arrangement of B-doped p-type SiNPs is beneficial for obtaining the higher PCE because of the efficient transport of the charge carriers between the NPs region.

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Plasma Processing
Room Naupaka Salon 1-3 - Session PS-TuP
Plasma Processing Poster Session

Moderator: Martin Nieto-Perez, CICATA Queretaro

PS-TuP-1 Synthesis of TiO2/CuOx Thin Film Composites by the Simultaneous Ablation of Ti and Cu Metallic Targets*, **A. Valeria García-Caraveo,* Instituto Tecnológico y de Estudios Superiores de Occidente, Mexico*; E Camps, E Campos-Gonzalez,* Instituto Nacional de Investigaciones Nucleares, Mexico*; A Perez-Centeno,* Centro Universitario de Ciencias Exactas e Ingenierías, Universidad de Guadalajara, Mexico*; M Santana-Aranda,* Centro Universitario de Ciencias Exactas e Ingenierías, Universidad de Guadalajara*; G Gomez-Rosas, L Rivera,* Centro Universitario de Ciencias Exactas e Ingenierías, Universidad de Guadalajara, Mexico*; D Cardona,* Instituto Tecnológico y de Estudios Superiores de Occidente, Mexico*; J Quiñones-Galván,* Centro Universitario de Ciencias Exactas e Ingenierías, Universidad de Guadalajara, Mexico

Titanium Dioxide (TiO2) is an n-type semiconductor material that has been used for different applications such as photo-catalysis, hydrogen separation and dye sensitized solar-cells. The band gap for TiO2 anatase phase is 3.2 eV, which means that UV light is needed to generate a photo-catalytic reaction. In this work, we proposed to generate a combined system of TiO2 with Copper Oxide (CuOx) to reduce the TiO2 band gap so that the photo-catalytic process can be induced under UV and Visible light.

We present the results obtained for the synthesis of a combined system of TiO2 and CuOx thin films deposited on glass substrates. We used a reactive Pulsed Laser Deposition (PLD) technique with a mixture of argon/oxygen. The produced plasma was diagnosed by means of the time of flight technique using a Langmuir planar probe; the voltage drop across a 20 Ohm resistance was measured and the current was calculated in order to estimate the ion density and its mean kinetic energy, with the aim of having a control on the deposition process.

A Nd:YAG pulsed laser with a wavelength of 1064nm was divided into two equal beams using a beam splitter. Each individual beam was focused on the surface of Titanium (Ti) and Copper (Cu) solid targets respectively for 15 minutes under an argon/oxygen pressure of 20 mTorr. Primarily we obtained an amorphous TiO2 thin film and a CuO thin film, afterwards we deposited a multilayered thin film of TiO2 /CuO/TiO2 and finally a combined system of TiO2 and CuOx by ablating both Ti and Cu targets simultaneously.

The obtained thin films were characterized by X-Ray Photoelectron Spectroscopy (XPS), X-Ray Diffraction (XRD), Raman Spectroscopy, Ultraviolet-Visible spectroscopy (UV-Vis) in order to know the stoichiometry and oxidation phases and Transmission Electron Microscopy (TEM) was used to define the morphology.

Characterization reveals that a TiO2 amorphous phase was deposited in any of the different experiments but Cu reacts in different ways depending on the plasma characteristics, it is shown that we can obtain different Cu oxidation states an even synthesize metallic Cu nanoparticles in a TiO2 matrix.

PS-TuP-2 Study of Carbon Fiber Manufacturing Process by Plasma Oxidation/stabilization and Microwave assisted Carbonization*, **Seok-Kyun Song**, B Kim, M Jung,* Cheorwon Plasma Research Institute, Republic of Korea*; S Lee,* Korea Institute of Science and Technology, Republic of Korea

Carbon fiber has a carbon content of 90~95% or more, and its strength is ten times that of steel. The manufacturing process proceeds with stabilization (chlorination), carbonization of the PAN fiber. In particular, the stabilization process is long-term treatment at high temperature which high cost is incurred. In order to low cost manufacture for carbon fiber, that is need reduction of stabilization process time. For that, we researched the oxidation/stabilization process using atmospheric pressure plasma and e-beam technology.

The atmospheric pressure plasma system developed by CPRI team suggests possibility to reduce oxidation/stabilization process time (from 120 min to 30 min, from 120 min to 10 min by add e-beam technology) and cost. Plasma oxygen radical accelerates the progress of fiber cyclization. After plasma treatment, the surface of oxidized/stabilized fiber had no damage.

In the nitrogen atmosphere, oxidated/stabilized fiber was used for low temperature carbonization of 300 ~ 1000 degrees Celsius, and energy consumption was reduced by directly supplying energy to the heating element near the fiber by the microwave assisted (MWA) method instead of the conventional resistance heating.

It has been suggested that energy can also be reduced by providing microwave assisted (MWA) energy directly to low temperature carbonized fiber for 1000 ~ 1600 degree Celsius high temperature carbonization.

PS-TuP-3 Design and Diagnosis of Atmospheric Microwave Plasma by Transmission Line Resonator*, **Jun Choi**,* Korea Institute of Industrial Technology (KITECH), Republic of Korea

Recently, atmospheric microwave plasmas (AMP) have attracted much attention as promising plasma sources for industrial applications such as material processing, surface treatment and biomedicine [1]. The AMP eliminates the need for a vacuum system and has a long operational time of the electrodes [2]. In this work, a plasma source using a two-parallel-wire transmission line resonator (TPWR) in atmospheric argon is described [3]. The E-field distribution and reflection coefficient of the resonator for the given frequency (~900MHz) are estimated by COMSOL Multiphysics software based on microwave theory to transfer maximum power from power supply to the resonator and enhance the power efficiency. The TPWR-AMP can sustain with low power less than 3 watts. The TPWR is fabricated to investigate the plasma characteristics such as excitation temperature, electron temperature and rotational temperature. The electron excitation temperature was measured by the Boltzmann plot and the rotational temperature was determined by comparing the spectra measurement and simulation of rotational lines of the OH band. The electron density was obtained by Stark broadening with the measurement of emission spectra. The characteristics of the TPWR-AMP shows that the device has the potential to be used effectively and widely in industry.

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PS-TuP-4 Nitridation of SiO_2 by using a VHF (162 MHz) Multi-tile Push-pull Plasma Source*, **You Jin Ji**, K Kim, K Kim, J Byun, S Lee,* Sungkyunkwan University, Republic of Korea*; A Ellingboe,* Dublin City University, Ireland*; G Yeom,* Sungkyunkwan University, Republic of Korea

Nitriding processes of SiO_2 thin film have been applied in various semiconductor device manufacturing. For example, in the fabrication of nanometer scale semiconductor devices, a nitriding process of SiO_2 for a nitride layer applied to gate insulator has become an important process to prevent the penetration of p-type dopant (boron) through the thin gate oxide. Typically, plasma and thermal nitridation methods are used to meet the requirement for the nitride layer. However, the thermal method has a bad influence on the device performance due to the high processing temperatures (600-1500 °C), and the plasma method tends to cause damage on the treated layer due to the ion bombardment and shows a low nitridation percentage in the film due to the difficulty in dissociating nitrogen molecules having a high electron-impact dissociation energy. Very high frequency (VHF; > 30 MHz) plasma is known to dissociate nitrogen molecules more effectively with a high dissociation rate at a low temperature due to a high electron energy tail in the electron energy distribution. Therefore, in this study, the nitridation of SiO_2 was performed to obtain a uniform silicon oxynitride (SiO_xN_y) layer using a VHF (162 MHz) multi-tile push-pull plasma source at room temperature. High nitrogen incorporation (~ 24.51 %) in the SiO_xN_y layer was confirmed by the X-ray photoelectron spectroscopy (XPS) analysis at the optimized nitridation condition. In addition, the EDS in TEM showed that a SiO_xN_y layer was uniformly formed after the nitridation of SiO_2 at the optimized condition. The leakage current of the MOS capacitor that has the SiO_xN_y layer formed by using the VHF (162 MHz) multi-tile push-pull plasma source was measured to be lower than that has the SiO_xN_y layer formed by the conventional CCP (60 MHz) plasma source.

PS-TuP-5 ***Fabrication of SnO Thin Films by Reducing Plasma on Atomic Layer Deposited SnO_2*****, *Jaehong PARK*,** *B PARK, H Kim,* Yonsei University, Republic of Korea

Oxide semiconductors have been intensively investigated in emerging applications, such as thin film transistor (TFT), flexible electronics and solar cell materials, owing to the added functionality using great diversity of materials and structures. There have been numerous studies on n-type semiconductors such as ZnO, SnO_2, and In_2O_3, whereas the research on p-type semiconductors is still ongoing due to the lack of synthesis technology. SnO is a representative p-type oxide semiconductor with wide band-gap and high mobility, but the poor stability of SnO limits the synthesis method to physical vapor deposition (PVD). PVD is difficult to apply in future integrated circuit process with aggressive scaling down and 3D structurization. Atomic layer deposition (ALD) is a promising technique owing to atomic-scale thickness controllability and great conformality. In this study, we synthesized p-type SnO thin film using ALD and consequent plasma treatment for reduction. We investigated the crystal structure, morphology, and electrical properties of SnO by using x-ray diffraction (XRD) and atomic force microscope (AFM). In addition, we evaluated the thermal and chemical stability of SnO film. As a result, SnO film shows highly stable SnO phase even after annealing at 400 °C with oxidation/reduction environment. This study will contribute to apply oxide semiconductor in future application by implementing various device structure, such as p-n junction, complementary metal oxide semiconductor(CMOS), and p-channel TFT.

PS-TuP-6 Plasma-Surface Interactions in Atmospheric Pressure Plasmas: In situ Measurements of Electron Heating in Materials*, S Walton,* Naval Research Laboratory*; B Foley,* Pennsylvania State University*; J Tomko,* University of Virginia*; D Boris, E Gillman, S Hernandez,* Naval Research Laboratory*; A Giri,* University of Virginia*; T Petrova,* Naval Research Laboratory*; **Patrick Hopkins**,* University of Virginia

The energy flux to a surface during plasma exposure and the associated surface heating are of long standing interest as they contribute to the physico-chemical changes that occur during plasma-based materials synthesis and processing. Indeed, the energy delivered to the surface, via a flux of particles and photons, in concert with a flux of reactive species serves to chemically modify, etch, and/or deposit materials, with an efficacy that depends on the plasma processing environment. A unique feature of plasma synthesis and processing is that most of the delivered energy is absorbed at or very near the surface over short (picosecond) time scales. The dissipation of thermal energy proceeds through electron-electron and/or electron-phonon interactions as they propagate through the material, with relaxation time scales that can be orders of magnitude slower. Typically then, the surface is not in thermal equilibrium with the bulk material. Fast, surface-sensitive techniques are thus required to fully appreciate the dynamics of the plasma-surface interaction. In this work, we employ pump-probe Time-Domain Thermoreflectance, a surface sensitive technique typically used to measure thermal properties of thin films, to determine electron heating of thin metal films during exposure to an atmospheric pressure plasma jet. The results, in conjunction with current measurements, are used to develop a first order understanding of plasma jet-surface interactions. The results show that the energy delivered by the plasma jet causes a localized increase in electron energy within the thin film over an area commensurate with the plasma jet radius. More details of this work an be found in the following recently published paper: Walton, S.G., Foley, B.M., Tomko, J., Boris, D.R., Gillman, E.D., Hernandez, S.C., Giri, A., Petrova, Tz.B., Hopkins, P.E., "Plasma-surface interactions in atmospheric pressure plasmas: In situ measurements of electron heating in materials," *Journal of Applied Physics* **124**, 043301 (2018).

PS-TuP-7 Classification of Aluminum Alloys by an Inexpensive Laser Induced Breakdown Spectroscopy System*, Kevin Renato Maldonado Dominguez,* *R Sangines del Castro,* CNyN-UNAM, Mexico

Laser induced breakdown spectroscopy (LIBS) has been widely used for elemental analysis of solid, liquid and gaseous samples due to its portability and the practical null sample preparation . Due to the changing nature of the induced plasma the necessity of using a time-resolved spectroscopy system, consisting of a Echelle spectrograph and an ICCD camera, is usually mandatory; however, these systems are delicate and the portability could be difficult. Although field spectrometers with a CCD detector could have relatively high spectral resolution, their main drawback is the trouble to synchronize the laser beam trigger to the beginning of the spectral acquisition. If the trigger issue is resolved with a relatively low jitter, these spectrometers could be an attractive alternative for characterization of material composition via LIBS.

In this work, a CCD spectrometer (Avantes, AvaSpec) is tested to determine the composition of several aluminum alloys and is compared to the results of an Echelle spectrometer by identifying spectral lines from the NIST database and applying statistical tools. Different experimental parameters were studied and results are discussed in terms of the correct identification of the Al alloy.

PS-TuP-8 Optimizing Deposition Parameters for Reactive Magnetron Sputtering by Monitoring the Plasma Optical Emission Spectroscopy.*, Genaro Soto-Valle Angulo,* *R Sangines,* CNyN-UNAM, Mexico

Thin films technology has grown during the last years due to its many applications. Extensive research has been focused on silicon oxides and nitrides for its excellent properties.

Although the wide variety of techniques for thin film deposition, reactive magnetron sputtering is still one of the preferred. However, one of the major drawbacks of this technique is the lack of repeatability of the film properties under the same deposition parameters as a result of the so-called target poisoning.

The aim of this work is to obtain the optimal deposition conditions for SiO_2 and Si_3N_4 thin films grown by reactive magnetron sputtering in order to guarantee specific film properties, particularly the refractive index for optical filters applications. Optical emission spectroscopy was used to monitor the deposition process in real time and to observe the species contained within the plasma. Information of the emission intensity was employed to obtain intensity ratios between certain emission transitions, and this information was then correlated with the film optical properties analyzed by spectroscopic-ellipsometry and XPS. Relation between these parameters can give valuable knowledge about the deposition rate and refractive index, which will allow to fabricate thin films with variable refractive index and with a high degree of repeatability.

PS-TuP-9 Origin of Plasma Damage during Sputtering of Ultrathin ITO Contact Layer on p-GaN for InGaN/GaN LEDs*, T Kim, Y Cha,* ***Joon Seop Kwak,*** Sunchon National University, Republic of Korea

We systematically examined the origin of plasma-induced damage on *p*-GaN surface during the sputtering of ITO transparent conductive electrodes (TCE) and its effects on the forward voltage and the light output power (LOP) of InGaN/GaN LEDs. Firstly, we investigated the effect of direct current (DC) power in radio frequency (rf) superimposed DC sputtering (RF+DC sputtering) of ITO on the forward voltage and and LOP of InGaN/GaN LEDs and found that the plasma-induced damage was sensitive to the DC power. The forward voltages of the LEDs at 20 mA drastically decreased from over 5 V to 3 V and the LOP of the LEDs was greatly enhanced by more than 20% at 250 mA, when the DC power was changed from negative to positive values. Secondly, electron flux as well as ion flux during the RF+DC sputtering of ITO with the various DC power were calculated based upon the plasma discharge parameters measured by cutoff probe and Langmuir probe. Changing the DC to positive power drastically reduced the electron flux in plasma, suggesting that plasma electrons play an important role in plasma-induced damage of *p*-GaN surface. Furthermore, the significant increase in forward voltage of the LEDs was observed, when electron-beam irradiation on *p*-GaN surface was employed. This confirms that the plasma electrons, not ions, can cause the plasma-induced damage on *p*-GaN during the sputtering of ITO. Lastly, physical mechanism for the generation of plasma-induced damage on *p*-GaN by the plasma electrons was suggested. The plasma electrons can compensate the deep level defects (DLDs) in the *p*-GaN surface and reduce the density of DLDs, which increase the effective barrier height at the ITO/DLD band of *p*-GaN. Furthermore, the plasma electrons yielded the energetic ad-atoms of ITO on *p*-GaN during sputtering by energy transfer of the electrons to the ad-atoms and increased the plasma-induced damage on *p*-GaN. We successfully demonstrated the plasma-induced-damage-free ITO TCE on the InGaN/GaN LEDs by sputtering, which showed 20 % improved LOP of the LEDs with comparable forward voltage of 2.9 V at 20 mA to the LEDs with conventional e-beam-evaporated ITO.

Thin Films
Room Naupaka Salon 1-3 - Session TF-TuP
Thin Films Poster Session I

Moderator: Darrell G. Schlom, Cornell University

TF-TuP-1 Oxidation Behavior of Sputtered $NiFe_2$ Coating on Ferritic Stainless Steel for SOFC Interconnect Application*, Shujiang Geng,* *F Wang,* Corrosion and Protection Division, Shenyang National Laboratory for Materials Science, Northeastern University

Ferrtic stainless steels are confronted with several problems during operation in SOFC cathode working condition such as the spallation of the oxide scale and cathode Cr-poisoning, leading to significantly degradation of the cell performance. To solve these problems, NiFe2 alloy coating has been deposited on SUS 430 ferritic stainless steel via magnetron sputtering method. Electrically conductive $NiFe_2O_4$ spinel coatings were thermally developed on the steels from the sputtered $NiFe_2$ coatings in air at 800°C. Initial oxidation behaviors of $NiFe_2$ coated bare and pre-oxidized steels were investigated for understanding the conversion process from the alloy coating to spinel. The phase structure and composition of coated steels after oxidation were characterized with XRD and SEM/EDS.

The oxidation kinetics analysis of the first 60min exposure demonstrated rapid mass gains were observed during the beginning 5-10 min for the coated bare and pre-oxidized steels, followed with slightly increase. The XRD and SEM/EDS results indicated Fe was preferentially oxidized resulting in un-reacted Ni residue in the coatings during the rapid mass gains stages. Scale formed on the coated bare steel presented multilayered structure, primarily consisting of a top Fe_2O_3 layer followed with $NiFe_2O_4$ layer and NiO layer. During the first 10 min, un-reacted Ni region beneath the NiO layer was decreasing with time. Cr-rich oxide was detected at the interface of scale/steel after 30min exposure. Similar scale structure was observed on the coated pre-oxidized steel except Cr-rich layer at scale/steel interface consistently. Compared with the coated bare steel, the bigger defect gap between columnar-grains in $NiFe_2$ coating on pre-oxidized steel serving as channel for oxygen inward diffusion will presumably provide higher oxygen capacity in coating, which accelerated Ni consumption during oxidation. Chromia layer formed after pre-oxidation treatment acted as a barrier to block Cr outwards diffusion into the alloy coating at the beginning of oxidation. Scales on both coated steels were well-bonded to steel substrate with a few tiny pores distributing discretely. The oxidation mechanisms were discussed.

**TF-TuP-2 Effects of Bias Voltage on the Structure and Corrosion Properties of Thick Cr Coatings Deposited Using Cathodic Arc ion Plating*, Jung-Hwan Park*, *Y Jung, D Park, H Kim, B Choi, Y Lee, J Yang,* Korea Atomic Energy Research Institute

After the Fukushima Daiichi nuclear accident, the major issue of nuclear researchers has been an improvement in the oxidation resistance under beyond-design accident conditions. Therefore, accident tolerant fuel (ATF) has been widely studied, which has high-temperature oxidation resistance. For the development of ATF claddings, several advanced cladding materials that have high-temperature oxidation resistance have been proposed, including advanced stainless steels, Mo alloys, and SiC/SiCf composites. However, they require changes in the engineering design of the reactor cores. An alternative approach to improving safety is to fabricate a cladding with a protective coating. A protective coating that has a high oxidation resistance also improves the corrosion performance during normal operation. Several coating materials have previously been suggested, including SiC, FeCrAl, TiN, TiAlN and Cr. Among the candidate materials for protective coating, Chromium coatings are well known for their high hardness, good corrosion, and wear resistance. In our previous work, Cr coating deposited on a zircaloy-4 cladding by cathodic arc ion plating was investigated to evaluate the corrosion protection of zircaloy-4 cladding in a high-temperature steam environment. Compared to pristine Zircaloy-4, Zircaloy-4 with a Cr layer exhibited superior oxidation resistance. However, an oxygen-stabilized alpha zirconium (α-Zr(O)) layer, which was formed through oxygen diffusion, was observed after a high-temperature steam oxidation test.

In this study, we tried to optimize the ion plating conditions to reduce the inward oxygen diffusion. Cr coatings were deposited on a Zircaloy-4 tube using arc ion plating at various substrate bias voltages. The effects of the substrate bias voltage on the corrosion behavior of arc ion plated Cr films has been investigated. We also investigated the relationships among the substrate bias voltage, physical properties, and corrosion resistance for Cr coated zircaloy-4. The internal stress was measured using an iso-inclination method with an x-ray diffractrometer at room temperature. A high-temperature steam oxidation test at 1473 K was executed.

**TF-TuP-3 Graphite Tribofilm Extracted from Base Oil by Self-Oxidizing Coating: A Highway for Friction and Wear Reduction*, Lina Yang*, State Key Laboratory of Superhard Materials, Department of Materials Science and Key Laboratory of Automobile Materials, MOE, Jilin University, Changchun 130012, People's Republic of China., China*; K Zhang,* State Key Laboratory of Superhard Materials, Department of Materials Science and Key Laboratory of Automobile Materials, MOE, Jilin University, Changchun 130012, People's Republic of China, China

Tailoring sliding interface is a vital pathway to minimize friction and wear, commonly, either fluid layers or solid tribofilms have been employed. Herein, the lubricating effects from both ones are combined via in situ formation of graphite tribofilm extracted from PAO base oil (without additives) when introduced catalytic TiN coating enabled by solute Ag atoms (super-hard nature). In this way, superior tribological properties with ultralow friction coefficient at 0.075 and wear rate at 2.28×10^{-11} mm^3/Nm can be obtained. Better yet, the incorporation of solute Ag atoms into TiN structure could induce a charge depletion state and active surface self-oxidation to a special Ag_2O/TiO_2 composite, as demonstrated by electron localization function (ELF) and XPS. Different from traditional metal catalysts, such metallic oxides from solid solution structure are suggested to dominant this catalyst and extraction action. Besides, the direct transfer of part of electrons from the unstable charge structure to oil molecules further ensures the catalytic effect. This study highlights the crucial role of solid solution coating in catalyzing and extracting tribofilms from lubricating oil, which would be a new insight towards a more efficient lubricating system.

**TF-TuP-4 Solute Ag Atom Incorporated into TaN with Excellent Tribological Property and Robust Antibacterial Activity*, Ping Ren*, *M Wen,* State Key Laboratory of Superhard Materials, School of Materials Science and Engineering and Key Laboratory of Automobile Materials, MOE, Jilin University, Changchun 130012, People's Republic of China, China

Nowadays, designing transition metal nitrides (TMN)-based films deposited on Ti-6Al-4V substrates with enhanced wear-resistance, anti-bacteria and a reduced friction represents urgent challenge for various application including bistoury scalpel, medical catheter, door handle and kitchen utensils et al. Generally, incorporating higher content (> 10 at.%) of antibacterial metallic phase (i.e. Cu, Ag) into TMN matrix to form the TMN/metal nanocomposite film has been considered as an effective approach to achieve improved toughness and antibacterial activity. However, in this system, hardness and wear rate are highly sensitive to soft metal content and can be significantly worsened. Herein, we provide a new strategy to introduce few solute Ag atoms (~ 3.08 at.% Ag) into TaN lattice to form a Ta-Ag-N solid solution structure, simultaneously achieving superhard (~ 40 GPa) yet high toughness, and improved wear-resistance, coupled with remarkable decrease in friction relative to Ag-free TaN film and TaN/Ag nanocomposition film with the same Ag content. In addition, the solid solution Ta-Ag-N film exhibits the excellent antimicrobial activity on Escherichia coli tested by measuring the diameters of the bacteriostasis circles. Obviously, introduction of few solute Ag atoms into TMN may open a new window to improve the comprehensive properties including hardness, toughness, friction, wear-resistance and anti-bacterial.

TF-TuP-5 Influence of Ag Content on the Tribological Properties of MoNbN-Ag Coatings at Elevated Temperature*, K Zhang,* State Key Laboratory of Superhard Materials, Department of Materials Science, Key Laboratory of Automobile Materials, MOE, and Jilin University, Changchun, People's Republic of China, People's Republic of China*; **Xuan Dai**,* State Key Laboratory of Superhard Materials, Department of Materials Science, Key Laboratory of Automobile Materials, MOE, and Jilin University, Changchun, People's Republic of China, China*; M Wen,* State Key Laboratory of Superhard Materials, School of Materials Science and Engineering and Key Laboratory of Automobile Materials, MOE, Jilin University, Changchun, People's Republic of China, China*; W Zheng,* tate Key Laboratory of Superhard Materials, School of Materials Science and Engineering and Key Laboratory of Automobile Materials, MOE, Jilin University, Changchun, People's Republic of China

In recent years, with the increasingly fierce and vigorous development of aviation technology, aerospace engine, as the "crown jewel of the aviation industry", has been constantly improving its requirements of technology and performance. Because the aerospace engines always work in high temperature environment, it is necessary for materials to have reliable tribological performance at high temperature. However, high temperature lubrication is still a considerable challenge for the tribology field, and it results that the damage and failure of motor components are always caused by high temperature friction. Here, a reduced friction coefficient from 25 to 800 ℃ was achieved successfully in MoNbN-Ag coating with tailoring Ag content. The deposited MoNbN coating is a ternary fcc-solid solution, and the transformation from solute Ag atoms to precipitate metal Ag can be realized through the increasing of Ag content. The reduced friction coefficient can be ascribed to silver, molybdenum and niobium reacted with oxygen at elevated temperatures and create lubricious phases molybdenum oxide, niobium oxide ,silver molybdate and silver niobite film on the coating. Amusing, compared with Ag in the form of precipitation in MoNbN coating, when silver exists in the form of solid solution, it has a lower friction coefficient at 25-450 ℃ and a similar friction coefficient at 450-800 ℃. In which, it's attributed to the contribution: solute Ag can activate easier self-oxidation forming Ag_2O+ MoO_3/Nb_2O_5 on the surface, which is beneficial for formation of $Ag_2Mo_4O_{13}/AgNbO_3$ during sliding at medium and low temperatures, thereby reducing friction.

**TF-TuP-6 High rate Reactive Sputter-deposition of WO_3 Films by using Two Different Deposition Methods*, Yoji Yasuda*, *Y Hoshi,* Tokyo Polytechnic University, Japan

Tungsten oxide (WO_3) is well known as a functional material with excellent gasochromic, electrochromic, and photocatalytic properties. Nano-structured WO_3 films prepared by glancing angle sputter deposition and high-rate gas flow sputtering were reported by Horprathum et al. and Oka et al., respectively. We have already reported that high-rate deposition of WO_3 films at a deposition rate (R_D) of more than 100 nm/min can be achieved by pulsed dc planar magnetron sputtering (PMS). However, poor gasochromic film was obtained near the center area of the substrate. This was due to bombardment by high energy negative oxygen ions that are sputtered from a target surface to the substrate surface during sputter-deposition. This ion bombardment is expected to be completely suppressed if the facing-target type low damage sputtering system (FTS) used for the deposition process.

In this study, we deposited WO_3 films using two different sputtering methods (a PMS and an FTS system), and compared the structure and properties of the resulting films. Typical sputtering conditions are presented in the poster session. R_D of more than 120 nm/min was easily realized with an increase in the sputtering voltage above 700 V. A typical WO_3 film obtained by PMS exhibited inhomogeneous gasochromic properties that depended on the location on the substrate, and films with excellent gasochromic properties were only obtained at the corner of the substrate. It was also found that the nonuniformity of the films can be improved by altering the angle of incidence of the particles on the substrate and relaxing the impact.

In contrast, uniform films were easily obtained by FTS. Details will be presented in the poster session.

TF-TuP-7 Initial Growth of Pentacene Thin Film on Si(001) Substrate*, **Takayuki Suzuki**, K Yagyu, H Tochihara,* Fukuoka University, Japan

Initial growth process of the pentacene molecules on the clean Si(001)-2×1 substrate were investigated by Scanning Tunneling Microscopy (STM) at room temperature (RT). The pentacene molecules were deposited onto the clean Si(001) surface held at RT, using a quartz crucible. We found that the wetting layer forms first by increasing the amount of the deposited pentacene molecules before starting the formation of the first layer, which is not crystalized, but disorder, where the molecules adsorb flatly. It does not have any ordered domain structure. The first pentacene layer that is crystalized with the standing-up pentacene molecules grows on the disordered wetting layer by increasing the deposited amount of the molecules more. The first layer consists of three domains at least, which have different crystal structures from each other: the ‘*α*’, the ‘*β*’ and the ‘*γ*’ domains. Among them, the ‘*β*’ domain has a new pentacene crystal structure that can form only on the first layer. The first layer does not have a dendritic shape at least at a field of view of 2 *μ*m. Second pentacene layer starts to form on top of the first layer by increasing the deposited amount more again, before the first layer completely covers the substrate surface. In contrast, the second layer has only single domain. The all other crystal structures found in the present study except for that of the ‘*β*’ domain, are similar to those of the four polymorphs reported previously [1]. Moreover, we investigated electronic properties of the various pentacene layers by the I-V measurements. The pentacene layers are semiconducting with a gap of about 4 eV from -1 eV to +3 eV.

Reference

[1] M. Kitamura, Y. Arakawa, J. Phys.: Condens. Matter 20, 184011 (2008), and references therein.

TF-TuP-8 Thermal Stability of Atomic Layer Deposition Precursors*, **Kyuyoung Heo**, J Son, G Jung,* Korea Research Institute of Chemical Technology, Republic of Korea*; W Lee,* Korea Research Institute of Chemical Technology, Republic of Korea, Republic of Korea

The development of high-k dielectric precursors for advanced semiconductor applications requires molecular engineering and chemical tailoring to obtain specific physical properties and performance capabilities. Some high-k precursors such as organometallic precursors for atomic layer deposition (ALD) that have metal atoms bound to cyclopentadienyl, are stored at a sufficiently high temperature due to their low volatility and consumed through continuous deposition for a commercial semiconductor process. In this case, thermal degradation slowly occurs due to storage at a high temperature for a long time, which causes deterioration of physical properties and reliability of the thin film. However, a technique for assessing the reliability of precursor has been undeveloped and thus causing the development of new precursors to be delayed. In this study, we have developed a reliability evaluation method for cyclopentadienyl tris(dimethylamino) zirconium [CpZr(NMe$_2$)$_3$] through accelerated thermal degradation test under severe environmental conditions in a short period of time. To evaluate the lifetime of precursor, we have investigated the thermal stability and degradation mechanism of precursor by using analysis of NMR and mass and viscosity measurements.

TF-TuP-9 Growth Behavior and Film Properties of Titanium Dioxide by Plasma-Enhanced Atomic Layer Deposition with Discrete Feeding Method*, **Heungseop Song**, D Shin, J Jeong, H Park, D Ko,* Yonsei University, Korea, Republic of Korea

Titanium dioxide (TiO$_2$) has emerged as an attractive dielectric material for electronic devices such as memory and thin film transistors due to its high dielectric constant and high thermal stability or its role as an important constituent of multi-metal oxide systems. TiO$_2$ thin films can be fabricated in many ways, such as physical vapor deposition, chemical vapor deposition and spin coating. Among these growth methods, plasma-enhanced atomic layer deposition (PE-ALD) technology becomes one of the most promising methods for nanoscale thin film deposition because of its advantage of conformal growth, precise control of the film thickness and relatively low substrate temperature. However, most PE-ALD TiO$_2$ processes show a low growth-per-cycle (GPC) of less than 1.0 Å, making them difficult for mass production. T. Park et al. reported the steric hindrance caused by the physical size and proximity of the neighboring parts of the precursor (or partially decomposed) molecule during precursor feeding time and introduced a “discrete feeding method” (DFM) of the metal precursor as a solution for improved GPC of HfO$_2$ film [1]. In this presentation, we report the growth behavior of TiO$_2$ film with the DFM-applied and the conventional ALD growing method, using tetrakis-dimethylamido-titanium [Ti(NMe$_2$)$_4$], as a Ti precursor. Our work focused on improving both physical and electrical properties of the film as well as increasing its growth rate through DFM application. In our experiments, TiO$_2$ films were deposited on Si (100) substrates at 250 °C. Spectroscopic ellipsometry (alpha-SE model, J. A. Woollam Co. Ltd.) and X-ray photoelectron spectroscopy (XPS, Thermo Scientific Inc., U.K) were examined to compare GPC. As a result, the GPC of the DFM group was increased by 18% compared to that of the conventional method group and the GPC difference from the ellipsometry measurement results of the two groups was also in agreement with the XPS analysis. In addition, we performed a wet etch rate test using 25: 1 HF chemical to compare the physical properties of the thin films and confirmed that the DFM group had a wet etch rate close to 6% of the wet etch rate for the conventional group. This confirms that the denser film was formed when DFM was applied, which was also consistent with the finding of the difference in Ti density observed through Rutherford backscattering spectrometry analysis. We expect that these differences in physical film properties would affect dry etch selectivity and consequently result in better dry etch selectivity compared to SiO$_2$ that has been most widely used in the semiconductor industry.

[1] T. Park et al., Chem. Mater. 2011, 23, 1654–1658.

TF-TuP-10 Properties of nm Scale Tungsten Thin Film Deposited using Inductively Coupled Plasma Assisted Sputtering*, **Soojung Lee**, T Kim, B Jeong, C Song, J Byun, J Kim, Y Ji, G Yeom,* Sungkyunkwan University, Republic of Korea

As the device width is reduced under 10 nm due to the high integration of semiconductor devices, resistivity of metallization line is significantly increased due to the decrease of the device width. Copper (Cu) is the most commonly used for metallization owing to the low resistivity and high conductivity. However, Cu metallization is known to show the limitation for the nm thickness due to the size effect linked to the long electron mean free path (EMFP) of 39nm. Also, the reliability of Cu is degraded as device operating temperatures and current densities are increased with each technology node. Since W has a smaller EMFP of 19nm, it is expected to reduce the size effect as it goes to nm dimension. Furthermore, W has a very high melting temperature of 3673K, there is a possibility to replace Cu for future metallization material for the metal thickness lower than tens of nm. In this study, ICP assisted sputtering of W has been investigated for lower resistivity of nm scale W film. An internal-type coil antenna has been used for a high ionization, and a DC sputter system has been used for the deposited W thin film. When the characteristics of W thin film deposited with and without ICP assistance were investigated, the decrease of the W thin film resistivity was decreased and, regardless of substrate heating, the deposition rate was increased due to the increase of plasma density. By using high density plasma, we could get dense structure of W thin film at low temperature. Using the XRD, the decrease of β peak which is A-15 structure and the increase of α peak which is bcc structure at both room temperature and 673K were observed with ICP-assisted sputtering. It means ICP assistance influence the decrease of the W thin film resistivity. In addition, analyzing with XPS, the O content in the W thin film which has great influence on the resistivity of W thin film was decreased with increasing the ICP power. As a result, the feasibility of tungsten deposited by ICP assisted sputtering as a next-generation metal interconnect material was investigated.

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TF-TuP-11 A New High Wear-resistant Conductive Coating Based on Transition Metal Nitrides with Solid Solution Structure*, **Yuankai Li**, C Hu,* State Key Laboratory of Superhard Materials, Key Laboratory of Automobile Materials of MOE, and School of Materials Science and Engineering, China

High wear-resistant conductive coatings have recently attracted increasing interest owing to their technological importance in the fields of high-speed railways, artificial joints and electrode materials. However, wear-resistance and conductivity of materials are a dilemma from the perspective of structures and chemical bonds. Thus, developing ideal wear-resistant conductive coatings remains a significant challenge. Here, we propose a novel strategy to design wear-resistant conductive coatings: a transition metal nitride is selected as a base, and its wear-resistance and electrical conductivity are simultaneously improved by doping transition metals or noble metals to form a solid solution structure. The new strategy is demonstrated to be practically feasible and effective by two experiments: doping tantalum and silver into hafnium nitride films. Doping with tantalum and silver can improve wear-resistance and conductivity of hafnium nitride films due to the formation of solid solution structures. The conductivity and wear-resistance of the silver precipitated Hf-Ag-N supersaturated solid solution are higher than those of the Hf-Ta-N solid solution, which is attributed to not only the solid solution strengthening effect but also the effects of precipitate silver including the precipitation strengthening, self-lubrication and additional conductivity enhancement. Combining a series of experiments with first-principle calculations and Drude-Lorentz fitting, we have proved that the formation of solid solution structures can achieve both wear-resistance and conductivity enhancement, apart from well-known strength enhancement. This work provides new insights in designing hard, wear-resistance yet high-conductivity coatings.

TF-TuP-13 Tribo-mechanical and Tribo -corrosion Properties of Thin-on-thick Duplex PVD/HVOF Coatings*, Jolanta Klemberg-Sapieha,* *F Pougoum, J Qian, L Martinu,* Polytechnique Montréal, Canada*; Z Zhou, K Li,* City University of Hong Kong*; R Schulz,* Institut de recherche d'Hydro-Québec

The tribo-mechanical, corrosion and, in general, multifunctional performance of metallic substrates can be significantly enhanced by applying a thin-on-thick duplex coating architecture. Specifically, in a very promising system consisting of a High Velocity Oxy-Fuel (HVOF) coating followed by a Physical Vapor Deposition (PVD) coating, the hard thick HVOF layer provides the load carrying capacity of the soft substrate, while the top dense thin PVD film improves the wear and corrosion resistance . In the present work, pure Fe_3Al coatings and composite Fe_3Al:BN coatings (~300 µm), with a hardness between 4.3 and 12.8 GPa, were prepared on SS304 substrates by HVOF. The top thin PVD layer of diamond like carbon (DLC, 1~2 µm) has been prepared by pulsed DC magnetron sputtering. The tribo-mechanical and tribo -corrosion properties of the DLC/SS304, DLC/Fe_3Al/ SS304 and DLC/Fe_3Al:BN / SS304 coating systems were then compared. Application of the DLC layer on top of the HVOF coating allowed one to decrease the friction coefficient from 0.7 to <0.1, and to significantly enhance the wear resistance. Particularly, the DLC/Fe_3Al:BN system exhibits the lowest wear rate of 8×10^{-8} $mm^3/N^{-1}\cdot m^{-1}$. The corrosion resistance of the DLC/Fe_3Al system was increased by 3 orders of magnitude. The wear, corrosion, and tribo -corrosion mechanisms are discussed in detail.

Biomaterial Surfaces & Interfaces
Room Naupaka Salon 6-7 - Session BI-TuE

35 Years of NESAC/BIO II

Moderator: Sally L. McArthur, Swinburne University of Technology, Australia

5:40pm **BI-TuE-1 History of Biomaterials and the Founding of NESAC/BIO**, ***Buddy D. Ratner,*** University of Washington **INVITED**

The history of biomaterials and the founding of NESAC/BIO is a big order for one abstract. The history of biomaterials can trace application back to the Neolithic period. But, more relevant to AVS, let's look at the early history relevant to considerations of the surfaces of biomaterials. Early pioneers in biosurface/biointerface studies include Agnes Pockels, Irving Langmuir, Katharine Blodgett, Henry Bull (proteins at interfaces), Leo Vroman, Robert Baier, Joe Andrade and Allan Hoffman. We also have pioneers in technique and instrumentation including William Zisman (contact angles), Kai Seigbahn, Alfred Benninghoven, Gabor Somorjai, Dave Clark, Ron Thomas, Michael Kelly, Chuck Bryson, Leroy Scharpen, Gerd Binnig and Heinrich Rohrer. In the late 1970's I became aware of the power of some of the newer methods for surface characterization for studying biomaterials, particularly electron spectroscopy for chemical analysis (ESCA). Inspired by the pioneers who were demonstrating the importance of surfaces for biology and powered by ESCA and a collaboration with Kelly and Scharpen of HP Corporation, I performed early studies that almost immediately began offering important insights into the biointerface. I came to realize that all biomaterials scientists should embrace biosurface studies, but most did not have access to the instrumentation and training in the use of the instrumentation. I learned about NIH National Resource Centers as a mechanism to provide services to the community and to advance my own studies. I applied to the NIH for such a center. After a failed application, on my second try, we were funded. That led to the formation of the National ESCA and Surface Analysis Center for Biomedical Problems (NESAC/BIO). Bringing on board Dave Castner and later Lara Gamble strengthened the intellectual and instrumental base of NESAC/BIO. Thirty five years later, it is with great pleasure and pride to look back on NESAC/BIO's successes and service to the biointerface community.

6:20pm **BI-TuE-3 The Evolution of Biomedical Surface Analysis at NESAC/BIO**, ***David Castner,*** University of Washington, USA **INVITED**

Biomedical surface analysis has undergone significant and numerous advances in the past decades in terms of improved instrumentation, introduction of new techniques, development of sophisticated data analysis methods, and the increasing complexity of samples analyzed. Comprehensive analysis of surfaces and surface immobilized biomolecules (peptides, proteins, DNA, etc.) with modern surface analysis instrumentation provides an unprecedented level of detail about the immobilization process and the structure of the immobilized biomolecules. Results from x-ray photoelectron spectroscopy (XPS or ESCA), time-of-flight secondary ion mass spectrometry (ToF-SIMS), near edge x-ray absorption fine structure (NEXAFS), surface plasmon resonance (SPR) and quartz-crystal microbalance with dissipation (QCM-D) biosensing, atomic force microscopy, and sum frequency generation (SFG) vibrational spectroscopy provide important information about the surface structure and composition of complex biomedical materials, as well as the attachment, orientation, conformation, etc. of biomolecules to those materials. However, even with the advances that have been achieved with these powerful surface analysis techniques, there still remain many significant challenges for biomedical surface analysis. These include characterizing the surface chemistry and structure of nanoparticles, determining the atomic level structure of proteins bound to surfaces, 3D imaging of cells and tissue sections, and maintaining biomolecules and materials in a biological relevant state when using ultra-high vacuum based analysis techniques. This talk will discuss the development of surface analysis tools at the National ESCA and Surface Analysis Center for Biomedical Problems (NESAC/BIO). Also discussed will be the role of well-defined standards to develop new biomedical surface analysis methods for characterizing more complex, biological relevant samples.

6:40pm **BI-TuE-4 Future Directions and Challenges in Biomedical Surface Analysis**, ***Lara Gamble,*** University of Washington **INVITED**

The NESAC/BIO center has been running as very successful NIH NIBIB funded P41 center since 1983. We are making plans for the future growth and expansion of the center resources and expertise. Our work and advances in ToF-SIMS imaging and analysis have prompted a lot of interest among biomedical academic as well as the clinical research community. As a result, we have developed many new tools and capabilities to improve sub-cellular resolution ToF-SIMS analysis of cells and tissues. In the future, the focus of the center will be to provide multimodal information in three dimensions addressing key questions to biomedical issues. While we have proposed instrumentation and research towards this end in the current proposal, we will also be building collaborations nationally with leading groups that have interests in cell and tissue 3D chemical analysis on a vertical and lateral scale that will take advantage of the resolution our NESACBIO surface characterization tools.

7:00pm **BI-TuE-5 Characterizing Protein Fiber Structures and their Interactions in Biological Environments with Vibrational Sum-frequency Scattering Spectroscopy**, ***Patrik Johansson,*** *D Castner,* University of Washington

Biological processes are typically regulated by interactions at the interface of 3D structures, such as the membrane of cells or protein fiber surfaces. Collagen (the most common protein in mammals) forms large fibers that are responsible for the structural integrity of tissues. The structure, organization and interactions of these fibers are furthermore important for the survival, communication, migration, and proliferation of cells.

Investigating protein fiber interactions is challenging, particularly under biological conditions where the fibers exist in a 3D aqueous environment. Many techniques cannot interrogate interfaces buried in the bulk of a solvent and therefore require 2D surface models, while others need extensive purification and sample preparation. These approaches may not capture all characteristics of the fiber structures and their interactions in the real sample. However, vibrational sum-frequency scattering (SFS) spectroscopy, with inherent contrast for local molecular ordering, can be utilized towards these important goals.

As a first demonstration, we applied SFS to protein fibers in aqueous environments, self-assembled from collagen type I. We detected signals from the amide I band and the N-H stretching vibrations, both of which are related to the specific protein backbone structure. Signals from the C-H stretching and bending vibrations were also identified, which are associated with the side-chains in the fibers. The angular scattering patterns for the backbone (amide I) and side-chain (C-H stretches and bends) signals are different, making the spectra dependent on the angle of detection. While the backbone signals are dominant in the phase-matched direction, the side-chain signals remain high also at large scattering angles. Distinctions in the organizational symmetry and the relative fiber surface contribution to the overall signal are hypothesized as reasons for this observation.

Finally, we are investigating how changes to the environment (pH, surfactants, etc.) affect spectra and scattering patterns for the SFS signals. This can yield new insights to the structure and dynamics of collagen fibers in biological settings and guide decellularization protocols in regenerative medicine. The relevance of such investigations is enhanced by the fact that detection of vibrations from the surrounding molecules is a direct observation of their interactions with the collagen fiber surface, which thus can be correlated with the fiber structure. The relative orientations for the detected groups may also be obtained via vibrational SFS polarization analysis, for a deeper understanding of biomolecular interactions in biological processes.

7:40pm **BI-TuE-7 Albumin and Fibrinogen Adsorption on New Fluorinated Polyurethanes as an Indication of Blood-compatibility**, ***Le Zhen,*** University of Washington, USA*; M Mecwan, S Zhang, F Simonovsky, B Ratner,* University of Washington

Clotting is a major complication for blood contacting biomaterials intended to sustain normal blood flow (biomaterials used in vascular grafts, stents, artificial hearts, etc.). FDA-approved devices for use in the blood stream suffer from thrombotic complications and can be blood reactive even after years of implantation. Thus, highly blood-compatible biomaterials have been long-sought after but not yet achieved. Polyurethanes, with their readily tunable chemical and mechanical properties, represent one of the most widely used classes of biomaterials. We synthesized fluorinated polyurethane materials via a one-step, solvent-free, catalyst-free reaction. The ratio of CF_3/CF_2 can be tuned by varying the composition of the monomers. Electron spectroscopy for chemical analysis (ESCA) and attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR) were used to confirm the success of the reaction. ^{125}I labeled albumin and fibrinogen are used in a competitive format to quantitatively study the adsorption of both proteins on the fluorinated polyurethanes. The retention of both proteins was quantified after elution with a sodium dodecyl sulfate (SDS) solution. Since fibrinogen is implicated in surface-induced clotting and albumin is a benign protein, we hypothesize that materials which tightly bind albumin and have reduced binding to fibrinogen will be less platelet activating and more blood compatible. Compared to non-fluorinated polyurethane and PTFE, the fluorinated polyurethane showed the highest albumin binding and retention. The albumin/fibrinogen ratio of the fluorinated polyurethane is higher than the non-fluorinated polyurethane and comparable to PTFE. These results show promise in blood-compatibility. We will further examine the albumin and fibrinogen adsorption to fluorinated polyurethanes with varying CF_3/CF_2 ratios and correlate composition to adsorption properties. The candidates optimized for high albumin binding and low fibrinogen binding from these experiments will be subjected to human platelet interaction studies to further test albumin hypotheses aimed at achieving enhanced blood-compatibility.

8:00pm **BI-TuE-8 Disclosing the Aggregation Mechanism and Orientation of Self-assembled Cysteine-modified Oligopeptides through Low Energy Dual Beam Depth Profiling Experiments***, **Luca Tortora**, S De Rosa,* National Institute of Nuclear Physics Roma Tre, Italy*; M Dettin,* University of Padua, Italy*; V Secchi, C Battocchio, G Iucci,* Roma Tre University, Italy

The use of short peptide-modified planar gold surfaces or gold nanoparticles is extensively reported in the literature regarding nanoscience and nanotechnology [1]. The mechanism by which these small biomolecules interact to form a film is a crucial information when a solid surface must be functionalized. At the same time, it must be taken into account that the final result in terms of chemical, topological, and functional features is strongly influenced by the orientation of the active layer. Here, a self-assembling peptide (SAP) with a Cys as a terminal residue was used to modify a planar gold surface. The SAP-Cys self-assembled monolayer (SAM) was obtained by o/n incubation of Au surfaces with 1mM SAP-Cys aqueous solution. The presence of alternating positively and negatively charged amino acids (H-Cys-Ala-Glu-Ala-Glu-Ala-Lys-Ala-Lys-Ala-Glu-Ala-Glu-Ala-Lys-Ala-Lys-OH) should guarantee the anchorage of the SAP to the metal surface preserving at the same time the ability of the SAP to self-assemble in antiparallel β-sheet structures. In recent studies [2], XPS analysis has allowed to estimate the film thickness as 4.45 nm and confirm the presence of sulfur atoms of Cys covalently bonded to the metal surface. In addition, an estimate of the mean angle between the peptide bond axis and the substrate surface of about 60° has been calculated by taking advantage of AD-NEXAFS investigations. In this work, we aim to obtain a more detailed understanding of the aggregation mechanism and orientation of SAP-Cys onto the gold surface through ToF-SIMS imaging and depth profiling experiments. Preliminary results obtained in static conditions showed the presence of SH negative ion signal coming from the top surface of the SAM, confirming the self-assembling of the SAP in antiparallel β-sheet structure. The signal intensities of the amino acid fragment ions were used to calculate the following ratios: Ala/Cys, Glu/Cys, Lys/Cys, and AuS/Au. In particular, AuS/Au peak intensity ratio values suggest a gold surface coverage percentage ranging from 8% to 12%. Low values of coverage could be strictly correlated with a strong presence of inorganic ions such as K, Na, spread over the gold substrate, as revealed by ToF-SIMS imaging. Finally, the SAP-Cys film was successfully profiled recording $SH^-$and S^-ion signal intensity variations during low energy dual beam depth profiling experiments.

References

1. D.Compagnone et al., *Biosens. Bioelectron.*, 2013, 42, 15, 618-625.

2. V. Secchi et al., *J. Phys. Chem. C*2018, 122, 6236−6239.

8:20pm **BI-TuE-9 Multimolecular Omics in Single Frozen-hydrated Cells using High-resolution Gas Cluster Ion Beam Secondary Ion Mass Spectrometry Imaging (GCIB-SIMS)***, **Hua Tian**, N Winograd,* Pennsylvania State University

The cross-talk between molecular network is central to signaling pathways that mediate cellular functionalities of all aspects. To understand the molecular mechanisms, it is necessary to unfold a complete spectrum of molecular species (e.g., lipids, metabolites and proteins) in parallel. Previously, independent molecular extraction is conducted to identify each classes using ensembles of cells. This poses a major limitation to study interconnection between lipid metabolism/protein based signaling from a global perspective and overlooks cell heterogeneity. Moreover, the spatial distributions, a vital piece for understanding biological processes is lost. It is a great technique challenge to detect all biomolecules in single cells near their nature state, and currently there is no method to directly detect metabolites in situ because of their rapid and dynamic nature and impossibility of amplifying. The development of high resolution CCIB-SIMS in our lab has positioned us to image multiple biomolecules in cryofixed cells in a single run. The approach takes advantage of three aspects of GCIB-SIMS - low chemical damage, high yield of intact biomolecules, and the possibility of sub-micron lateral resolution. In this work, we utilize a DC beam buncher-ToF SIMS instrument to achieve high lateral resolution. Moreover, this configuration simplifies depth profiling since erosion and spectral acquisition are performed with a single beam.

To illustrate this instrumental protocol, single HeLa cells expressing purine de novo biosysthesis (PDNB) are imaged in 3D using a novel 70 keV $(CO_2)_{14000}^+$ beam with a spot size of 1 µm. Purine de novo biosynthesis (PDNB) is essential for supporting cellular proliferation, survival and metabolic adaptation under varying nutritional environment. Using isotope tracer experiments, the stable PDNB intermediates are localized as distinct isolated punctate within cellular boundary. The simultaneous imaging of enzyme to catalyze the pathway is also developed to show the interactions of enzyme and protein. The approach provides a complete chemical picture of single cells at near original physiological and morphological state, opening the opportunities for single cell omics and heterogeneity studies using SIMS.

8:40pm **BI-TuE-10 Pretty Gross: Surface Analysis Illustrating How Beauty Tools Aren't Only Biocompatible for the Human Face***, P Nguyen, V Mitchell, J Romero-Kotovsky, B Mattheson, L Ista,* ***Heather Canavan****,* University of New Mexico

Tools such as "beauty blender" sponges have become a multi billion dollar product in the cosmetic industry. Introduced in 2007 as reusable utensils for the reliable application of liquid foundation, these applicators have become the largest growing area of the cosmetic industry. Current sales in the USA alone equate to $445B USD/yr in 2017, and are expected to climb to $805/yr by 2023. Although the manufacturers recommend that their sponges be cleaned prior to each use, and have a limited lifetime, many users are relatively complacent about the hygiene of their utensils. In this work, we evaluate how the surface properties of the various makeup blending sponges on the market correlate with their utility and propensity to harbor unwanted bacteria and other microbes. Using traditional surface analysis tools such as X-ray photoelectron spectroscopy, atomic force microscopy, Fourier transform infrared spectroscopy, and scanning electron microscopy, the surface chemistry, porosity, tensile and Young's modulus of the dominant sponges currently sold on the market were evaluated. In addition, the relative hospitality of the sponges to culture bacteria such as *E. coli, Staphlococcus aureus, and Propionibacteriumacnes* were evaluated using confocal microscopy, dilution colony cell counts, and XTT analyses. Preliminary results indicate that these sponges, which are primarily poly(urethane)-based, are capable of forming colonies of these bacteria, as well as other microbial such as fungi, within days if not hours.

Nanomaterials

Room Naupaka Salon 5 - Session NM-TuE

Magnetic Properties and Nanocomposites

Moderator: H. Henry Lamb, North Carolina State University

5:40pm **NM-TuE-1 Voltage-Assisted Magnetic Switching in MgO/CoFeB-Based Magnetic Tunnel Junctions by Way of Interface Reconstruction***, J Ko,* ***Jongill Hong****,* Yonsei University, Republic of Korea **INVITED**

Engineering of interfacial structures has become important to find new scientific observations and to create novel applications more than ever before. In this presentation, we show that the interface reconstructed by sub-monolayer-thick Mg insertion improved the magneto-electrical properties of perpendicular magnetic tunnel junctions essential for modern spintronic applications. The 0.2−0.4 nm-thick Mg inserted between MgO tunnel barrier and CoFeB ferromagnet restructured the interface in such ways as to protect the CoFeB from over-oxidation, to strengthen the texture, to make the interfacial roughness smooth, and to relax the mechanical stress. Observed were great increases in the perpendicular magnetic moment and perpendicular magnetic anisotropy of the CoFeB by 2.1 and 1.8 times, respectively, which can be ascribed to the optimum interfacial condition because of the least possible chemical damage. Furthermore, strong enhancement of (010) in-plane and (001) out-of-plane texture and of interfacial roughness led to a significant increase in the tunnel magnetoresistance by 4.4 times from 13.2 to 57.6% by the insertion. Most importantly, the electric field-controlled magnetic anisotropy coefficients became *symmetrically bipolar* to the electric field, which is essential for device applications, and they were increased over 100 fJ/V·m, which is 6 times larger than one found before the Mg insertion owing to optimum chemical and physical structures at the interface. As a result, we could successfully demonstrate the voltage-induced magnetization switching for the perpendicular magnetic tunnel junctions with the help of an external magnetic field. We strongly believe that our findings will ignite further study on the new way of electrical control over magnetic switching and provide an essential ingredient to realize electric field-driven energy-effective magneto-electronic devices.

6:20pm **NM-TuE-3 A Theoretical Outlook on the Exotic Properties of Spin Ice and Other Magnetic Pyrochlore Thin Films*, Michel Gingras,*** University of Waterloo, Canada

Frustrated magnetic materials and strongly correlated electron systems are a forefront of research in modern condensed matter physics and materials science. Despite almost three decades of investigations, the theoretical understanding of these fascinating systems remains incomplete. The most prominent theoretical frameworks used to tackle these systems take the form of an *emergent gauge theory* akin to the gauge theory that describes conventional electromagnetism.

Spin ice is an unusual substance in which the magnetic moments of individual atoms behave very similarly to the protons in conventional water ice — hence the name spin ice — failing to align even at very low temperatures and displaying the same residual entropy that Linus Pauling calculated for water ice and which is measured experimentally. Spin ices, which belong to the broad class of compounds called magnetic pyrochlores, actually have something in common with electromagnetic fields; both can be described by a gauge theory. Many aspects of conventional electromagnetism are sensitive to constraints from enclosure boundaries, such as total internal reflection used in communication with optical fibers. It is then reasonable to wonder if spin ices have similar sensitivities to boundary effects and confinement. Motivated by the recent experimental realizations of spin ice and other magnetic pyrochlore thin films, I will explore in this talk some of the exotic physical phenomena that arise when considering spin ice thin films such as, for example, a novel magnetic charge crystallization on the film surface while the bulk remains thermally disordered **[1]**. From a broader context, magnetic pyrochlore thin films offer a natural platform to study the confinement of emergent gauge fields describing strongly correlated systems and the evolution of nontrivial magnetic correlations as one moves from three to two dimensional spin textures **[2]**.

[1] L. D. C. Jaubert, T. Lin, T. S. Opel, P. C. W. Holdsworth, and M. J. P. Gingras, Phys. Rev. Lett. **118**, 207206 (2017).

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6:40pm **NM-TuE-4 Extending Compound Semiconductor Nanowire Functions by the Introduction of Additional Elements*, Fumitaro Ishikawa,*** Ehime University, Japan **INVITED**

Semiconductor nanowires are promising as building blocks in nanoelectronics and nanophotonics. The introduction of III–V compound semiconductor heterostructures into NWs provides dynamic control for the electronic band structure of these systems. On the other hand, oxides displaying advantageous dielectric, thermal, and resistive properties, which cannot be achieved in semiconductors, make their combination with semiconductors appealing. GaAs and related heterostructure have realized various optical and electronic devices with high speed and efficiency, e. g., transistors, lasers, and solar cells. To extend the functions of the materials system, diluted nitride and bismide has been paid attention over the past decade. They can largely decrease the band gap of the alloys, providing the greater tunability of band gap and strain status, eventually suppressing the non-radiative Surface and/or Auger recombinations. Selective wet oxidation for Al-rich AlGaAs is a vital technique for vertical surface emitting lasers. That enables the introduction of precisely controlled oxides in the system, enabling the optical and electrical confinement, heat transfer, and mechanical robustness.

We introduce the above materials into GaAs nanowires.[1] GaAs/GaAsN core-shell nanowires showed clear redshift of the emitting wavelength toward infrared regime. Further, the N introduction passivates non-radiative surface recombination, demonstrating laser emission from the single nanowire.[2,3] GaAs/GaAsBi core-shell structure was also obtained, showing a characteristic modification of the nanowire morphology.[4] Selective and whole oxidations of GaAs/AlGaAs core-shell nanowires produce semiconductor/oxide composite GaAs/AlGaOx. Possibly sourced from molecular species, the oxide shell shows white luminescence. [5,6]

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7:40pm **NM-TuE-7 Single-molecule Study on Nanocarbon Materials*, Shintaro Fujii,*** Tokyo Institute of Technology, Japan **INVITED**

Understanding charge transport through nanocarbon materials across the metal–molecule interface is a fundamental issue in organic devices. In recent years, single-molecule scale studies on charge transport through the metal–molecule interface have been made possible by break junction techniques. Here, we present our recent single-molecule transport studies on nanocarbon meterials using scanning tunneling microcopy (STM) and break junction techniques in combination with current-voltage measurements and fist principle simulations [1-4].

Bowl-shaped π-conjugated nanocarbons, or buckybowls, are a novel class of sp^2-hybridized nanocarbon materials. In contrast to tubular carbon nanotubes and ball-shaped fullerenes, the buckybowls feature structural flexibility. Bowl-to-bowl structural inversion is one of the unique properties of the buckybowls in solutions. Bowl inversion on a surface modifies the metal–molecule interactions through bistable switching between bowl-up and bowl-down states on the electrode surface, which makes surface-adsorbed buckybowls a relevant model system for elucidation of the mechano-electronic properties of nanocarbon materials. We demonstrate that the bowl inversion can be induced by approaching the STM tip toward the molecule. By tuning the local metal–molecule interaction using the STM tip, the sumanene buckybowl exhibits structural bistability with a switching rate that is two orders of magnitude faster than that of the stochastic inversion process.

Aromaticity of nanocarbons is a fundamental concept in chemistry. Antiaromatic nanocarbons are predicted to exhibit remarkable transport properties and high redox activities. However, it has only been possible to measure compounds with reduced aromaticity but not antiaromatic nanocarbons due to their energetic instability. We addressed these issues by investigating the single-molecule charge transport properties of a genuinely antiaromatic nanocarbon, showing that antiaromaticity results in an order of magnitude increase in conductance compared with the aromatic counterpart. Single-molecule *I-V* measurements and first principle transport calculations reveal that this results from a reduced energy gap and a frontier molecular resonance closer to the electrode potential in the antiaromatic species. The conductance of the antiaromatic complex is further modulated electrochemically, demonstrating its potential as a high-conductance transistor.

References

[1] Y. Komoto et al., Sci. Rep. 6, 26606 (2016). [2] Y. Isshiki et al., J. Am. Chem. Soc., 140, 3760 (2018). [3] S. Fujii et al., J. Am. Chem. Soc., 38, 12142 (2016). [4] S. Fujii et al., Nat. Commun., 8, 15984 (2017).

8:20pm **NM-TuE-9 Interfacial Defect Vibrations Enhance Thermal Transport in Amorphous Multilayers with Ultrahigh Thermal Boundary Conductance*, Ashutosh Giri,*** *J Braun, J Gaskins,* University of Virginia*; S King,* Intel Corporation*; A Henry,* Massachusetts Institute of Technology*; W Lanford,* University at Albany*; P Hopkins,* University of Virginia

The role of interfacial nonidealities and disorder on thermal transport across interfaces is traditionally assumed to add resistance to heat transfer, decreasing the thermal boundary conductance (TBC). However, recent computational works have suggested that interfacial defects can enhance this thermal boundary conductance through the emergence of unique vibrational modes intrinsic to the material interface and defect atoms, a finding that contradicts traditional theory and conventional understanding. By manipulating the local heat flux of atomic vibrations that comprise these interfacial modes, in principle, the TBC can be increased. In this work, we provide experimental evidence that interfacial defects can enhance the TBC across interfaces through the emergence of unique high frequency vibrational modes that arise from atomic mass defects at the interface with relatively small masses. We demonstrate ultrahigh TBC at amorphous SiOC:H/SiC:H interfaces, approaching 1 GW m^{-2} K^{-1} and are further increased through the introduction of nitrogen defects. The fact that disordered interfaces can exhibit such high conductances, which can be further increased with additional defects, offers a unique direction to manipulate heat transfer across materials with high densities of interfaces by controlling and enhancing interfacial thermal transport.

8:40pm **NM-TuE-10 Icephobic and Hydrophobic Behaviour of Laser Patterned Polyurethane Nanocomposite Coatings***, **Bartlomiej Przybyszewski**,* Warsaw University of Technology, Poland*; R Kozera,* Technology Partners Foundation, Poland*; A Boczkowska,* Warsaw University of Technology, Poland*; A Gonzalez-Elipe, A Borras,* Instituto de Ciencia de Materiales de Sevilla, Spain

Laser Patterning (LP) is a versatile tool for the fabrication of micro and sub-micropatterns on different materials. Inspired by typical plant surfaces with super-hydrophobic character such as lotus leaves and rose petals, structured hydrophobic surfaces have been prepared to discuss the wettability properties. In this work, LP was used to produce periodic surface structures on modified polyurethane (PU) coatings with periods ranging from 10 to 30 µm. The influence of the different modifications of PU as well as topographical characteristics of the produced micropatterns on coatings' wettability and icephobicity was investigated. The morphologies of structured samples include linear, square and rhombic protuberances. 2024 Al alloy and commercially available polyurethane topcoat, an extensively used materials in aircrafts and marine vessels, were employed as the substrates. To characterize the surface topography of the produced structures Scanning Electron Microscopy and Laser Profilometry were utilized. Static contact angle (SCA) and contact angle hysteresis (CAH) have been determined using standard wettability tests. Ice accretion, ice adhesion and freezing delay time tests have been carried out to assess icephobic properties of investigated coatings. It was found that prepared structured surfaces showed hydrophobic property with a WCA as high as 170° and CAH lower than 10°. Measurements of the contact angle of water on the treated surfaces allowed to identify an wetting behavior depending mainly on the laser period, surface roughness and chemical composition of investigated surfaces.

Thin Films

Room Naupaka Salons 4 - Session TF-TuE

Next-generation Protective Coatings and Tribological Applications

Moderator: Lars Hultman, Linkoping University

5:40pm **TF-TuE-1 Effects of Ar:N_2 gas ratio on TiN and TiAlN Thin Films Synthesized via RF Magnetron Sputtering***, **Jason Audrey Licerio**, A Alibadbad, M Vasquez,* University of the Philippines, Philippines

There is a growing interest in using titanium nitride (TiN) and titanium aluminum nitride (TiAlN) as a hard coating in recent years because of their high hardness, low friction coefficient, and good wear and oxidation resistance. Lifetime of machining tools significantly increase when coated with these transition metal nitrides. Radio frequency (RF) magnetron sputtering was used to synthesize the films. In this study, the Ar:N_2 ratio of synthesized TiN and TiAlN films were varied and characterized using a single target magnetron. That is, thin film growth is achieved using either a Ti target or 1:1 TiAl composite target. Argon:nitrogen (Ar:N_2) partial pressure ratios were varied at 9:1, 8:2, and 7:3 to grow the TiN and TiAlN films. Scanning electron microscope (SEM) images of TiN showed rough, 'pyramid-like' grains. Higher N_2 content resulted in more compact grains. The TiAlN films formed were dense 'cauliflower-like' grains. Cross-sectional SEM images showed both films having columnar structure with increasing grain diameter as N_2 content is increased. Energy dispersive x-ray spectroscopy mapping of TiN showed over-stoichiometric TiN_x. TiAlN maps showed almost 1:1 Ti:Al ratio but an abundance of N, confirming the formation of $TiAlN_x$ films. X-ray diffraction (XRD) results of TiN showed presence of (111), (220), and (311) TiN crystallographic planes. Decreasing N_2 content in the system resulted in the increase in intensity of (111) and (220) planes while increase in N_2 resulted in broadening of (111) plane. TiAlN XRD results showed formation of (111), (200), and (220) peaks. Increasing N_2 enhances the (220) peak. The 80:20 Ar:N_2 ratio resulted in increase of (200) peaks. The performance of drill bits coated with TiN showed three-fold increase in number of holes drilled while TiAlN films showed a two-fold increase as compared to that of uncoated drill bits. This work succeeded in the synthesis of TiN and TiAlN films and improving drill bit performance.

6:20pm **TF-TuE-3 Formation Mechanism of Tribofilm of Silicon Carbide under Water Lubrication: Molecular Dynamics Simulation***, **Fumiya Nakamura**, Y Wang, N Miyazaki, Y Ootani, N Ozawa, K Adachi, M Kubo,* Tohoku University, Japan

Water lubrication has the characteristic of low environmental burden. It is known that silicon carbide (SiC) shows low friction coefficient due to the formation of a tribofilm by chemical reaction at sliding interfaces under water lubrication. Thus, understanding of the chemical reaction mechanism is essential to improve friction characteristic for practical use and application. However, it is difficult to observe directly such a complicated phenomenon including friction and chemical reaction by experiments. Therefore, in this study, molecular dynamics (MD) simulation using reactive force field, which can simulate chemical reaction, was conducted to analyze the structure and formation mechanism of tribofilm in the friction process of amorphous SiC under water environment.

In the simulation, we used a model in which amorphous SiC ball and disk were rubbed in water (See supplementary document (SD) Fig.1). The SiC ball was slid on the SiC surface with nominal pressure of 0.5 GPa and sliding speed of 100 m/s.

During the friction, the surface wears as the SiC ball and the SiC disk come into contact with each other. Silica (SiO_2) particle and hydrocarbon were confirmed as wear debris. It was also observed that the SiO_2 particles dissolved in water and forms colloidal silica. Firstly, we investigated the changes in number of water molecules and Si-O-Si and C-H bonds during the friction (See SD Fig. 2, Fig.3). It was found that the number of water molecules decrease continuously while the number of Si-O-Si and C-H bonds increase correspondingly. This result indicates that hydrolysis reaction of SiC ($SiC + H_2O \rightarrow Si\text{-}OH + C\text{-}H$) occurs at the sliding interface. Next, we investigated the change in the number of Si and C contained in the wear debris (See SD Fig. 4). We found that the number of Si in the debris was always larger than that of C in the debris. This result indicates that the Si atoms are easily dissolved from the SiC surface as SiO_2 particle, whereas the C atoms tend to remain on the SiC surface. The distribution of C, Si, H, and O atoms except H_2O molecules shows that the C and H atoms were concentrated on the surface of the SiC disk and SiC ball (See SD Fig. 5, Fig. 6). On the other hand, the Si and O atoms were dissolved in water, forming the colloidal silica. Meanwhile, the Si and O atoms also located between the SiC disk and SiC ball. This fact indicates that the colloidal silica prevent the contact of the surfaces, leading to low friction. Thus, we concluded that colloidal silica, which is produced by the hydrolysis reaction of SiC surface, lowers the friction of SiC in water lubrication.

6:40pm **TF-TuE-4 Recent Advances in Surface Engineering***, **Ivan Petrov**,* Linköping University, Sweden, Frederick Seitz Materials Research Laboratory, University of Illinois **INVITED**

Surface Engineering (SE) is the science and technology of improving the surface properties of materials for protection in demanding contact conditions and aggressive environments. SE also encompasses engineering new multi-functional surface properties, such as electrical, optical, thermal, chemical, and biochemical properties. It involves multiple or hybrid processes which include substrate modification and deposition of overlayers in complex architectures. These processes enhance adhesion and optimize composition or microstructure to enhance protective properties coupled with other functionality. The substrates may be of complex shapes, like metal-cutting tools and automotive or aerospace components, and range in size from micrometers, such as in MEMS or NEMS devices, to meters, such as in architectural glass. The applications are wide-ranging, and include, for example, control of friction, wear-resistance, corrosion-resistance, thermal-barrier coatings, decorative coatings, bioimplants, antimicrobial layers, web-coatings, and thin films with engineered electrical and optical responses. Areas of scientific interest range from first-principle atomistic studies of new materials, to scientific and technological advances in synthesis methods, structural and chemical characterization techniques, property measurements, and performance characterization of surface-engineered parts. I will highlight a few selected SE advances from the past three years which include: complex SE architectures for joint-replacement implants [1], duplex coating for superior wear resistance of Ti alloy compressor blades or landing gear components [2], fracture-resistant thin-film metallic glass [3] and non-stick syringe needles[4]. TiB_x thin films grown from compound TiB_2 targets by magnetron sputter deposition are typically highly over-stoichiometric due to differences in Ti and B preferential ejections angles and gas-phase scattering during transport. I will describe two methods to control of the B/Ti ratio in sputter deposited titanium diboride coatings, involving preferential ionization of sputter-ejected Ti atoms [5,6]. The ability to obtain stoichiometric TiB_2 films is a prerequisite to obtaining high-quality epitaxial transition metal diboride layers. Overall, Surface Engineering continues to be a vibrant interdisciplinary field in the area of interest of AVS.

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[3] CC Yu et al, APL MATERIALS 4, 116101 (2016)

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7:40pm **TF-TuE-7 Influence of Defect Structures in MoS_2 Tribo-film Generated from MoDTC at DLC/DLC Interface on Friction Behavior: A Molecular Dynamics Simulation***, **Masahiro Saito,** N Miyazaki, Y Ootani, N Ozawa, M Kubo,* Tohoku University, Japan

MoDTC friction modifier for engine oil is well known to reduce friction under boundary lubrication where friction surfaces locally contact each other. MoDTC decomposes during friction and then, tribo-film of 2D-MoS_2 layers oriented at sliding interface is formed from the decomposition products of MoDTC, leading to low friction [1] . It is well known that the effect of MoS_2 largely depends on sliding condition. However, understanding of the dependency is not sufficient because of the difficulty of *in situ* observation at the sliding interface although sliding condition optimization is important to improve friction property. As one cause of this dependency, it is considered that the defect structure in MoS_2 tribo-film has some influence on friction. Thus, in order to investigate influence of defect structures in MoS--$_2$ tribo-film generated from MoDTC at sliding interface on friction behavior, we performed molecular dynamics simulation by using reactive force field (ReaxFF), which takes into account the chemical reactions.

In the simulation, we prepared models in which some MoS_2 layers are sandwiched between two diamond-like carbon (DLC) substrates because DLC is a coating material used in engine cylinders. Here, we investigated the influence of the defects by comparing the friction behavior of the MoS_2 layers with and without defect structures. As the defect structures, we considered grain boundary structures in the MoS_2 layer and a distorted layer structure in which layers unoriented at the interface. In order to simulate friction process, one DLC substrate was fixed and the other was slid at 100 m/s with 3 GPa of a contact pressure.

The friction simulation the model without defect showed that the contact surface of DLC and MoS_2 was the sliding interface. The simulation the model with grain boundaries showed that the contact surface of MoS_2 and MoS_2 was the sliding interface since C-S bonds were formed between DLC and MoS_2 around grain boundaries. In addition, the MoS_2 layers with grain boundaries showed higher friction force because the grain boundaries in neighboring MoS_2 layers interact each other. The simulation the model with distorted layer structure showed that the MoS_2 edge adhered to DLC since C-S and Mo-C bonds were formed between DLC and MoS_2. The shear stress acting on the unstable MoS_2 edge accelerated the chemical bond formation. In summary, we found that interactions between MoS_2 grain boundaries and formation of chemical bonds between MoS_2 and DLC sliding surface around defect are significant frictional resistance.

[1] J. Graham et al., J. Tribol., 44 (2001) 4

8:00pm **TF-TuE-8 Diamond-like Carbon Thin Film Deposition using Low-energy Ion Beams***, A Cuevas, M Ramos, A Catapang, **Magdaleno, Jr. Vasquez,*** University of the Philippines, Philippines

Diamond-like carbon (DLC) is a metastable form of carbon that has characteristics similar to diamond. High hardness, low wear rate, and chemically inert are some desirable properties of DLC that find a host of industrial applications. Diamond-like properties are greatly dictated by sp^2/sp^3 ratio of hybridized carbon and hydrogen atoms that are present in the DLC matrix. High sp^3 content in DLC can be achieved when carbon ion energy incident on a substrate is in the range of 100 eV. In this work, we developed a two-electrode ion source system capable of extracting broad ion beams with mean ion energies around 100 eV. The ion reservoir is made of stainless steel with permanent magnets around the cylindrical body to realize a multicusp configuration. Quiescent plasma was produced using 0.3 mm dia tungsten wires as hot cathodes. Acetylene (C_2H_2) was used as the carbon source with argon (Ar) as background gas. Doping was also done by introducing nitrogen (N_2) gas into the system. Retarding potential analyzer measurements suggest the successful generation of tunable broad ion beams with mean energies around 100 eV and current densities of around 10^{-6} A/cm^2. The dissociation of Ar/C_2H_2 and Ar/C_2H_2/N_2 plasma were obtained using a residual gas analyzer. The mass spectra of the Ar/C_2H_2 ion beam showed the presence of mostly hydrocarbon radicals such as $C_2H_2^+$, C_2H^+, CH^+, as well as heavier $C_XH_Y^+$ radicals and monatomic carbon and Ar. For Ar/C_2H_2/N_2 ion beam, CN radicals, monatomic and diatomic N were also observed. Compositional analyses of the films via Raman spectroscopy revealed the successful growth of DLC with sp^3 content of up to 80%. Energy-dispersive x-ray spectroscopy measurements show up to 10\% doping implying the successful and uniform incorporation of N in the DLC matrix. Improvement in adhesion was also observed for N-doped DLC films. X-ray photoelectron spectral measurements suggest the presence of sp^2 and sp^3 on the surface which supports the subplantation growth scheme of DLC. X-ray diffractometry suggests the presence of diamond and graphite phases in a generally amorphous films . Surface analyses employed using scanning electron microscopy showed good conformity of the DLC films with increasing thickness upon the subsequent increase in C_2H_2 content. Hardness testing via nanoindentation show acceptable hardness values of around 8 GPa. These films may find applications in tribological coatings.

8:20pm **TF-TuE-9 A Study on Copper/Silver Core-shell Microparticles with Silver Nanoparticles Hybrid Ink and its Sintering Characteristics with Flash Light for High Oxidation Resistance***, **Jong-Whi Park**, Y Jang, H Kim,* Hanyang University, Seoul, Korea

In this study, a silver(Ag) coated copper(Cu) core-shell microparticles ink were fabricated and screen-printed on Polyimide(PI) substrates. It was sintered via flash light sintering technique. Flash light irradiation condition (i.e. pulse duration, irradiation energy) was optimized to obtain high conductivity and good oxidation resistance characteristics of Ag coated Cu core-shell pattern. To increase the packing density of the electrodes and its oxdiation resistance, Ag nanoparticles(NPs) were added to Cu/Ag core-shell microparticles (MP) ink. To determine optimal amount of the Ag NPs, the hybrid ink having different mass ratios of the Ag NPs and Cu/Ag core-shell MP were fabricated and tested. The sheet resistance of the hybrid ink was measured using the four-point probe method. To analyze the sintering behavior and degree of oxidation of hybrid pattern, a scanning electron microscope (SEM) was used. To demonstrate the mechanism of the sintering process on hybrid ink, multiphysics COMSOL simulation and temperature monitoting was conducted. As a result, hybrid pattern sintered with flash light showed excellent oxidation resistance (resistance increase rate in 300℃ for 5 hours: 54.34 %), and high electrical conductivity (9 μΩ·cm).

Acknowledgments

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Biomaterial Surfaces & Interfaces
Room Naupaka Salon 6-7 - Session BI-WeM

Soft Surfaces and Biofunctional Coatings

Moderator: Tobias Weidner, Aarhus University, Denmark

8:40am **BI-WeM-3 Surface Micropatterning Techniques for Reconstituting Functional Neuronal Networks in Culture***, **Hideaki Yamamoto**, A Hirano-Iwata,* Tohoku University, Japan **INVITED**

Nerve cells in culture take irreplaceable roles in molecular and cellular neuroscience. However, the fact that neurons form random connections, which are substantially different from the actual brain, has limited the wide application of cell culture in systems-level studies.

Surface modification combined with microfabrication has a high potential to circumvent this limitation of cell culture technology in neuroscience [1-2]. By patterning biomolecules that scaffolds cellular growth, a glass coverslip can be functionalized so that growth of primary neurons can be controlled extrinsically, at the level of both individual cells [3-5] and cell populations [6]. Taking advantage of the cell micropatterning technology, we reconstitute functional neuronal networks of rat cortical neurons and investigate how meso-scale connectivity among neurons determines network dynamics. We focus on the modular organization of brain networks, characterized by the presence of densely-connected subsystems, i.e., modules, that are weakly interacting with each other [7]. Analysis of spontaneous neural activity by fluorescence calcium imaging shows that an atypical dynamics of the cultured networks, characterized by a bursting activity that is highly-synchronized across the whole network, is suppressed by the induction of modular organization in the networks. Increasing the degree of modularization causes the networks to generate activity patterns that are spatiotemporally more complex. Our results demonstrate that surface micropatterning expands the cell culture system as a unique tool to model and study the structure-function relationships in living neuronal networks.

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9:20am **BI-WeM-5 Inhibiting Bacterial and Fungal Growth *via* Biomimetic Nanopillared Surface Structuring***, **Rachel Rosenzweig**, V Ly, K Perinbam, M Marshall, E Pearlman, A Siryaporn, A Yee,* University of California, Irvine

Bacterial and fungal contamination occur in our everyday lives from food spoiling, oral disease, appliance clogging, and industrial naval and aviation fuel-line dependent transportation. More perilously, human pathogenic bacteria and fungi often contaminate medical device surfaces leading to 1.7 million annual nosocomial infections in the US alone. Such infections result in 99,000 annual deaths and $20 billion in healthcare costs. Current solutions that are declining in efficacy due to antimicrobial resistance (AMR) include chemical antimicrobials applied topically to or impregnated onto devices and implants. The rise of AMR has created an urgent need for alternative strategies. In this work, the physical antimicrobial effects of nanoimprinted polymer surface structures inspired by insect wing nanotopography are investigated.

Natural nanopillared surface structures found on dragon fly and cicada wings have been found to cause bacterial cell lysis, yet their possible effect has not been studied when applied to eukaryotic filamentous fungi. In this work, AMR prokaryotic bacteria, *Pseudomonas aeruginosa*, and clinical isolates of AMR eukaryotic filamentous fungi, *Aspergillus fumigatus* and *Fusarium oxysporum*, were cultured on flat and engineered biomimetic nanopillared surfaces on a material often used in medical devices, *viz*., poly(methyl methacrylate). Surfaces of nanopillared arrays with varying periodicities of 200nm, 300nm, 500nm, and 600nm were fabricated using nanoimprint lithography. Notably, this surface structuring technique is a low-cost and scalable lithographic method translatable to flat and curved surfaces. Cell growth and survival were measured using fluorescence microscopy of GFP tagged bacteria and fungi with propidium iodide DNA stain to indicate compromised cell membranes. The cell-nanosurface interface was further analyzed with scanning electron microscopy. A decrease in *P. aeruginosa, A. fumigatus,* and *F. oxysporum* cell growth and an increase in cell death were observed on the biomimetic nanopillared surfaces compared to the flat. This work presents the first demonstration of a scalable, nanostructured, antimicrobial surface against both drug resistant prokaryotic bacteria and eukaryotic fungi. This biofunctional coating can be applied to a broad range of applications in healthcare, industrial transportation, and environmental conservation.

9:40am **BI-WeM-6 Chemo-enzymatic Pathways for Sustainable Terpene-based Polymeric Materials***, **Arne Stamm**, L Fogelström, P Syren, E Malmström,* KTH Royal Institute of Technology, Sweden

Polymers play an essential role in everyday life as materials in automotive, packaging and electronics and as compounds in medicine. Nevertheless, the finite supply of fossil fuels leads to an increased need for development of more sustainable materials from renewable sources. Renewable natural products from forestry, especially hemicellulose and terpenes, offers a highly versatile platform for green building blocks. By using Nature's own biofunctionalizations, enzymes can be used as green catalysts for the valorization of abundant terpenes from pine-wood extractives. Enzymatic biotransformations enable mild processes for "activating" inert molecular building blocks in a highly controlled manner to afford renewable monomers. By combining *in vitro* synthetic biology and polymer chemistry, we have generated a novel class of bio based polymers, star ting from a naturally abundant terpene found in wood. Specifically, the terpene sobrerol, which can be achieved both enzymatically and by traditional organic chemistry, represented a promising starting compound for the preparation of such bio based monomers. Sobrerol consists of a multiple substituted cyclohexene unit, containing secondary and tertiary hydroxyl functionalities. The functionalities of sobrerol enable certain chemical modifications, whereas the cyclic structure provides hardness in subsequent polymeric products. Especially, the stereoselective methacrylation of the secondary hydroxyl group constituted a suitable monomer for radical polymerization. We were able to demonstrate that the enzymatic functionalization under benign conditions showed superior properties concerning yield, stereo selectivity and workup procedures of the methacrylated sobrerol (SobMa). Further, SobMA could be polymerized using both traditional and enzymatic procedures enabling a completely green route from a natural abundant product to a highly versatile polymer. Due to the remaining functional groups in the side chain, polySobMA provides a variety of possibilities for post-functionalization reactions and crosslinking. Polymeric films were obtained by crosslinking reactions using either the ene-, or the hydroxyl functionality of the sobrerol unit and their properties evaluated. Thus, the unaffected second functionality could be used for a broad range of further modifications to produce tailor-made polymer films targeting different fields of application. In conclusion we were able to present that the use of enzymatic or chemo-enzymatic processes is an ideal approach to convert terpenes into highly versatile polymeric coating materials.

10:20am **BI-WeM-8 Chemical Surface Modification of Carbon Nanostructures Towards Biological Applications***, **Mildred Quintana**,* Universidad Autónoma de San Luis Potosí, México **INVITED**

The unique combination of properties of carbon nanostructures, such as high specific surface area, chemical stability, mechanical strength, flexibility, high electrical and thermal conductivity, and tunable band gap and shape, make them ideal materials for the development of a number of bio-applications including biosensors [1], photodynamic therapy agents [2], and active surfaces for cellular growth [3]. However, for applicability several problems arise, including scalability, dispersibility, stability, and reproducibility. Several authors have proposed chemical functionalization as a feasible solution to render carbon nanostructures dispersible in many solvents, comprising water, and readily for its integration in hybrids materials [4]. Furthermore, by performing chemical organic reactions on carbon nanostructures, it is possible to exactly adjust the interfacial properties to increase biocompatibility [5] or to prompt lipid membrane translocation [6]. In this work, I will describe our recent efforts on the chemical functionalization of carbon nanotubes and graphene towards the development of SERS biosensors, photodynamic therapy agents and active surfaces for cellular growth. The importance of the tailored design of the chemical surface of the nanostructure for the desired application will be extensively discussed.

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11:00am **BI-WeM-10** ***Roles of Anodic Oxide Layer on the Improvement of Cellular Response of Titanium Implant , Naofumi Ohtsu****, T Kuji, M Hirano,* Kitami Institute of Technology, Japan

Anodic treatment of titanium (Ti) has been used to improve its biocompatibility. The process leads to the formation of TiO_2 layer and the layer growth can be controlled by varying the processing voltage. Concomitantly, the surface roughness increases accompanying with the layer growth. Some researchers have believed that the enhanced biocompatibility through anodization is derived from the chemical property of TiO_2 itself, whereas other groups have insisted that the roughness increase relates with the biocompatibility. To obtain the valuable clue regarding this argument, in the present study, we prepared a TiO_2 layer with different roughness through the anodization in H_3PO_4 electrolyte with various voltages ranging from 5 to 500 V and thermal oxidation at 723 K in air. Thereafter, surface roughness and cellular response were compared to discuss the dominant property contributing the enhancement.

The surface image of the anodized substrates, observed by SEM, revealed that the surface roughness increased with increasing the voltage. To investigate the cellular response, MC3T3-E1 cells, an osteoblast-like cell line, were seeded on the sample surface and cultivated for 72 h, after which the numbers of the attached cells were counted. The numbers of the cells on the anodized surfaces were larger than those on an untreated and the thermally oxidized surfaces, whereas the difference depending on the processing voltage was hardly observed. Ii was conjectured that the enhanced biocompatibility is due to the anodized TiO_2 itself, of which surface property is different with that of TiO_2 prepared by thermal oxidation.

11:20am **BI-WeM-11 (Electro)Chemically Synthesis et Characterization of New Coating having N-Halamine Groups giving them Regenerative Antibacterial Properties*, Vincent Humblot*,** *N Nazi,* LRS - CNRS Sorbonne Université, France*; C Debiemme-Chouvy,* LISE - CNRS Sorbonne Université, France

In the presence of moisture, surfaces are an ideal support for the development of biofilms containing bacteria that can be pathogenic. This poses a real public health problem, economic or even environmental in view of the use of biocides to fight against this phenomenon. The first step in the formation of a biofilm is the adsorption of molecules, especially proteins, followed by the colonization of surfaces by bacteria.

The goal of this study is the development of **new regenerative antimicrobial coatings**, **containing haloamine (or N-halamine) functions(> N-Cl or> N-Br)** that have oxidative properties due to the degree of oxidation +I [(a,b)]. N-halamines are broad-spectrum biocidal groups; due to their mode of action, i.e. oxidation, bacteria should not develop resistance, unlike after repeated use of antiobiotics. The protection of surfaces with N-halamine compounds requires the immobilization of amine, amide or imine functions that will be transformed into haloamine either during synthesis or by post-treatment in the presence of NaOCl or NaOBr.

In this study, we will present a new approach of gold surfaces functionalization with the use of a biopolymer: **polydopamine**. The synthesis of the polymer has been implemented with two original approaches: a chemical and an electrochemical synthesis. We will present a comparative study of both chemical and electrochemical polymerisation and functionalization of gold surfaces characterized by means **of PM-RAIRS, XPS and (E)-QCM surfaces techniques**. The control of the polymer thickness shows a clear dependence of the antibacterial response with the degree of chlorination or bromination. Finally, the simple regeneration of the biocidal surfaces will be presented together with the biocidal activity upon re-use of the surfaces.

(a) Antimicrobial *N*-halamine polymers and coatings: A review of their synthesis, characterization and applications. F. Hui, C. Debiemme-Chouvy, *Biomacromolecules* **2013**, 14, 585-601. (b) N-halamine coating formed via the electroreduction of *in situ* generated diazonium cations: toward antimicrobial surfaces. S. Gao, H. Cachet, C. Debiemme-Chouvy. *Surf. Interface Anal*. **2016**, 48, 630-635.

11:40am **BI-WeM-12 Effect of Salts on Friction of Zwitterionic Polymer Brush: Molecular Dynamics Simulation*, Shuichi Uehara*,** *Z Liu, N Miyazaki, Y Ootani, N Ozawa, M Kubo,* Tohoku University, Japan

In recent years, concentrated polymer brush (CPB), which is constructed by grafting polymers onto a substrate at high density, has been developed [1]. Especially, zwitterionic CPB produces ultra-low-friction surface and has biocompatibility in aqueous environment. Thus, zwitterionic CPB has attracted much attention for application to a low friction material as artificial joints. Recently, experiment showed the friction force of zwitterionic CPB decreases with increasing ionic strength for salts [2]. However, the details of this mechanism are still unknown because the in-situ observation is difficult. For enhancing the performance of zwitterionic CPB as a low friction material in biological applications, it is important to understand the effect of salt existing in biological environment. Thus, computational simulation is required.

In the present study, we performed molecular dynamics friction simulation between CPB and Au tip to elucidate the effect of salts on friction force of zwitterionic CPB. In the CPB model, 9 zwitterionic polymer chains of 10 monomers were grafted to a silicon (111) substrate (area, 5.75nm×5.98nm) via covalent bonds. For comparison, we prepared two systems: with salts (80 KCl) and without salts. Both system of CPB solvated in 6000 water molecules.

At a low load (up to 10 MPa), zwitterionic CPB with salt showed lower friction force than system without salts. This result is qualitatively consistent with experimental data [2]. The mean square displacement of water in the system with salts is lower than that in system without salts. This result suggests that waters in the system with salts have higher viscosity. Whereas, we find that zwitterionic chain with salts is harder to move in the sliding direction than system without salts. Therefore, we revealed that the binding of salts to polymer chain made polymer chains hard to collapse in spite of increasing viscosity of waters. Thus, zwitterionic CPB with salt reduced contact area between Au tip and polymer chains. Our previous study showed that the reduction of contact area of CPB in friction interface leads to low friction [3]. On the other hand, at a high load (20 MPa), the friction force of zwitterionic CPB with salts and system without salts were comparable. This is because salts desorb from inner layer of zwitterionic CPB due to the severe load. Therefore, to enhance performance of zwitterionic CPB as a low friction material, it is necessary to design of CPB so as to hold salts which make CPB hard to collapse in the severe load.

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Energy Harvesting & Storage
Room Naupaka Salon 5 - Session EH-WeM

Efficient Power Conversion/Cells
Moderator: Paul Braun, University of Illinois at Urbana-Champaign, USA

8:00am **EH-WeM-1 Linear and Multi-photon Fluorescence of Thiophene based Copolymer as Novel Potential Material for Photovoltaics***, L Slusna,* Comenius University, Bratislava, Slovakia*; L Haizer,* International Laser Center, Bratislava, Slovakia*; E Jane,* Institute of Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia*; D Bondarev,* Polymer Institute, Slovak Academy of Sciences, Bratislava, Slovakia*; V Szocs, M Drzik,* International Laser Center, Bratislava, Slovakia*; E Noskovicova,* Comenius University, Bratislava, Slovakia*; D Lorenc,* International Laser Center, Bratislava, Slovakia*; M Jerigova,* ***Dusan Velic***, Comenius University, Bratislava, Slovakia

Currently, the most important applications for polythiophenes are in the area of solar cells, thin-film transistors, light-emitting diodes, sensors and nonlinear optics with low-cost and low-temperature processing [1]. On the other hand, polythiophenes show a great promise also in the area of nonlinear optics and photonics [2] with enhanced second and third order nonlinearities. Hence, dynamics of polythiophenes gained an increased interest, because it is providing detailed understanding of the complex processes occurring in π-conjugated polymers.

A novel copolymer (poly(thiophene-2,5-diyl-2,5-di-n-octyloxycarbonyl-1,4-phenylene)) denoted as P33 is introduced as a potential material for photovoltaics. P33 dissolved in chloroform was investigated by steady-state absorption, linear/non-linear fluorescence spectroscopies and time-resolved fluorescence spectroscopy.

Molar extinction coefficient of P33 was determined as 18315 $cm^{-1}.M^{-1}$. The P33 fluorescence quantum yield and P33 singlet fluorescence lifetime were determined as 0.4 and 810 ps, respectively. The P33 fluorescence fast decay component shows decay times of 1.2 ps, 2.0 ps, and 0.5 ps for increasing wavelengths of 480 nm, 500 nm, and 520 nm, respectively. The fast component has been previously attributed to transport of nearly instantaneously formed excitons to localized states known as downhill energy transfer. Multi-photon excited fluorescence has been observed for the P33 solutions in chloroform and for 800 nm and 1200 nm pumping. The P33 TPA cross-section was evaluated as 6.9 GM. This spectroscopic study provides basic fluorescence characteristics of the novel thiophene copolymer P33.

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8:20am **EH-WeM-2 Novel Semi-Transparent Inorganic Sb_2S_3 Thin Film Solar Cells*, Shi-Joon Sung*,** *S Lee, K Yang, J Kang, D Kim,* DGIST, Republic of Korea

In recent years, researches on transparent photovoltaics has been attracting immerse interests as a key component of multifunctional window applications. Until now, there were enormous researches on transparent photovoltaics were based on organic materials, such as dye sensitized solar cell (DSSC) or organic solar cell (OSC), because of wide bandgap of the organic materials. However, these organic-based transparent solar cells are still suffering from the stability problem, which is one of critical obstacles for the commercialization of organic-based solar cells. In order to overcome this problem, some researchers are nowadays interested in the inorganic-based transparent solar cell technologies, such as ultra-thin film solar cells, patterned aperture solar cells, and so on. However, in these cases, device fabrication process is complicated and the device performance is limited because of restricted physical dimensions.

Because inorganic Sb_2S_3 has wide bandgap (1.6 ~ 1.8 eV) and higher absorption coefficient (10^5 cm) compared with other inorganic materials, Sb_2S_3 might be a good candidate for inorganic semi-transparent absorber materials. In our work, we adopted ultra-thin and high quality Sb_2S_3 thin films as a semi-transparent absorber layer. The high quality Sb_2S_3 thin films with different thickness were deposited using atomic layer deposition (ALD) technique, which showed bandgap of 1.78 eV, absorption coefficient of 1×10^5 cm, and light transmittance up to 30 %. In order to fabricate semi-transparent solar cell devices, ALD Sb_2S_3 thin film with 80 nm thick were firstly deposited on transparent TiO/ITO substrates. Transparent P3HT and ultra-thin transparent Au electrode were also deposited onto the ALD Sb_2S_3 thin film. This semi-transparent Sb_2S_3 solar cell device showed power conversion efficiency of 3.44% and average light transmittance (from 400 to 800 nm) of 13%. The semi-transparent Sb_2S_3 solar cell device also showed excellent device stability over 180 days, which might be attributed to the inorganic Sb_2S_3 absorber material. Semi-transparent inorganic thin film solar cells based on Sb_2S_3 has a great potential to be a novel robust and stable transparent solar cell technology.

8:40am **EH-WeM-3 In situ Scanning Tunneling Microscopy of the Electrocatalytic Reactions*, Dong Wang,*** ICCAS, China

The electrocatalytic reactions at the electrode/electrolyte interface play a critical role in the performance of electrochemical energy storage and conversion devices. Understanding the structure and reaction processes at solid/liquid interface is of great importance in surface science and electrochemistry. In view of the dynamic and complex nature of the interface, in situ research approaches can provide valuable information of interfacial phenomena. In situ scanning tunneling microscopy (STM) is a powerful technique used for the interfacial investigation of electrochemical energy devices.

In this presentation, we employed high resolution electrochemical STM to investigate the typical electrochemical catalytic reactions, such as oxygen reduction reactions, oxygen evolution reactions, using the model molecular catalysts. The self-assembled metal porphyrin and phthalocyanine compounds show notable electrocatalytic activity. The real-time STM imaging provides direct evidence to study the interfacial electrochemical reactions at molecular level.

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9:00am **EH-WeM-4 Fabrication of Free-standing Thin Film by Injecting Polymer into Porous Substrate for Thin Film Solid Oxide Fuel Cells*, Yusung Kim*,** *S Cha, W Yu, W Jeong, J So,* Seoul National Univeristy, Republic of Korea

Free standing thin films were fabricated by injecting polymer into porous substrate for thin film solid oxide fuel cells(TF-SOFCs). To apply thin film on porous substrate with pores of more than 1 micrometer, anode functional layer(AFL) is needed to reduce pore size. However, it is difficult to supply gas when the AFL is thickened due to the reduced pore size and porosity. To solve this problem, free standing under 1 micrometer thin film AFL was fabricated on a porous support. Based on the Si-based free standing thin film sofc, which is a field of TF-SOFCs, the pores of the porous NiO-YSZ support were blocked through injecting polystyrene, the NiO-YSZ thin film was deposited thereon, and the polystyrene was removed to make the free-standing thin film by pyrolysis. The pore blocking through the polymer was obviously a major influence on the thin film covering the pore. On the other hand, since the pore size of the support is about 10 μm, the pore size is not reduced when the thin film is deposited without pore blocking. In the process of melting and solidifying into a liquid to insert the polymer, a nanoscale gap was created due to the volume change due to the phase change, and the thin film deposited thereon also has this shape. Also it is verified that the NiO-YSZ thin film was successfully fabricated on the porous NiO-YSZ substrate by FIB-SEM analysis.

9:20am **EH-WeM-5 First-Principles Study on Influence of Metal Oxide on H_2S Poisoning Tolerance of Pt Nano-Particle Catalyst in Polymer Electrolyte Fuel Cell*, Kota Kuranari*,** *N Miyazaki, Y Ootani, N Ozawa,* Tohoku University, Japan*; M Kubo,* Institute for Materials Research, Tohoku University, Japan

Pt catalysts are used as anode catalysts for polymer electrolyte fuel cell (PEFC). The fuel in PEFC contains a small amount of impurities such as CO and H_2S. These impurities adsorb on active sites of Pt surfaces and degrade the hydrogen oxidation reaction activity of the anode catalyst. This loss of catalytic activity caused by impurities is known as impurity poisoning. Therefore, the development of the anode catalyst with the high impurity tolerance is strongly required. Takeguchi et al. experimentally found that adding SnO_2 as support material improves the CO tolerance of the Pt-based catalyst[1]. Furthermore, it is known that adsorbed impurities on the Pt catalyst can be removed by oxidation reaction. Kakati et al. reported that oxidation reaction by O and OH can recover from the H_2S poisoning[2]. In order to develop the high impurity tolerant catalyst, it is necessary to reveal the effect of SnO_2 nano-particles on H_2S tolerance and the recovery mechanism from H_2S poisoning by oxidation reaction. In this study, we analyzed the adsorption states of H_2S on Pt/SnO_2(110) model and the recovery process from H_2S poisoning by oxidation with OH using first-principles calculation.

For the calculation model, we put a Pt_{29} cluster on SnO_2(110). The Pt_{29} cluster exposes Pt(111) on the top (See supplementary document Fig. 1). We calculated the adsorption energy of H_2S on Pt/SnO_2(110) and compared with the one on Pt(111) to reveal the effect of SnO_2 on H_2S poisoning process. The adsorption energies of H_2S were -18.38 and -24.73 kcal/mol on the Pt cluster of Pt/SnO_2(110) and Pt(111), respectively. Thus, it was found that the adsorption of H_2S on Pt is suppressed by addition of SnO_2. Next, we analyzed the recovery process from H_2S poisoning by OH generated from dissociation of H_2O. It is known that H_2S adsorption on Pt is dissociative and adsorbed sulfur atom is generated. The sulfur atom adsorbed on the surface decreases the activity of the Pt catalyst. In this study, we considered the reaction process (See supplementary document Fig. 2) based on the intermediate stable species during the H_2S oxidation cascade in the gas phase[3] and calculated the activation energies of each elementary process. We found that the water dissociation is the rate-determining step on both Pt/SnO_2(110) and Pt(111) and the activation energies were 18.78 and 23.70 kcal/mol, respectively. Therefore, we demonstrated that an addition of SnO_2 promotes an oxidation reaction of adsorbed sulfur on the Pt catalyst.

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9:40am **EH-WeM-6 Impurity Tolerance of Pt/ Metal-Oxide Anode Catalyst for Polymer Electrolyte Fuel Cell: First-Principles Calculation***, **Nobuki Ozawa**, K Kuranari, M Kubo,* Tohoku University, Japan

Polymer electrolyte fuel cell (PEFC) needs anode materials with high tolerance to poisoning by impurities such as CO, NH_3, and H_2S in the fuel, which degrades performance of the PEFC. Recently, a composite of Pt and WO_3 (Pt/WO_3) is used as a catalyst in the anode, and this catalyst is effective for CO removal by oxidation [1]. For theoretical design of anode materials with high tolerance to impurity poisoning, the mechanism of high tolerance of Pt/WO_3 to CO should be revealed. In this study, we investigated CO oxidation processes on Pt/WO_3(001) by first-principles calculation. At first, we calculated the adsorption energies of CO on Pt/WO_3(001) and an isolated Pt cluster, to discuss an effect of WO_3 on CO tolerance of Pt. For a Pt/WO_3(001) model, a Pt_{20} cluster is put on a WO_3(001) surface. The adsorption energy of CO on the Pt_{20} cluster is 36.40 kcal/mol, while that on an isolated Pt_{20} cluster is 45.65 kcal/mol. These results indicate that the combination of the WO_3 surface and Pt cluster decreases the adsorption energy of CO on the Pt cluster. To investigate the reason why the adsorption energy of CO decreases by the WO_3 surface, we calculated d-band center [2] of the Pt atom on Pt/WO_3(001) and Pt cluster. In general, downward shift of the d-band center increases the adsorption energy of CO. Here, the d-band center values of the Pt atom on Pt/WO_3(001) and isolated Pt cluster are -2.28 and -2.15 eV, respectively. This means that WO_3 modifies the electronic states of the Pt cluster and leads to the downward shift of the d-band center, which decreases the adsorption energy of CO. Next, we discuss CO oxidation on Pt/WO_3(001). The CO oxidation by H_2O proceeds as follows; (i) $H_2O \rightarrow OH^- + H^+$ and (ii) $CO + OH^- \rightarrow CO_2 + H^+ + 2e^-$. Here, we firstly investigated H_2O dissociation on Pt/WO_3(001). In this calculation, the H_2O molecule adsorbs on the interface between the Pt cluster and WO_3(001) surface, and dissociates to H^+ on the Pt atom and OH^- at the interface. The activation energy for the H_2O dissociation is 19.87 kcal/mol, which is lower than that on a pure Pt(111) surface (23.70 kcal/mol). Thus, we suggest that WO_3(001) can decrease an adsorption energy of CO and activation energy for H_2O dissociation on Pt catalyst during CO oxidation process.

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10:20am **EH-WeM-8 Harvesting Sunlight for Photoelectric and Photothermal Conversions with Titanium Nitride Nanostructures***, **Satoshi Ishii**,* National Institute for Materials Science, Japan*; S Shinde, R Sugavaneshwar, M Kaur, T Nagao,* National Institute for Materials Science **INVITED**

Harvesting sunlight enables conversion of photon energy to electronic energy and thermal energy. Among different classes of materials, metals have unique properties in light harvesting. Since metals are highly conductive and do not have bandgaps, metals can generate hot carriers even with low energy photons to be injected into an adjacent semiconductor. The excited hot carriers eventually become heat and heat the metals themselves and their surroundings. These photoelectric and photothermal effects can be enhanced by the optical resonances i.e. surface plasmon resonances. Hence, number of researches have taken advantage of plasmon resonances in photoelectric and photothermal conversions. As gold and silver are known to be excellent plasmonic materials, nanostructures made of these noble metals have been widely used in the recent studies.

In contrast, we have been working with titanium nitride (TiN) nanostructure to show that it can also be used in photoelectric and photothermal conversions. Titanium nitride is chemically stable and much cost-effective than gold or silver, making it a practical choice of material. In addition, TiN is plasmonic in visible and near infrared and superior to gold and silver in absorbing broad spectrum. In the first part, we present that TiN nanostructures can generate photocurrent by the irradiation of visible light, and can enhance the visible photocatalytic activities of carbon nitride which is a UV-active metal-free photocatalyst. In the second part, we show that TiN nanoparticles are efficient sunlight absorbers to generate solar heat. Since each TiN nanoparticle act as a nanoscale heater, solar heated TiN nanoparticles offer efficient water distillation and chemical reactions such as oxidation of carbon monoxide. Our results demonstrate that TiN nanostructures have the potential to replace gold and silver nanostructures in sunlight harvesting applications with better efficiencies.

11:00am **EH-WeM-10 Solar Printing: From Benchtop to Rooftop***, **Paul Dastoor**,* University of Newcastle, Australia **INVITED**

Organic photovoltaics (OPV) are poised to play a major role in the global energy portfolio driven by their capability to be printed at high speeds across large areas using roll-to-roll (R2R) processing techniques; creating the tantalising vision of coating every roof and other suitable building surface with photovoltaic materials at extremely low cost. Indeed, recent full economic modelling of the balance of materials (BOM) and balance of system (BOS) costs, have highlighted the long-term commercial viability of OPV-based technology in today's energy marketplace.

However, the chlorinated solvents that are used in current OPV technology are under continual regulatory pressure due to their hazardous and toxic nature. Indeed, increasingly harsh technical requirements for using these solvents means that their implementation in high speed printing lines will be highly problematic if not economically impractical. In addition, tailoring device morphology across large areas is fraught with difficulty due to the challenge of controlling phase segregation of polymer mixtures using conventional printing. Water-based polymer nanoparticle dispersions (solar paint) offer the prospect of simultaneously controlling the nanoscale architecture of the active layer whilst eliminating the need for hazardous organic solvents during device fabrication. However, the behaviour of these nanoparticulate devices is complex and thus understanding their structure-function relationships requires characterisation techniques that can probe chemical structure on the nanoscale. In this paper we review our progress in understanding the structure-function relationships of organic electronic nanoparticulate thin films. In particular, I will discuss how scanning transmission X-ray microscopy is an invaluable tool for characterising these materials.

Finally, I will explore the future prospects and economics for large scale manufacture of solar cells based on printing. I will discuss our recent achievements in the development of a fully operating R2R printing line and the installation of several large scale (> 100 m^2) demonstrations of printed solar modules.

Thin Films
Room Naupaka Salons 4 - Session TF-WeM

Nanostructural and Surface Morphological Evolution: Experiment and Theory

Moderator: Andres De Luna Bugallo, CINVESTAV-Unidad Queretaro, Mexico

8:00am **TF-WeM-1 Nanostructure and Morphological Evolution During Thin Film Growth of Metals and Silicides Using Real-time Diagnostics***, **Gregory Abadias**, C Furgeaud,* Institut Pprime, CNRS-Université de Poitiers, France*; B Krause,* KIT, Germany*; A Jamnig,* Institut Pprime, CNRS-Université de Poitiers and IFM Linköping University, Sweden*; K Sarakinos,* Linköping University, Sweden*; J Colin, L Simonot, A Michel, C Mastail,* Institut Pprime, CNRS-Université de Poitiers, France **INVITED**

Thin metallic films deposited on Si are still largely used in many technological areas, such as microelectronics, catalysis, architectural glazing or plasmonics. In the case of high-mobility metals on weakly interacting substrates (e.g. Ag on SiO_2), the growth proceeds in a 3D fashion, known as Volmer-Weber. The control of islands size and shape at the beginning of growth is vital for many applications as the characteristic length scales and physical attributes of ultrathin films are mostly set-in during the coalescence stage.

By employing a panel of *in situ* and real-time diagnostics, we could obtain valuable insights on the thin film growth dynamics, as well as stress evolution, in a variety of sputter-deposited metallic systems (Ag, Cu, Au, Pd and Mo). More particularly, the characteristic thickness of film percolation and film continuity can be determined from a combination of real-time electrical resistivity and wafer curvature measurements. This will be highlighted for the case of Ag and Cu deposited on amorphous carbon as a function of deposition rate *F* and deposition temperature T_s.

We will also provide examples on how chemical alloying or interface reactivity can affect the growth morphology and stress evolution of Ag and Cu films. Growth monitoring was performed *in situ* by employing either surface differential reflectance spectroscopy or spectroscopic ellipsometry.

We will show that strategies based on interfacial or alloying design can be efficiently employed to manipulate growth and obtain ultra-thin, ultra-smooth, continuous layers.

Finally, we will discuss the case of silicide formation during growth of metal layers with lower adatom mobility (e.g. Mo) on silicon. By coupling simultaneously X-ray diffraction, X-ray reflectivity and wafer curvature during sputter-deposition of metal layers on amorphous Si, information about thickness-dependent crystalline phases, texture, grain growth and microstrain can be gained. This will be demonstrated for Mo/Si and Pd/Si systems. A complex nanostructure formation is uncovered from these synchrotron studies, pointing out to different silicide formation mechanisms and subsequent structural development.

8:40am **TF-WeM-3 Seeding and Growth of Metallic Ultra-thin Film Deposited on Amorphous Polymeric Substrates*, Jitesh Hora, D Evans, E Charrault, P Murphy,*** Future Industries Institute, University of South Australia, Australia

Abstract: In order to add a new functionality to materials**,** applying thin film coatings is among one of a feasible route. Ultra-thin films deposited by physical vapor deposition techniques on plastic substrates have found significant roles in a variety of industrial applications like in electronics, automotive, etc. [1] This is due to their attractive properties such as high electrical conductivity and transparency, light weight, mechanical flexibility and so forth.[1] There are challenges involved for deposition of a film on polymers, like limitation related to the deposition temperature, due to the low thermal stability of the polymers and to control the formation of cracks on coating due to mechanical stress and environmental effects like the effect of humidity and moisture uptake [2]. In order to overcome the challenges, also to minimise the material use and to get the same functionality as that from thick film, there is a fundamental need to understand the seeding and growth of films deposited by physical vapour deposition technique on different polymeric substrates (stiff and flexible) by exploring the effect of compliance of substrates. This research work aims to understand the structure-property relationships of an ultra-thin film (UTF) on different amorphous polymeric materials. Investigating the structure-property relationships of these advanced materials will lead to an understanding of the link between the growth and seeding with the effect of substrates nature and its effect on composite material properties. In this work, we present the effect of amorphous polymeric substrate mechanical properties on seeding and growth of ultra-thin metallic film deposited using magnetron sputtering, (DC) technique. When same material is deposited under similar conditions on different compliant polymeric substrates we observed different coating growth morphology.

Acknowledgments

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This work was performed in part at the South Australian node of the Australian National Fabrication Facility under the National Collaborative Research Infrastructure Strategy.

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9:00am **TF-WeM-4 *In situ* Studies of Surface Morphological Evolution During Indium Nitride Growth by Atomic Layer Epitaxy*, Charles Eddy, Jr.,*** *N Nepal, S Rosenberg,* U.S. Naval Research Laboratory*; V Anderson,* Sotera Defense Solutions*; J Woodward,* U.S. Naval Research Laboratory*; C Wagenbach,* Boston University*; A Kozen,* U.S. Naval Research Laboratory*; Z Robinson,* College at Brockport - SUNY*; L Nyakiti,* Texas A&M University*; S Qadri,* U.S. Naval Research Laboratory*; M Mehl,* U.S. Naval Academy*; K Ludwig,* Boston University*; J Hite,* US Naval Research Laboratory

Nitride semiconductors have had significant commercial success, but full bandgap engineering of these materials is prohibited by the high temperatures used in conventional growth methods. Recently, we have developed a growth method –low temperature atomic layer epitaxy (ALEp) – that has empirically produced crystalline semiconductor films with properties comparable to those from conventional growth processes, but at roughly half the growth temperature [1,2]. This has eliminated miscibility gaps in ternary III-N semiconductor films and enabled the realization of full bandgap engineering from 0.7 eV to 6.1 eV.

Despite these empirical successes, the fundamental mechanisms involved in ALEp are unknown and the full promise of the method unrealized. To obtain such enabling knowledge we have employed synchrotron-based grazing incidence small angle x-ray scattering (GISAXS) to study the low temperature atomic level processing (ALP) of GaN substrate surfaces for epitaxy and ALEp nucleation and growth of InN on said surfaces. GISAXS allows real-time, in situ monitoring of the surface morphology during these processes.

In this presentation, we will introduce the GISAXS method and the apparatus we have developed to conduct in situ GISAXS measurements of the aforementioned ALP and ALEp processes. We monitor the evolution of GaN substrate surface morphology during a series of low-temperature ALPs including: gallium flash off (GFO), hydrogen plasma clean, and nitrogen plasma nitridation. We learn that the optimum surface results from a GFO conducted at 500° C for only 10 cycles followed by a hydrogen plasma clean. Further, we learn that conventional plasma nitridations are detrimental to smooth surface evolution. When employed to study ALEp InN nucleation and growth, GISAXS data, coupled with Porod[3] and 2D Fourier Transform analysis, affords a clear picture that the growth proceeds by island nucleation and growth and not by the conventionally accepted layer-by-layer growth associated with atomic layer deposition. We have monitored the evolution of island nucleation density, island spacing, island shape and island size as a function of key ALEp growth parameters. We observe that the islands are generally tens of nm or less in size and evolve from a spherical mound shape to a cylindrical shape. Finally, we will present the variations between 2D and 3D growth modes with growth parameter variations that provide insights on process modifications to promote higher quality electronic materials growth.

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9:20am **TF-WeM-5 Nanostructured Material Surface and Thin Film Interface Characterization by X-ray Photoelectron Spectroscopy*, Jisheng Pan,*** Institute of Materials Research and Engineering, A*STAR (Agency for Science, Technology and Research), Singapore

It is well known that X-ray photoelectron spectroscopy (XPS) is a very powerful tool for understanding the nature of solid surfaces. Although many newly developing tools with high spatial resolution play important role in the analysis of individual nanostructured features of materials XPS is still considered as an essential tool for understanding several important aspects of nanostructured materials that cannot easily be observed using other techniques. However, the question of how the nanostructured material features impact XPS data have been heavily debated in the scientific community, which limits its application in characterization of nanostructured materials. For example, there is consistent observation of cluster-size-dependent binding energy (BE) shifts. But there is substantial disagreement over the assignment of these shifts to initial or final state effects. As a result, the measured PES data can’t directly match to the electronic property of clusters because among the initial and final state effects, only the initial state effect involves information of changes in the electronic structure before photoemission, and hence is directly related to nanostructured material properties and is relevant for understanding other chemical process and reactions. In the first part of the presentation, I will talk to you the issues raised specifically for XPS analysis of nanostructured materials and followed by the method to overcome limitations through some examples of application of XPS to study nanostructured materials. In the second part, band energy alignment of different material interfaces such as semiconductor/semiconductor, metal/semiconductor, metal/insulator, semiconductor/insulator, 2D material interfaces determination by XPS will be presented. The performance of any type of hetero-junction device is determined by band energy alignment (band offsets) of material interfaces which form the hetero-junction. Therefore, accurately determining heterojunction band offsets and tuning them to a desired application would have an obvious impact on the optimization of the devices. The effects of chemical shift, differential charging, band bending and photoemission final state on the XPS measurement accuracy and reliability will be discussed.

9:40am **TF-WeM-6 Sputter Epitaxy via Inverse Stranski-Krastanov Growth Mode: A Method of Single Crystal Growth *beyond* Lattice Matching Condition***, **Naho Itagaki**, D Yamashita, K Kamataki, K Koga, M Shiratani,* Kyushu University, Japan

Success in semiconductor devices has been limited thus far because of lattice-mismatch problems between growth layers and substrate. Here, we report on a new method of single crystal growth beyond lattice matching condition, sputter epitaxy via "inverse Stranski-Krastanov (SK) growth mode". Regarding heteroepitaxy on large lattice mismatched substrates, there are two primary modes by which thin films grow: 1) Volmer–Weber (VW: island formation) mode and 2) Stranski–Krastanov (SK: layer-plus-island) mode. In both modes, crystal growth ends up in formation of three-dimensional (3D) island (Fig. S1), making fabrication of single crystalline films challenging. On the other hand, in "inverse" SK mode, 3D islands are initially formed, and subsequent growth of 2D layers occurs on the 3D islands (Fig. S1 (c)). This 3D-2D transition, which is just opposite to the 2D-3D transition in SK mode, is caused by introducing impurity atoms into the growth atmosphere during the initial stage of crystal growth. In this study, we demonstrate the inverse SK growth of ZnO films on 18%-lattice mismatched sapphire substrates, where nitrogen is employed as impurity.

First, 3D island layers of 10 nm thickness were deposited by N$_2$/Ar sputtering. Next, 2D layers of 1 µm thickness were deposited on the 3D island layers by O$_2$/Ar sputtering.

We have successfully grown ZnO single crystals on sapphire substrates via inverse SK mode. XRD and AFM analyses revealed that the 3D island layers consist of nm-sized islands with high crystal quality (Fig. S2 (a)). Since the strain induced by the lattice mismatch is relaxed through the island formation, smaller islands have lower density of misfit dislocation, resulting in high crystal quality. In a conventional method, however, such small islands hardly grow because of the cost of additional surface energy due to the increased surface area. Therefore, we consider that the role of nitrogen is to reduce the surface energy through the adsorption on the island surface, taking the advantages of its active but ZnO-insoluble natures. In fact, our calculation indicates that nitrogen addition leads to 4-nm-sized island growth owing to the lowered surface energy (Fig. S3). Furthermore, we found that after cessation of N$_2$ supply, crystal grains that grow originating from the 3D islands rapidly coalesce to form 2D layer, and eventually grow in a layer-by-layer (2D growth) fashion (Fig. S2 (b)).

We believe that our findings on this growth mode will offer new opportunities for designing materials with unprecedented properties.

This work was supported in part by JSPS KAKENHI 18H01206 and NTT collaborative research.

10:20am **TF-WeM-8 Self-organized Nanostructure Formation in Functional Nitride Alloy Thin Films – Playing Games with Physical Metallurgy***, **Lars Hultman**,* Linkoping University, Sweden **INVITED**

This presentation reviews a multitude of tricks that can be used to promote self-organized nanostructuring in materials. These are used to enhance mechanical and electronic properties for transition metal and group-III nitride alloy thin films prepared by physical vapor deposition. The structural design is obtained by surface- and bulk-driven phase transformation in metastable TiAlN, ZrAlN, HfAlN, TiSiN, MoVN, VWN, and InAlN model systems, and analyzed by XRD, HREM, FIB, APT, and phase field modeling. *Ab initio* calculations are employed to assess phase stability and decomposition behavior from lattice mismatch and electronic band structure effects. The concept of age hardening in transition metal nitride alloys is reviewed for isostructural model systems. Spinodal decomposition is thus established for TiAlN by the formation of cubic-phase nm-size domains in a checker-board-pattern of TiN and AlN at temperatures corresponding to cutting tool operation. 2-D-nanolabyrinthine structuring in ZrAlN is obtained from with intergrowth of non-isostructural phases *c*-ZrN/*w*-AlN: {110}║{11-20} interfaces. Superhardening in TiN/Si$_3$N$_4$ nanocomposites takes place due to Si segregation forming a few-monolayer-thick SiN$_x$ tissue phase, which is a vacancy-stabilized cubic-SiN$_x$ layer. A hardness maximum at 34 GPa – short of ultrahard - is observed in TiN/SiN$_x$(001) superlattices at the epitaxial-to-amorphous thickness-limit for the SiN$_x$ layers. Thermodynamically-driven Si segregation in c-Ti$_{1-x}$Si$_x$N is proven in atom probe tomography on the sub-nm scale using ^{15}N isotopic substitution to resolve mass spectral overlap between Si and N. For In$_x$Al$_{1-x}$N, we report curved-lattice epitaxial growth of nanospirals with controllable chirality as well as core-shell nanorod formation. Finally, the possibility to intercalate atomic layers of Au in non-Van-der Waals nanolaminated Ti$_3$SiC$_2$ (MAX phase) is demonstrated.

11:00am **TF-WeM-10 Effect of Atomic Layer Deposition Grown VO2 Film Morphology and Crystallinity on Opto-Electronic Phase Transition.***, **Jason Avila**,* ASEE postdoc fellow*; M Currie, B Downey, V Wheeler,* Naval Research Laboratory

VO$_2$ is a promising material for a variety of opto-electronic applications due to its metal-to-insulator phase transition occurring near room temperature. Atomic layer deposition (ALD) is an advantageous technique to deposit VO$_2$ due to its excellent conformality and ability to deposit thin films at low temperatures allowing for growth on a variety of substrates and device architectures. Such conformality is especially useful for complex optical devices with non-planar structures such as waveguides or diffraction gratings. There is, however, no current ALD method for direct growth of crystalline VO$_2$, therefore post deposition annealing is required to achieve crystallinity. In this study, we examine the impact of annealing conditions on the resulting phase, crystallinity, composition, morphology, and metal-to-insulator transition of as-grown amorphous ALD VO$_2$ films on sapphire. By controlling annealing conditions such as temperature, time, and O$_2$ pressure, this study demonstrates a control over film morphologies and phase transition properties of the VO$_2$ film. One such example is decreasing the VO$_2$ film roughness by an order of magnitude by changing the annealing temperature by 100 °C, which simultaneously improves the hysteresis of the metal-to-insulator film transition. Through these efforts, the structure-property relationship of VO$_2$ will be revealed, which can then provide a guide for tailoring of optimal film properties for specific electronic and optical applications.

11:20am **TF-WeM-11 Relationship between Relaxation ratio and growth temperature of GaInN by RF-MBE***, **Yusuke Nakajima**, T Honda, T Yamaguchi, T Onuma,* Kogakuin University, Japan

Full-color micro-LED displays [1] requires a monolithic integration of blue, green and red LEDs. In this case, realization of GaInN-based red LEDs with high efficiencies is one of the technical issues. One of the difficulties of these fabrications is due to lattice mismatch between GaN and GaInN layers as the indium composition is increased [2]. At present, the GaInN substrate is still in the research stage. Thus, fabrication of GaInN underlying layers is one of the technique to overcome the lattice-mismatch problems. The lattice-relaxed underlying layers are required for the red LEDs. On the other hand, the lattice relaxation requires the generations of threading dislocations (TDs). These points show the GaInN underlying layers require the lattice relaxation and reduction of TDs. We consider that growth temperature is an important parameter in GaInN growth.

In this paper, lattice relaxation in GaInN layer growth by RF-MBE with different growth temperature is reported. Their photoluminescence (PL) spectra are also discussed. The growth temperatures were fixed at 520, 540, 560, 580 and 600 ° C. The indium compositions were of grown layers 25±5%. The lattice relaxations of these layers were estimated using the patterns of reciprocal space mapping in X-ray diffraction (RSM).

GaInN layers on GaN templates were grown by RF-MBE. GaN templates were grown by MOVPE. The growth time was 60 minutes. The thickness of all grown layer was approximately 0.4µm. The RSMs show that the high relaxation was observed from the low-temperature grown layer nevertheless indium compositions were constant of 25%. On the other hand, PL peaks were shifted towards higher energy side as a function of growth temperature. These mean that the high indium segregation will be occurred in the layers grown at low temperature. Detailed relaxation ratio depended on growth temperature will be discussed.

Acknowledgment

The authors would like to thank Spring-8, Dr. Sasaki and Takahasi of QST and Profs. Nanishi and Araki of Ritsumeikan University for their help with the experiments.

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11:40am **TF-WeM-12 The Effect of Interface Structure on MgO/Al/MgO Multilayer Photocathodes***, **Jeff Terry**, Z Lee, L Spentzouris,* Illinois Institute of Technology

Early research and development of photocathode material was based on characterizing compounds with low work function and high quantum efficiency. Recent theoretical and experimental work has shown that the metal-insulator junctions can give rise to changes in the band structure at the interface, which in turn leads to a change in work function and quantum efficiency.

In addition to concerns about work function and quantum efficiency, many modern photoinjector designs also require low beam emittance. Beam emittance is an intrinsic property of the photocathode, therefore it is important to be able control the growth and quantify the factors that lead to such growth. Nemeth [Phys. Rev. Lett. 104, 046801 (2010)] used DFT to model metal- insulator multilayer junction. The model indicate that it is possible to reduce the emittance of the photoemitted beam. Velazquez et al [Appl. Surf. Sci. 360, 762 (2016)] has demonstrated that the work function of lab grown thin film multilayers had trends that match the theory. However the model predicted an exponential decrease of work function, but experimental measurements suggests a linear decrease.

It has been suggested that the surface roughness of the lab grown thin film multilayers might be the main cause of the discrepency. Our multilayer then films are synthesized using Pulsed Laser Deposition. We have developed growth methodology to systematically control the surface roughness. We characterize these interfaces with photoelectron spectroscopy, Kelvin-probe measurements, and quantum efficiency measurements. We track these measured changes with the interface roughness to better understand the role of chemistry at the interfaces.

Nanomaterials
Room Naupaka Salon 1-3 - Session NM-WeP

Nanomaterials Poster Session II

Moderator: Paul Stoddart, Swinburne University of Technology

NM-WeP-1 Fabrication of Morpho Butterfly Structure using Standing Wave Effect*, **Tomoki Nishino**, H Tanigawa,* Ritsumeikan University, Japan*; A Sekiguchi,* Litho Tech Japan Corporation, Japan

In recent years, biomimetic technologies have been extensively studied. Morpho butterflies are representative examples of structural colors, and many scientists have done research. On the wing, small thin plates called scales with a size of 70 x 150 µm and a thickness of a few microns are spread like roof tiles. When one scaled powder is enlarged, it has a streaky structure on the scale, this streak is called ridge. It is a characteristic of morpho butter that each of the ridges (lid interval: 1 µm) appears blue.

In this paper, the morpho structure can be fabricated by using lithography technology. The standing wave effect is exposure unevenness generated in the resist film when the photoresist on the Si substrate is exposed with monochromatic exposure light. Two reflected lights of the resist surface and the Si substrate cause interference waves. It strengthens and weakens according to the film thickness. No interference wave is generated by the reflected light of the Si substrate, and constant reflection intensity of light is always obtained.

Patterning was performed on the resist, cross-sectional development was performed, and the standing wave effect in the resist film was confirmed.

We propose that the morpho structure can be fabricated by using lithography technology.

NM-WeP-2 Photovoltaic Performance of Organic Polymer Solar Cells using Silicon Nanoparticles with Various Phosphorus Contents*, **Naoki Ikeda**, K Sato,* Tokyo Denki University, Japan

Silicon nanoparticles (SiNPs) are used for solar cell applications because they not only enhance light absorption efficiency of the photoelectric conversion layer but also expand the absorption bands of sunlight. We have fabricated the phosphorus (P)-doped SiNPs using an electroless chemical etching, which is inexpensive and simple techniques. When the P powders was used as n-type dopant, it was difficult to uniformly incorporate the P atoms in the SiNP core. To overcome this challenge, we performed the P doping into SiNPs using P dispersed solvent. In this presentation, we report the photovoltaic performance of the organic polymer solar cells using SiNPs with various P contents. The P-doped SiNPs were fabricated by etching the Si powders with a diameter of 100 nm in a hydrofluoric acid/nitric acid mixture solution using high-speed mixer and by thermally diffusing the P atoms at high temperature. The P contents in the SiNPs were controlled by varying the annealing temperature. The solar cells were prepared by individually coating the P-doped SiNPs and poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT: PSS) on the micro-pyramidal structured Si substrate. The current density-voltage characteristics of undoped SiNPs/PEDOT:PSS solar cells and the P-doped SiNPs/PEDOT:PSS solar cells were shown in Figure 1. The solar cell using undoped SiNPs showed a power conversion efficiency (PCE) of 4.81% with a short circuit current density (J_{sc}) of 27.7 mA/cm^2, an open circuit voltage (V_{oc}) of 0.361 V and a fill factor (FF) of 0.482. On the other hand, these cell parameters dramatically increased by doping the P atoms into SiNPs; that is, the values of J_{sc}, V_{oc}, FF and PCE were 29.7 mA/cm^2, 0.349 V, 0.560 and 5.79%. These results are attributable to the uniform incorporation of P atoms into SiNPs by the use of the P dispersed solvent and the improvement of transport efficiency of photogenerated charge carriers between the SiNPs.

NM-WeP-3 Effect of Phosphorus-doping on Photovoltaic Performance of Si Nanoparticles/Polymer Hybrid Solar Cells*, **Masataka Takase**, K Sato,* Tokyo Denki University, Japan

Semiconductor nanoparticles (NPs) are increasingly gaining attention as suitable materials to enhance photovoltaic performance for solar cell applications because the absorption regions of solar light can control by tuning the band gap due to quantum confinement effect. We have investigated the photovoltaic performance of solar cells using phosphorus (P) doped n-type silicon NPs (SiNPs) so as to improve the transport efficiency of photogenerated charge carriers, and we have compared to that of the undoped SiNPs. In this presentation, we report the effect of P-doping on the photovoltaic performance of solar cells using n-type silicon NPs (SiNPs). The n-type SiNPs were prepared by doping P dopant in commercially available NPs of 100 nm in size using thermal diffusion process at high temperature. The doping states of P atoms in the obtained n-type SiNPs were confirmed by X-ray photoelectron spectroscopy (XPS), indicating that the P atoms exist as the P-Si bonds at the substitutional sites of Si atoms in the crystalline core of n-type SiNPs. We prepared the solar cells in which the undoped SiNPs layer or n-type SiNPs layer applied on the micro-pyramid-shaped Si substrate was covered with poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), which is p-type conducting polymers. The solar cells using the undoped SiNPs showed the low power conversion efficiency (PCE) of 1.44% with open circuit voltage (V_{oc}) of 0.318 V, short circuit current density (J_{sc}) of 10.1 mA/cm^2 and fill factor (FF) of 0.451. When the active layer in the solar cells replaced the undoped SiNPs by the n-type SiNPs, the values of PCE, J_{sc} and FF dramatically increased to 4.79%, 22.3 mA/cm^2 and 0.520, respectively. These improvements are because the reduction in the value of the series resistance (R_s) (0.23 Ω·cm^2 for the solar cells using the n-type SiNPs) due to the increase in the number of photogenerated charge carriers by P doping. This result demonstrates that the P-doped n-type SiNPs is beneficial for obtaining the higher PCE.

NM-WeP-4 Effect of Amino Modification on Photovoltaic Performance of Silicon/Polymer Solar Cells with Porous Desert Structures*, **Kento Saito**, K Sato,* Tokyo Denki University, Japan

Various micro-texture structures have been reviewed in silicon (Si)/polymer solar cells. Our research group have suggested a facile approach to forming micro-desert structure (MDS) on the Si substrate surface by enclosing Si substrate, phosphorus (P) powders and hydrofluoric acid (HF)/nitric acid (HN) mixed solution in a sealed container. However, the MDS is confronting serious problem for antireflection effect, which affects the power conversion efficiency (PCE) of the solar cells, showing the reflectance of 29.8 % in the incident wavelength range of 500-1000 nm. To drop the reflection of the MDS, we fabricated a porous desert structure (PDS) with ordered cylindrical mesopore in the MDS by treating in a mixed solution containing silver perchlorate (AgCl)/sodium hydroxide (NaOH). Additionally, the inside wall of the mesopore of the PDS was modified with amino group to infiltrate the polymer into the mesopore. In this presentation, we report the effect of the amino modification on the photovoltaic performance of the Si/polymer (poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)) solar cells with PDS. The PDS with the pore diameter of approx. 20 nm and the depth of approx. 500 nm was confirmed by scanning electron microscopy (SEM). Such PDS showed the low reflectance of 1.93 % or less in the incident wavelength range of 500-1000 nm, indicating an excellent antireflection effect. When the PDS was modified with amino group, the photovoltaic performance was dramatically improved. The Si/ PEDOT:PSS solar cells with the amino-modified PDS attained the PCE of 4.53% with a short-circuit current density (J_{sc}) of 27.9 mA/cm^2, an open-circuit voltage (V_{oc}) of 0.362 V and a fill factor (FF) of 0.450 compared to the solar cells having the unmodified PDS with the values of J_{sc} of 22.9 mA/cm^2, V_{oc} of 0.261 V, FF of 0.375 and PCE of 2.24 %. This is due to the fact that affinity between the Si with the PDS and the water-soluble PEDOT:PSS enhanced by the modification of hydrophilic amino group.

NM-WeP-6 Indoor Light Photocalytic Performance of Graphene Quantum Dot-TiO_2-PAN Composite based on Electrospinning Matrix*, **Hyonkwang Choi**, W Yang,* KwangWoon University, Korea, Republic of Korea

TiO_2 is one of the most promising catalysts owing to its relatively low cost, superior photocatalytic performance, long-term stability, low cost, and low toxicity under UV illumination.

However, the inherent drawbacks of the TiO_2, e.g. the poor response to visible light due to its large bandgap of 3.2 *eV*, and the fast recombination of photogenerated electron-hole pairs, have significantly impeded the photocatalytic application. To address these matters, the absorption of TiO_2 has been extended into the visible range using chemical doping. Nitrogen doping, especially, can alter the band structure or suppress the recombination efficiency of the photogenerated electron-hole pairs, resulting in an enhanced photocatalytic capacity of TiO_2 in the visible light region.

We present a facile method to the fabrication of nitrogen-doped GQDs/TiO_2 via polyacrylonitrill (PAN)-based carbon fibers (PAN-CFs). Electrospun PAN-CFs have here been selected to produce an electrochemically-active carbon-network matrix containing in-frame incorporated nitrogen, because of its high carbonization yield and high controllable residual nitrogen content. Also, an improvement in visible light absorption is enabled at the GQDs/TiO_2 heterostructure due to bandgap narrowing of TiO_2 by Ti–O–C bond formed between GQDs and TiO_2. PAN plays a dual role, nitrogen doping during its cyclization as well as acting an electrical conducting substrate of a support that enhances the performance of other decorated active catalysts. Thus, nitrogen-doping process of GQDs/TiO2 heterostructure and its corresponding structural and optical properties were investigated through a series of experiments(SEM, TEM, FTIR, XPS, XRD, UV-Vis, PL). We also demonstrate that GQDs/TiO2/PAN electrodes exhibit enhanced photochemical and electrochemical activities advantageous by indoor light methylene blue test and solar-driven hydrogen evolution reaction.

NM-WeP-7 Multispectral Optical Imaging Retrofitted to XPS and SIMS Instruments*, **Peter Cumpson**, I Fletcher, N Sano,* Newcastle University, UK

All X-ray Photoelectron Spectroscopy (XPS) and Time-of-Flight Secondary Ion Mass Spectrometry (ToFSIMS) instruments have optical cameras to image the specimen under analysis, and often to image the sample holder as it enters the system too. These cameras help the user find the appropriate points for analysis of specimens. However they seldom give as good images as stand-alone bench optical microscopes, due to the limited geometry, source/analyser solid angle and Ultra-High-Vacuum (UHV) design compromises. This often means that the images displayed to the user necessarily have low contrast, low resolution and poor depth-of-field.

To help identify the different regions of the samples present we have found it useful to perform multispectral imaging by illuminating the sample with narrow-wavelength-range light emitting diodes (LEDs). By taking an image under the illumination of these LEDs in turn, each at a successively longer wavelength, one can build-up a set of registered images that contain more information than a simple Red-Green-Blue image under white-light illumination. We show that this type of multispectral imaging is easy and inexpensive to fit to common XPS and ToFSIMS instruments, using LEDs that are widely available. In our system we typically use 14 LEDs including one emitting in the ultraviolet (so as to allow fluorescent imaging) and three in the near infra-red. The design considerations of this system are discussed in detail, including the design of the drive and control electronics, and three practical examples are presented where this multispectral imaging was extremely useful in XPS and SIMS.

NM-WeP-8 Synthesis of Small Cubic Metal Nanoparticles of Fe^0, Co^0 and Ni^0 by using Calcium Hydrate as Reducing Agent*, **Maria Volokhova**, A Boldin, L Seinberg,* National Institute of Chemical Physics and Biophysics, Estonia

Metal oxide nanoparticles (NPs) are widely used in different biomedical fields, such as tissue engineering [1], MRI contrast enhancement [2] and detection of proteins [3]. In the current study we are focusing on synthesizing metal nanoparticles (size ~20 nm). In comparison with their oxide counterparts, metal NPs with improved magnetic properties could be used as a MRI contrast agent. Our metal NPs were synthesized using metal oxide NPs, which have been synthesized beforehand by using simple one-pot pyrolysis [4]. Metal hydrate salt and polyvinylpyrrolidone (PVP) in DMF were used as starting materials. The reaction is carried out in a teflon tube that is heated in a furnace (< 200^{o}C). The metal oxide NPs were covered with SiO_2 and reduced using CaH_2 in a vacuum sealed tube [5]. Therefore, NPs with a cubic metal core and a SiO_2 shell coating were obtained. The crystal structure and morphology of the NPs were analyzed using X-ray diffraction (XRD) and transmission electron microscope (TEM). Using the physical properties measurement system (PPMS), we have studied the magnetic properties of the NPs at the room temperature. As far as biomedical applications are concerned, we improved the solubility of the NPs in water. For this purpose zwitterionic dopamine sulfonate (ZDS) [6] was synthesized and used as a coating material for the NPs. Preliminary toxicology experiments of the NPs confirmed their suitability for biomedical application.

NM-WeP-9 Synthesis And Characterization Of Hydrogel With Ag Nanoparticles For 3-D Printable Prosthetics*, **Karí Martínez Reyna**, G García Valdivieso, H Navarro Contreras,* Universidad Autónoma de San Luis Potosí, México

The objective of this work is the synthesis of a hydrogel with Ag nanoparticles, like a biopolymer (hydrogel/Ag), as well as its characterization, to be used in prosthetics in 3D printing.

Hydrogels are of great interest due to their unique properties such as high content of water, softness, flexibility and biocompatibility. Some of the applications of these materials are the delivery of drugs, pesticides and tissue engineering. Silver nanoparticles are used in biomedical applications for their antibacterial property. The purpose of an anti-bacterial hydrogel is that, in addition of being biocompatible, it avoids prosthetic infection.

To get Hydrogel, Laponite was dispersed in water in a proportion of 3% by mass. MBBA (cross-linker), I2959 (initiator), and the monomer AMPS were added later, under rigorous agitation. Ag nanoparticles, previously synthesized by the method of Turkevich, were added to the solution obtained. The Hydrogel/Ag obtained was used to build a model piece with a 3D printer, finally held a curing through UV radiation to provide it rigidity.

We proposed to characterize the mechanical properties of tension, compression, and rigidity. As well as the viscosity to hold in a range of 14.48-37.22 kPa, to ensure the viability in 3D printing. The morphology was characterized by scanning electron microscopy (SEM). The composition and antibacterial activity were characterized by Raman Spectroscopy and Gram test, respectively.

Key Words: Biocompatible Hydrogel, Ag nanoparticles, 3D printing.

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NM-WeP-10 Control of Fluorescence Color and Magnetic Intensity of Magnetofluorescent Microparticles*, **Takafumi Yasuzawa**, K Sato,* Tokyo Denki University, Japan

In recent years, magnetofluorescent materials have attracted attention as one of a powerful tool to provide simultaneously diagnosis and treatment of cancer cells such as image diagnosis using fluorescence property and thermotherapy using magnetism property. We have developed the magnetofluorescent microparticles in which fluorescent ammonium silicon fluorides ($(NH_4)_2SiF_6$) were formed on the surface of the ferromagnetic magnetite (Fe_3O_4) layer, which applied on the Si substrates. This microparticles have some serious challenges; for instance, emission of only single light (red-orange color) and poor magnetic response due to the formation of the diamagnetic ferric fluoride (FeF_3) by the chemical reaction between the Fe_3O_4 and hydrofluoric acid/nitric acid mixture solution during the preparation process. To overcome these challenge, we suggest the approach to combine the phosphorus (P)-doped $(NH_4)_2SiF_6$, as a novel fluorescent materials, with Fe_3O_4 without the formation of FeF_3. In this

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presentation, we report the fluorescence color and chemical composition of the magnetofluorescent microparticles. The P-doped $(NH_4)_2SiF_6$ microparticles were linked with the Fe_3O_4 using ultrasound cleaner. To vary the fluorescent color of the P-doped $(NH_4)_2SiF_6$ microparticls, they were immediately treated in vacuum or in atmospheric environments. The fluorescence properties and chemical composition of the obtained microparticles were investigated by using photoluminescence (PL) and X-ray photoelectron spectroscopy (XPS) measurements. The fluorescent color varied from yellow to green light due to the oxidation of the P-doped $(NH_4)_2SiF_6$ in atmospheric environment. Furthermore, the magnetic component in the micropaticles was composed of only Fe_3O_4 without the formation of FeF_3. Therefore, we suggest that the particles become a highly effective tool of diagnosis and treatment of cancer cells as a novel magnetofluorescent materials.

NM-WeP-11 Nonideality in Atomic Layer Deposition and Its Implication in Efficient Electrolysis*, **Changdeuck Bae**, T Ho, H Shin,* Sungkyunkwan University, Korea, Republic of Korea

We describe the spontaneous formation of a composite chalcogenide materials that consist of two-dimensional (2-D) materials dispersed in bulk and their unusual charge transport properties for application in hydrogen evolution reactions (HERs). When MoS_2 as a representative 2-D material is atomic layer deposition-deposited on transition metals such as Cu in a controlled manner, the sulfidation reactions also occur with the metal. This process results in remarkably unique structures, i.e., bulk layered heterojunctions (BLHJs) of Cu-Mo-S that contain MoS_2 flakes inside, which are uniformly dispersed in the Cu_2S matrix. The resulting structures were expected to induce asymmetric charge transfer via layered frameworks and tested as electrocatalysts for HERs. Upon suitable thermal treatments, the BLHJ surfaces exhibited the efficient HER performance of approximately 10 mA/cm^2 at a potential of as low as -0.1 V versus a reversible hydrogen electrode (RHE). The Tafel slope was approximately 30 to 40 mV/dec. The present strategy was further generalized by demonstrating the formation of BLHJs on other transition metals such as Ni. The resulting BLHJs of Ni-Mo-S also showed the remarkable HER performance and the stable operation over 10 days without using Pt counter electrodes by eliminating any possible issues on the Pt contamination.

NM-WeP-12 Stretchable Temperature Sensor Based on Elastomeric rGO/PU Nanoomposite Fiber*, **Tran Quang Trung**,* Sungkyunkwan University, Republic of Korea*; N Lee,* Sungkyunkwan University, Republic of Korea, , Republic of Korea

Developing fiber-based sensors and integrating them with textile to develop smart textile smart clothes, and smart gloves for monitoring physiological and biological signals of human body are promising for next generation of wearable electronic platform. In recent, there have been many efforts on development of stretchable temperature sensors. However, they still presented some limitations such as requirement of complicated fabrication process, high cost, low yield, and unstability in output performances under mechanical deformation. Herein, we proposed a stretchable temperature sensor with simple fabrication process based on elastomeric rGO/PU nanocomposite fiber. By incorporating high thermal-responsive material (reduced graphene oxide (rGO)) into outstanding mechanically stretchable elastomer polymer (polyurethane (PU)), we generated a free-standing rGO/PU elastomeric composite fiber with high thermal responsivity and good mechanical deformation via a simple fiber spinning method. The fiber with outstanding mechanical deformation helps it easily moulded in serpentine shape and encapsulated by polydimethylsiloxane (PDMS) to generate a free-standing stretchable temperature sensors. Fabricated device presented high responsivity, stretchability, and stability in sensitivity under applied stretching. The free-standing stretchable temperature sensor can embedded on PDMS substrate, sewn on stretchable fabric and bandage, and laminated on human body to monitor the temperature changes of skin during doing exercise. These results demonstrate that the free-standing, fiber-based, stretchable temperature sensor has great potential for development of smart textile for personal healthcare.

NM-WeP-13 Study on the Application of Raman Spectroscopy for Early Detection of Cervical Cancer*, **Alondra Hernández Cedillo**,* Universidad Autónoma de San Luis Potosí, Mexico

Cancer is a disease in which cells in the body multiply without control. When this starts in the neck of the uterus, is called cervical cancer, or cancer of the cervix. Cancer can spread to the other parts of the body later. Cervical cancer is one of the leading causes of death from cancer among women around the world. Most of these deaths occur in low and middle-income countries. The primary cause of precancerous lesions and cervical cancer is persistent or chronic infection with one or more of the “elevated risk” (or oncogenic) types of human papillomavirus (HPV). In these patients a tumor marker system could be an additional tool to derive the status of the tumor. Subsequently, these markers may be useful to correlate with response to anti-cancer treatment and recurrence of the disease. Increases in the levels of sialic acid can be considered as potential inflammatory marker which would serve to aid in the diagnosis, prognosis and monitoring cancer therapy. Thus, using spectroscopy Raman with silver nanoparticles (NPsAg) is seeks to determine the concentrations of sialic acid in patients with cancer women with benign and precursor lesions and invasive cervical to determine the stadium of the people about development of cancer. Already existing previous tests with this technique which has already measured the concentration of sialic acid in women with other types of conditions which have provided saliva samples, and which found them the concentration of sialic acid.

NM-WeP-14 Au Nanoparticle Decorated rGO/MoS$_2$ Sandwich Catalyst for Photodegradation*, **Jyh-Ming Ting**,* National Cheng Kung University, Republic of China

With the development of industry and the rapidly innovative technology progress, various pollution issues have thus occurred. For example, management of wastewater is obe on the critical issues. Therefore, waste water purification by semiconductor or semiconductor composite photocatalyst has been attracting much attention. In the study, we have investigated a novel catalyst for use as photocatalyst. The photocatalyst is a novel visible light response Au nanoparticle decorated rGO/MoS_2 material. The synthesis of such photocatalyst involves the use of a supercritical fluid carbon dioxide process. The processing conditions were studied to obtained desired characteristics of the photocatalyst. The obtained photocatalyst was for the degradation of MB.

NM-WeP-15 Surface Modification of CFRP by CNT-Doped Buckypapers*, **Bartlomiej Przybyszewski**, K Dydek, P Latko-Duralek, A Boczkowska,* Warsaw University of Technology, Poland

One of the latest trends in the development of new materials is to improve the electrical and thermal conductivity of Carbon Fiber Reinforced Polymers (CFRP). Instead of metallic meshes, lightweight structures are searching as more promising candidates that decrease the total weight of composite laminates and are electrically conductive in order to be able to provide electromagnetic shielding.

Thin sheets made from an aggregate of carbon nanotubes (so called buckypapers) are novel CNT-based materials which mainly consist of carbon nanotubes that are bonded together by thermal treatment. They can improve the electrical conductivity of CFRP composites due to the presence of carbon nanotubes (CNTs), which are known to be highly conductive nanoparticles.

In order to investigate the effect of surface modification of CFRP by CNT-doped buckypapers on the electrical and thermal conductivity of CFRP, two types of laminates were fabricated with different buckypaper types. All panels were made from carbon prepregs using a vacuum bag (Out of Autoclave method). Electrical conductivity was measured in three directions of the fabricated panels. The differences in the results were explained by microscopic observations. In addition, the effect of CNT-doped buckypapers on the thermal properties of the panels was analyzed.

NM-WeP-16 Characterizing the Quality of Molten Al Alloys with Hydrogen, Porosity and Bifilm Content*, H Jang, P Youn, H Kang, G Lee, J Jeon, J Park, E Kim, **Sunmi Shin**,* Korea Institute of Industrial Technology, Korea

In response to the recent strengthened environmental regulations, high strength aluminum alloys have been actively studied as a substitute for steel material for light weight of vehicle. In particular, Al-Mg alloy is a typical high-strength aluminum alloy, and it is used as a structural material with excellent strength and deformation resistance. Mg alloying element induces solid solution hardening and precipitation hardening depending on coexistence of Si and Zn. On the other hand, Mg element weaken the fluidity of the molten alloy and increase the amount of inclusions due to the strong bonding force with oxygen. In order to reduce the internal defects and improve the mechanical properties of Al-Mg alloys, the quality of molten Al-Mg alloys should be precisely controled. In this study, the melt quality of Al-Mg alloys was characterized by measuring hydrogen, porosity and bifilm content and the effect of Mg content and melting process parameters on the melt quality was discussed.

NM-WeP-17 Molecular Confinement on Nanostructured Polymer Surfaces*, **Sara Heedy**, A Yee,* University of California, Irvine

Polymers have a characteristic size (lamella thickness, molecular orientation, etc.) which may depend on processing, especially when fabricated into structures that range from 10's to 100's of nm. These dimensions may be important in certain properties such as electrical or thermal conductivity. These properties will be strongly affected when fabricated polymer nanostructures have dimensions comparable to the critical length scale of physical phenomena (unconstrained radius of gyration, mean free path of charge carriers, mass transport, etc.). Enhanced mechanical, optical, and electrical properties of nanostructures, including arrays of nanopillars and nanolines less than 1 µm tall, have been well documented. Scientists and engineers who desire to control such properties are often unable to characterize and predict the nanoscale surface chemistry change due to surface topography. This research aims to significantly update the current knowledge of nanoscale surface chemistry, allowing the alteration of physical properties in a defined and predictable manner to obtain unique bio-electronic interfaces. Here, we aim to both quantify and control interface chemistry and molecular confinement to allow researchers the ability to alter surface chemical composition on a given polymer substrate in a methodical and predictable manner.

We fabricated nanostructures using nanoimprint lithography on the synthetic polymer poly(methyl methacrylate) (PMMA), which is often used for biomedical devices. A consequence of such a process is confinement induced reordering of polymer chains which is strongly affected by the mold geometry, mold surface properties, and imprinting process variables. Using thermal imprinting, and the combined topographical and nanoscale chemical mapping of photoinduced force microscopy (PiFM) (Nowak et al. Sci. Adv. 2016), we found that nanopillars (100-700 nm range) confine functional groups differently depending on the pattern geometry used. These findings are very surprising, and suggest that surface chemistry, as well as nanoscale phenomena, can be controlled for use in adhesion and bio-electronic interfaces.

NM-WeP-18 Non-volatile Memory Based on Negative Capacitance and Photovoltaic Effect*, **Kai-Wen Chen**, S Chen, Y Tseng, S Chang,* National Chiao Tung University, Republic of China

The investigation for solid-state non-volatile memory has triggered great research into new materials combination. Here we demonstrate that the significant photovoltaic effect of the multiferroic heterostructure. This work $GdFe_{0.8}Ni_{0.2}O_3/SrTiO_3$ (GFNO/STO) ferroelectric capacitors have been successfully fabricated on an Nb-doped $SrTiO_3$ substrate, in which the GFNO and STO film were prepared by magnetron sputtering. When GFNO layer was combined with an STO layer, the total capacitance appeared increased, which suggested the negative value of the ferroelectric capacitance. In addition, the amplified photocurrent was induced by positive poling which led to polarization pointing down and vice versa. The direction of photocurrent could be reproducibly switched along with the polarization flips. Using x-ray absorption spectroscopy (XAS) with in-situ electrical characterization, we investigated the poling dependence of transport properties at an interface of a GFNO/STO devices. We found that electrons were pushed upward or downward by dipole moment inside GFNO thin film with the occurrence of polarization flipping which decreased the rate of recombination of electron-hole pairs. In addition, photoelectron spectroscopy (PES) indicated that oxygen vacancies accumulated mainly at one side of GFNO with polling dependence and motivated the change of Schottky barrier height at the interface. With the combination of modern x-ray technique and photocurrent measurement, our results pave a way for ferroelectric electro-optic memory by manipulation of multiferroic interfaces. This work was financially supported by the "Center for the Semiconductor Technology Research" from The Featured Areas Research Center Program within the framework of the Higher Education Sprout Project by the Ministry of Education (MOE) in Taiwan. Also supported in part by the Ministry of Science and Technology, Taiwan, under Grant MOST-107-3017-F-009-002.

NM-WeP-19 Particle Embedded Slippery Surface for Icephobic Paint*, M Kim,* Korea Electronics Technology Institute, Republic of Korea*; B Lee, D Kim,* Kangnam Jevisco Co., LTD., Republic of Korea*; J Kim, B Yoon, **Young-Seok Kim**,* Korea Electronics Technology Institute, Republic of Korea

Heavy ice or wet-snow accretion on the surface of solar panels, wind turbines, aircrafts, heat pumps, power lines, telecommunication equipment, and submarines, may lead to major service outages. Icephobicity is usually defined as the ability to delay and prevent ice nucleation and formation on surfaces induced either by pouring a supercooled water. Formation, adhesion, and accumulation of ice, snow, frost, glaze, rime, or their mixtures can cause severe problems. Recently, extremely low ice adhesion was introduced by tailoring the cross-link density of different elastomeric coatings and by enabling interfacial slippage of surface. But, the icephobicity for such surfaces can be short-lived, as the oil may be displaced and removed by water droplets or frost, or during accreted ice removal.

Here, we introduced oil-impregnated silica particles into modified hydrophobic polyurethane. The swelling capacity of oil was greatly increased by the porosity of particles, which promises durability of slippery surface. The roughness of particle-disperedd surface also enhanced hydrophobicity. The measured the interfacial friction force between the ice and the film agreed improved icephobicity with durability.

NM-WeP-20 Effect of the Addition of Ti^{4+} Ions on Magnetic and Dielectric Properties of $BaFe_{12}O_{19}$ Ceramics Prepared by Coprecipitation Method*, **Carlos A. Rodriguez Garcia**, M Bravo-Sanchez, M Cano Gonzalez, O Blanco Alonso,* Universidad de Guadalajara, Mexico

Barium ferrite is a well-known ferromagnetic material, and it has a major role on the industry of data storage, sensors, speakers, electric generators, among others. Nowadays, the research for multiferroic materials is essential for the development of multi-function electronic devices.

In this work, the ferrite was modified with the addition of titanium ions having general formula: $Ba\ (Fe_{12-x}Ti_x)\ O_{19}$, with x values 0, 0.005, 0.01, 0.03 and 0.05. These have been synthetized by coprecipitation method and then sintered on ceramics to study the effect of titanium addition over its dielectric and magnetic properties. Structural characterization, through by XRD and SEM studies, reveal a change of morphology in the samples with the Ti^{4+}substitution. Surface analysis was assessed with XPS, where survey and high resolution spectra were obtained for calculation of total and relative composition, showing consistent values for titanium and iron. Magnetic properties were characterized by magnetic susceptibility and magnetization curves (Hysteresis); the thermal scanning curves of magnetic susceptibility, from 50 K to 400 K, show that magnetic susceptibility and saturation magnetization change with the addition of titanium ions. Dielectric characterization was performed by thermal scanning of dielectric permittivity, from 90 K to 400 K; the curves reveal the increase in the dielectric constant with the Ti^{4+}insertion.

Thin Films

Room Naupaka Salon 1-3 - Session TF-WeP

Thin Films Poster Session II

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

TF-WeP-2 Effect of Modulation Structure on the Microstructural and Mechanical Properties of TiAlSiN/CrN Thin Films Prepared by HiPIMS Process*, H Liu,* Institute of Advanced Wear & Corrosion Resistant and Functional Materials, Jinan University, China*; F Yang,* Center for Plasma and Thin Film Technologies, Ming Chi University of Technology, Taiwan*; Y Tsai,* Department of Materials Engineering, Ming Chi University of Technology, Taiwan*; **Chi-Lung Chang**,* Department of Materials Engineering, Ming Chi University of Technology, Taiwan, Taiwan, Republic of China

The TiAlSiN/CrN multilayer coatings were deposited on silicon Si (100) substrates and cemented carbide (WC-10 wt.%, Co) substrates at 80°C using both metallurgical TiAlSi alloy target and Cr target, with varying modulation period (Λ) from 27 nm to 2 nm, by reactive high power impulse magnetron sputtering technique (HiPIMS). The modulation structure characteristics of the TiAlSiN/CrN multilayer was first investigated, and then the microstructure evolution and mechanical properties of TiAlSiN/CrN coatings with decreasing modulation period (Λ) were analyzed by TEM, SEM, XRD, Scratch test, Rockwell hardmeter and nanoindenter. It was found that the grain size of TiAlSiN/CrN multilayer increased with a decreasing modulation period (Λ). The hardness and elastic modulus of the multilayer reached their maximum when Λ is about 8.5 nm. The hardness, H3/E*2 ratios and critical loads LC in scratch test showed an initial increase, followed by a decrease with a decreasing modulation period (Λ). The modulation period (Λ) at 8.5 nm exhibited the highest hardness, H3/E*2 ratios and critical loads.

TF-WeP-3 Effect of α-$(Al_xGa_{1-x})_2O_3$ Overgrowth on MSM-Type α-Ga_2O_3 Ultraviolet Photodetectors Grown by Mist CVD*, Kenichiro Rikitake, T Yamaguchi, T Onuma, T Honda,* Kogakuin University, Japan

Ultraviolet (UV) photodetectors using high Al content AlGaN have been studying towards applications such as flame detection, sterilization and so on [1]. However, the growth of high-quality AlGaN with increased Al content required for UV photodetector has difficulty in epitaxy. Therefore, we have been focusing on corundum-structured gallium oxide (α-Ga_2O_3) as an alternative material. a-Ga_2O_3 has a wide bandgap of 5.3 eV, and the bandgap engineering is possible in whole composition range of $(Al, Ga, In)_2O_3$ alloys [2, 3]. A β-Ga_2O_3 based UV photodetector has been shown to have high responsivity [4], and Al_2O_3 deposition on β-Ga_2O_3 for surface passivation has been reported [5]. In contrast, α-Ga_2O_3 detector has so far not yet been reported.

In this study, a metal-semiconductor-metal (MSM)-type UV photodetector using α-$(Al_xGa_{1-x})_2O_3$ on α-Ga_2O_3 is fabricated by mist CVD.

1-μm-thick unintentionally doped α-Ga_2O_3 film was grown on *c-plane* sapphire substrate by mist CVD. Ga acetylacetonate was used as a source material for this mist CVD growth, and it was solved in deionized water with a small amount of hydrochloric acid. The concentration of Ga was 0.05 mol/L. It was followed by 20-50-nm-thick $(Al_xGa_{1-x})_2O_3$ growth using Al and Ga acetylacetonate as source materials. Then, α-Ga_2O_3-based MSM-type photodetector was fabricated by employing Ni (50 nm)/Au (100 nm) pads as Schottky electrodes.

Figure 1 shows XRD 2θ-ω scan profile. (0006)α-Al_2O_3 and (0006)α-Ga_2O_3 diffraction peaks were observed. 2θ-ω and phi scan profiles indicate growth of single crystalline epitaxial film. As shown in Fig. 2, the full-width at half maximum of the X-ray rocking curve for (0006)α-Ga_2O_3 diffraction peak is 39.8 arcsec. The absorption coefficient a was determined by optical transmittance measurements. Then, $(\alpha h\nu)^2$-hν plots give bandgap energy of 5.3 eV. Figure 3 shows photo-responsivity of the MSM-type photodetector. Increase in responsivity above the bandgap energy of 5.3 eV was successfully observed. Maximum photo-responsivity was estimated to be 1.0 A/W. However, the photo-responsivity decreased in the energy range between 5.6 and 5.8 eV due to surface effect of the α-Ga_2O_3 film. Surface effect on MSM-type UV photodetectors using α-$(Al_xGa_{1-x})_2O_3$ on α-Ga_2O_3 structure will be shown at the cofference.

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TF-WeP-4 Continuous Dielectric Function of Monolayer $MoSe_2$ for Temperature Range from 31 to 300 K by Spectroscopic Ellipsometry*, **Tae Jung Kim**, H Park, V Le, H Nguyen, X Nguyen, Y Kim,* Kyung Hee University, Republic of Korea

Molybdenum diselenide ($MoSe_2$) is a layered material with strong in-plane bonding and weak out-of-plane interactions like many transition metal dichalcogenides (TMDCs). These interactions lead to exfoliation into two-dimensional layers of single unit cell thickness. $MoSe_2$ is well known as one of TMDCs that has a potential substitute for silicon or organic semiconductors in high-tech transistors, sensors, and photodetectors. Several works reported the dielectric function of monolayer $MoSe_2$ at low and room temperatures by using spectroscopic ellipsometry (SE). However, In order to apply properly for device applications, the dielectric function of monolayer $MoSe_2$ had better be well known for continuous temperature.

In this work, monolayer $MoSe_2$ is formed by selenization of MoO_3 which is fabricated on a sapphire substrate by using pulsed-laser sputtering. We report dielectric function parametric model (DFPM) of optical properties of $MoSe_2$ over the energy range of 0.74 to 6.42 eV and the temperature range from 31 to 300 K that measured by SE. We could clearly observe the existence of twelve critical point (A^-, A^0, B_1, B_2, C_a, C_b, E, F, and $E_{\mathrm{I\text{-}IV}}$) structures. The parameters were extracted by fitting the spectra with the reconstruction from twelve dispersive oscillators at each measured data. The dependence of temperature is achieved from the model parameters that are fitted by polynomial and then the dielectric functions of $MoSe_2$ for continuous temperature is determined. These results are expected to be useful in design and understanding in applied device technologies based on $MoSe_2$.

TF-WeP-5 Formation of Microwire Arrays with Dot Structure on Sol-gel Derived Cu_2O Surfaces by Thermal Annealing*, **Katsuhiro Uesugi**, K Matsumoto, W Ikesugi, Y Nakata, Y Hoshiyama, K Obara, H Fukuda,* Muroran Institute of Technology, Japan

Cu_2O is recognized as the most promising p-type oxide semiconductor because of its desirable optical properties in the visible region and high Hall mobility. It has been widely studied for the applications such as gas sensors, solar energy conversion, photocatalyst, and photosynthesis. Although Cu_2O films can be synthesized by using chemical- and physical-deposition methods and thermal oxidation of metallic Cu surfaces, nano-microscale modifications on the surfaces are important to improve the surface reaction rate of the photoelectrodes. In this study, the self-assembled growth of Cu_2O microwire arrays with dot structures was performed on the sol-gel derived Cu_2O films by thermal annealing.

A metal precursor solution was prepared by the mixing of copper (Ⅱ) acetate monohydrate and monoethanolamine in 2-propanol at 50 ºC. After thin films were deposited on glass substrates, they were annealed in the furnace at 270 ºC for 40 min. Cu_2O(111) peak was observed by the X-ray diffraction measurement of the samples. A lot of wires spread through from dot structures were observed on the surfaces. A typical structure of the wires was 1.6 μm in width and 200-340 μm in length. The number of the wires was proportional to the circumference of the dot, and 10-100 wires per one dot were formed. Although the wires were isotropically grown from the isolated dot, the wire arrays were formed between neighboring dots. The lateral fusion of the wires did not occur, and the wire grown from the different dots was connected directly and formed the microwire array structures. These results suggest that the surface diffusion of the atoms during the thermal annealing was promoted to the parallel direction of the wires.

TF-WeP-6 Surface Plasmon Excited on Metallic-Glass Nanotube Arrays for Surface-Enhanced Raman Scattering Applications*, **Yi-Chi Lu**,* National Taiwan University of Science and Technology, Taiwan, Republic of China*; H Ho, C Hsueh,* National Taiwan University, Republic of China*; J Chen,* National Taiwan University of Science and Technology, Republic of China*; J Chu,* National Taiwan University of Science and Technology, Taiwan, Republic of China

Metallic glass (MG) is a new class of alloys with the amorphous structure and unique characteristics, including high strength, smooth surface, absence of grain boundaries, and corrosion resistance. MG materials can exhibit a plastic-like flow property at temperatures between glass transition (T_g) and crystallization (T_x). It has been reported that Au-based MGs possess negative dielectric constants and could be used as plasmonic materials. Furthermore, with a low T_g temperature of Au-based thin-film MGs (TFMGs), large dimensions of nanostructures can be thermally imprinted in air [1]. Both measurements and simulations have shown that designed nanostructures were suitable for surface-enhanced Raman scattering (SERS) applications. In addition, in the absence of grain boundaries in amorphous TFMGs, damping due to increased scattering at grain boundaries does not occur, and SERS could be improved. In addition to the thermal imprint method, the metallic glass nanotube (MGNT) array on Si has been successfully fabricated by a widely-used lithography and sputter deposition process for very large-scale integration [2]. Like other nanostructured surfaces, MGNT array surfaces show water repelling and attracting properties. In this presentation, as-prepared nanotubes are 500-800 nm tall and 500-800 nm in diameter and they are used for the SERS property evaluations. The MG alloys selected include Pd-, Ti-, and Zr-based systems. The characterization results are obtained and will be discussed in the presentation. Hence, our result shed lights on the possibility of MGNT array for plasmonic applications.

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TF-WeP-7 Study on Characteristics of the REBCO Thin Film Superconducting Wire according to the Thickness and Properties of the Wire's Stabilization Layer*, **Ho-Ik Du**, S Yang, H Jeong,* Chonbuk National University, Republic of Korea

To protect REBCO layers that are weak against thermal impact after quenching, REBCO thin-film superconducting wires are manufactured with a complex structure of a substrate layer (metal), a superconducting layer (ceramic), and a stabilizing layer (metal). The stabilizing layer is positioned at the outermost layer of the REBCO thin-film superconducting wire to cover the REBCO superconducting layer, and is made mainly of Ag. The stabilizing layer normally protects the REBCO superconducting layer from thermal stress.

Therefore, in this paper, a REBCO thin film superconducting wire was fabricated by depositing materials with different specific resistance values (Ag) on REBCO thin-film superconducting wire, using the "RF Sputtering Deposition Method" with micro-range thicknesses to form a outer layer. Then the fabricated REBCO thin film superconducting wire were subjected to basic characteristics tests (measurement of their temperature distribution according to their changing resistance) and over-current transport- current tests to investigate their phase transition. Finally, the results of the basic characteristics tests and the over-current transport-current tests were analyzed to present the applications of superconducting power application devices of the REBCO thin film superconducting wire according to the thickness and properties of the wire's stabilization layer.

TF-WeP-8 Arginine and Aspartic Acid on Cu(110) to Predict RGD Adsorption*, **Vincent Humblot**, R Totani, C Methivier,* LRS - CNRS Sorbonne Université, France*; H Cruguel,* INSP - CNRS Sorbonne Université, France*; C Pradier,* LRS - CNRS Sorbonne Université, France

Peptides are versatile molecules, whose properties can be conveniently tailored through genetic engineering and chemical functionalization. For this reason they are employed as building blocks for functional materials with applications in nanotechnology, medicine and biotechnology [1].

The knowledge of amino acids (peptides subunits) adsorption processes on metallic surfaces is mandatory to implement peptides and proteins in these applications, but also to collect information on the obtained functional materials and to control the biointerfaces behavior [2].

In this work, we examined the interaction mechanisms of aspartic acid and arginine, the main components of the polypeptide RGD (arginine-glycine-aspartic acid), with a Cu(110) single crystal surface. The molecular films have been obtained by means of an electrospray ionization source (ESI) [3]: with respect to the traditional Knudsen cells, ESI allows an adsorption from an aqueous solution at room temperature, avoiding the high sublimation temperatures and all molecular damages related to them [4].

The chemical state and the anchoring points of the molecules on the surface have been investigated with X-ray Photoelectron Spectroscopy (XPS) and Polarization Modulation Infrared Reflection Absorption Spectroscopy (PM-RAIRS). Scanning Tunneling Microscopy (STM) furnished complementary information about the structures of the adlayers.

We show that the adsorption occurs differently for the two molecules: via the amine reactive groups for arginine and via both the carboxylate and the amine reactive groups for aspartic acid. In accordance, they self-assemble in a very different way:

- Aspartic acid creates islands of dimers showing a 2D pattern whose unit cell is disorientated from the crystallographic axes,

- While arginine assembles in line along the Cu [001] direction.

Thus, for arginine the molecule-substrate interactions dominate on long-range distances, influencing the molecular arrangement along one of the crystallographic axis. Conversely, for aspartic acid and, intermolecular interactions are predominant and are responsible for the dimerization process and the creation of extended 2D arrays.

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TF-WeP-10 Improvement of Pumping Characteristics of Oxygen-Free Palladium/Titanium Non-Evaporable Getter (NEG) Coating Based on Removal of Carbon Contamination*, **Tetsuya Miyazawa**,* SOKENDAI, Japan*; Y Kano, Y Nakayama,* Tokyo University of Science, Japan*; K Ozawa,* Tokyo Institute of Technology, Japan*; T Kikuchi, K Mase,* KEK, Japan

Non-evaporable getter (NEG) coatings are widely used for accelerators because they are ideal for maintain ultrahigh vacuum (UHV), and are oil free, magnetic-field free, vibration free, economical, and energy saving. Recently, we have developed a new NEG coating for pumping H_2 and CO, and named it as oxygen-free Pd/Ti coating. In oxygen-free Pd/Ti coating Ti thin film is deposited and overcoated by Pd thin film under clean UHV conditions in the range of 10^{-7}–10^{-8} Pa [T. Miyazawa, M. Kurihara, S. Ohno, N. Terashima, Y. Natsui, H. Kato, T. Kikuchi, and K. Mase, J. Vac. Sci. Technol. A, in press.]. When the oxygen-free Pd/Ti thin film is exposed to the atmosphere, the Pd surface is contaminated with organic compounds to some degree, resulting in a decline of the pumping speeds. In the present paper, we report removal of the carbon contamination and improvement of the pumping speeds of the oxygen-free Pd/Ti thin film using UHV or O_2 annealing. Unannealed, UHV annealed, and O_2 annealed (annealed under O_2 pressure of 1.3×10^{-4} Pa) oxygen-free Pd/Ti thin films were analyzed with X-ray photoelectron spectroscopy using synchrotron radiation. The carbon coverage of the unannealed sample was estimated as 0.90 ML. On the other hand, the carbon coverages of UHV annealed and O_2 annealed samples were estimated as 0.41 and 0.10 ML, respectively. The pumping speed of the oxygen-free Pd/Ti for H_2 and CO after baking under O_2 pressure of 1.3×10^{-4} Pa was improved by a factor of 3.7 and 16.3 in comparison with UHV baking, respectively [T. Miyazawa, Y. Kano, Y. Nakayama, K. Ozawa, T. Kikuchi, and K. Mase, in preparation.].

TF-WeP-11 Development of a New NEG Pump Using Oxygen-Free Pd/Ti Thin Film that can be Activated by Baking at 150 °C for 12 h*, T Kikuchi,* KEK, Japan*; T Miyazawa,* SOKENDAI, Japan*; H Nishiguchi,* Baroque International Inc., Japan*; **Kazuhiko Mase**,* KEK, Japan

Non-evaporable getter (NEG) pumps are widely used in synchrotron radiation facilities because they are free of oil, evaporation, sputtering, sublimation, magnetic field, and vibration as well as economical, compact, lightweight, and energy efficient. However, conventional NEG pumps have the following drawbacks: 1) decreased pumping speed after repeated venting–activating cycles; 2) relatively high activation temperature (typically 450 °C for 10 min when ZrVFe alloy is used, and typically 180 °C for 24 h when TiZrV film is used); and 3) a dedicated power supply is required. In order to overcome these disadvantages, we developed a new NEG pump with a DN 160 conflat flange using a new NEG material, i.e., oxygen-free Pd/Ti thin film, for evacuating residual H_2 and CO (Fig. 1) [1]. After baking at 150 °C for 12 h, the pumping speeds of the NEG pump were measured with the orifice method. Pumping speeds of 500–320, 370–260, 400–300, and 310–170 L s^{-1} were estimated for H_2 after the first, second, third, and fourth venting–activating cycles in a pumped-quantity range of 0.01–10 Pa L . On the other hand, pumping speeds of 510–440, 590–470, and 880–690 L s^{-1} were estimated for CO after the sixth, seventh, and eighth venting–activating cycles in a pumped-quantity range of 0.003–0.03 Pa L (Fig. 2). After baking at 150 °C for 12 h under O_2 pressure of 1.3×10^{-4} Pa, pumping speeds of 680–240 L s^{-1} and 900–470 L s^{-1} were estimated for H_2 and CO, respectively (Fig. 2). The advantages of the new NEG pump are as follows: 1) it does not oxidize even after repeated venting–activating cycles; 2) it can be activated by baking at 150 °C for 12 h; 3) no dedicated power supply is required; 4) it is more economical than conventional NEG pumps because no electric feedthroughs are required; and 5) the pumping speeds can be improved by baking under O_2 pressure of 1.3×10^{-4} Pa. The new NEG pumps are a suitable alternative to conventional NEG pumps or titanium sublimation pumps.

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TF-WeP-12 The Effect of Cu Oxide Shell on the Flash Light Sintering of Cu Nanoparticle-ink on Si Wafer Substrate for Solar Cell Electrode*, **Chung-hyeon Ryu**, J Chu, A Supriya, H Kim,* Hanyang University, Seoul, Korea

In this study, flash light sintering method of Cu nanoparticle (NP)-ink on Si wafer substrate and the effect of Cu oxide shell type and thickness on flash light sintering process were investigated. The Cu NPs were oxidized in a heat chamber and the oxidation temperature was varied from 100 °C to 300 °C. The Cu NP-ink was fabricated using the oxidized Cu NPs and the fabricated Cu NP-ink with was printed on Si wafer substrate using screen printing method. To sinter the printed Cu NP-ink, multiple pulsed flash light irradiation was employed. The flash light irradiation conditions were optimized to obtain a high electrical conductivity of Cu NP-ink. In order to characterize the microstructures, scanning electron microscopy (SEM) was performed. X-ray diffraction (XRD) was conducted to investigate the oxidation or reduction of oxidized Cu NPs. The thickness of Cu oxide shell was measured using transmission electron microscopy (TEM). The sheet resistance and thickness of sintered Cu NP-ink was measured to calculate the resistivity of sintered Cu NP-ink.

Finally, the Cu NP-ink was successfully sintered on Si wafer substrate using multiple pulsed flash light and it had a 15.42 μΩ·cm resistivity.

Acknowledgments

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TF-WeP-13 Realization of Three Optical States with High Contrast by Doping Nitrogen into $Ge_2Sb_2Te_5$*, **Chaobin Bi**, C Hu,* Jilin University, China

Phase change materials (PCMs) are widely used in non-volatile photonic applications due to the large optical contrast (ΔR) caused by phase transitions. However, only ΔR between amorphous and metastable phase are used to achieve the modulation of two optical state, which limits the performance of the photonic device, such as the storage density of the optical disk, the multi-absorption band of the perfect absorber, and the channels of optical switch. Channels. And the ΔR between metastable phase and the stable phase is too small to be considered as a third-order optical state. Therefore, it is necessary to develop new PCMs with three optical state of large ΔR. Here, combined with experiments, theoretical calculations and Tauc-Lorentz model, we reveal the microscopic mechanism and propose a method to increase the ΔR among the three phases. The results show that ΔR is proportional to the change of material disorder and band gap before and after phase transition. On this basis, by introducing an appropriate amount of N (5.8%) into $Ge_2Sb_2Te_5$, the ΔR between metastable and stable phase is significantly increased from 7% to 22%, exceeding the commercial requirement; meanwhile, the ΔR between amorphous and metastable phase is also increased from 20% to 37%, meaning that the tertiary optical state of large ΔR is obtained. This study not only reveals the origin of ΔR, but also provides new PCMs for research on improving the performance of photonic devices.

TF-WeP-14 Self-Assembly of Nanocrystalline@amorphous Core-Shell Nanostructure in the TA-19 Alloy Film to Achieve High Strength*, M Wen, **Meijia Wang**, M Wu,* Jilin University, China

Improving the strength of alloy materials and simultaneously retaining high toughness are strongly desirable by various engineering applications. Nanocrystalline-amorphous dual-phase nanostructure consisting of nanocrystalline-cores encapsulated with amorphous-shells has been regarded as one of most effective routes to achieve high strength yet high toughness, which is better than either single-phase nanocrystalline alloys or single-phase metallic glasses because of reverse Hall-Petch effect or shear-band deformation. Herein, nanocrystalline@amorphous core-shell nanostructure has been successfully assembled in the sputtered TA-19 alloy film only by regulating bias voltages (V_b), and then V_b induced microstructure and property evolution was further investigated by combined experiments of X-ray diffraction (XRD), atomic force microscope (AFM), scanning electron microscope (SEM), select electron diffraction (SAED), transmission electron diffraction (TEM) and nanoindentation. The results show that the bombardment of energy ions can promote formation of amorphous zones in TA-19 alloy film, successfully achieving ordered core-shell nanostructure at −120 V of V_b, while single-phase nanocrystalline occurs at V_b= −40 V and amorphous dominated structure appears at V_b= −200 V. Maximum hardness value of 11.2 GPa achieves at V_b= −120 V when the ordered core-shell nanostructure is formed with invisible shear bands around indenter, but more amorphous resulting in disappearance of core-shell nanostructure at V_b= −200 V worsens hardness, accompanying with presence of obvious shear bands around indenter. This novel core-shell-like structure succeeded in achieving high strength or hardness by providing strong resistance to hinder movements of both grains and shear bands due large amount of nanocrystalline/amorphous interfaces. It is suggested that the V_b as a key factor controlling the core–shell-like structure of TA-19 films, which may provide a new strategy to improve mechanical properties of alloy films.

TF-WeP-15 On the Deposition and Properties of Carbon-based Single- and Multilayer Systems Prepared by PLD*, **René Bertram**, D Haldan, S Weissmantel,* University of Applied Sciences Mittweida, Germany

The layer deposition technique Pulsed Laser Deposition (PLD) provides a feasible way to produce pure carbon films with a wide range of mechanical properties. These properties cover, depending on the deposition parameters, indentation hardness H_{IT} from 20 GPa to 60 GPa and indentation modulus E_{IT} from 300 GPa to 620 GPa what could be correlated with Raman spectra determined on these films. Thus, the ratio of the disordered and the graphitic peaks provides an efficient w ay to estimate the mechanical properties of the hydrogen free amorphous carbon films.

Furthermore, it will be presented, that a layered structure consisting of sublayers of alternating or continuously changing mechanical properties results in mechanically highly-resistant layer systems. In scratch tests, these multilayers show beside an excellent adhesion to various substrate materials, a significantly improved, very high cohesive breaking strength. In addition, by testing the abrasive wear of such coating systems against pc diamond suspension in calotte grinding and various ceramics and metals in tribological investigations superior durability was identified, surpassing conventional wear protection layers, in part, by 3 orders of magnitude.

These outstanding layer properties such as high hardness, elasticity, toughness and wear resistance show the great potential of such carbon-based coating systems, i.e. for application as wear protection coatings.

TF-WeP-16 Microstructure and Phase Transformation Behavior of High Carbon M4 Steel Layers Prepared by Direct Energy Deposition Process*, **Jong Bae Jeon**, T Nam, G Park, H Jo, W Lee,* Korea Institute of Industrial Technology, Korea

Metal 3D printing has recently attracted attention as a new technology to replace existing processing processes because of its ability to directly produce complex shapes. Direct energy deposition method has potential to be used for remanufacturing, repairing, and surface modification of molds and broken parts, and recent studies have been carried out on the DED process of high carbon steels. However, due to the unique microstructural complexity of carbon steels, systematic understanding of microstructure and phase transformation behavior during the lamination process has not been systematically understood. Therefore, in this study, the microstructural characteristics and the phase transformation behavior of the thin layers fabricated by DED were studied. M4 steel powder was deposited on D2 steel base material and then the microstructure of the layers were characterized with SEM, EBSD and EDS. Through this study, it was found that the microstructure of DED processed layers dramatically differs from conventional bulk carbon steel. Especially, the nanocarbide formation and phase transformation behavior were different from those of conventional bulk materials. Therefore, this study suggests that understanding microstructure and phase transformation behavior during DED process is essential for controlling microstructures to obtain target properties of DED processed layers.

TF-WeP-23 Development of Low-Emissivity Optical Filters Using Double Cannon Sputtering*, **Ramon Rodriguez Lopez**, N Abundiz Cisneros,* Centro de Investigación Científica y de Educación Superior de Ensenada, México*; R Sangines de Castro, J Cruz Cardenas, R Machorro Mejia,* Universidad Nacional Autonoma de Mexico, México

The implementation of Low emissivity (Low-E) filters in windows for buildings reduces de energy costs employed to compensate the thermal interchange in the structure, hence saving up to 30% of the energy used to keep the building's temperature. The actual designs of this filters use a silver layer between two protective layers, which is expensive and can be easily oxidized when it gets in contact with the atmosphere, also when moisture reaches the thin silver layer, an agglomeration effect is produced due to the migration of the silver to the surface, causing peeling and losing its low emission property (Ando and Miyazaki, 1999).

The aim of this work is the construction of a Low-E filter made up of stack layers: glass/Si_3N_4/Al/Al_2O_3/Si_3N_4, with a high transmittance in the visible region > 80% and high reflectance in the infrared region. This filter has the novelty of employing aluminum (Al) instead of silver (Ag) as a reflector of IR to obtain a cheaper, efficient and durable Low-E filter. The Al is protected with silicon nitride (Si_3N_4) for hardness, high density, and high refraction index (Signore, et al, 2012), furthermore, alumina (Al_2O_3) is a protective layer for the aluminum, and that quality is exploited to enhance its durability.

The Low-E filter is grown using reactive magnetron sputtering technique with double cannon; the reason for this is to be able of synthesizing the whole stack without opening the chamber, hence of avoiding different layers interact with the atmosphere. With this procedure, we can ensure the intended optical properties of the filter. Plasma optical emission spectroscopy and in-situ spectroscopic ellipsometry are employed to find the optimal deposition conditions for each layer and also control and monitor the stack fabrication process for its reproducibility (Abundiz, 2013).

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TF-WeP-25 Investigation of CO_2 Sensing Efficiency and Mechanism Based on P-type MoS_2, *Kuan-Sheng Li, C Yang,* National Chiao Tung University, Republic of China*; C Wang,* National Synchrotron Radiation Research Center*; Y Tseng, S Chang,* National Chiao Tung University, Republic of China

Two-dimensional materials have attracted tremendous attention die to their unique electronic structures, as well as extraordinary physical and chemical properties for sensing gas. In this work, we investigated the CO_2 sensing efficiency and sensing mechanism based on P-type MoS_2 which was doped with niobium (Nb). With a relatively high Nb dopant concentration, the sensor response showed decreased sensitivity, which could be attributed to a higher metallic NbS_2 ratio in the semiconducting MoS_2 film. Using in-situ x-ray absorption spectroscopy (XAS) and ambient-pressure x-ray photoelectron spectroscopy (ARXPS) techniques at national synchrotron radiation research center (NSRRC), we found that CO_2 acted as electron acceptor. However, the resistance of P-type MoS_2 would increase in sensor measurement, which was different from charge-transfer mechanism that acceptors would lower down the resistance of p-type semiconductor. The different behaviors between spectrum results and electric measurements may be the result of different sensing mechanism. The dominated mechanism in this research could be intercalation mechanism which gas molecules intercalated into the structure and changed the conducting path. This work was financially supported by the “Center for the Semiconductor Technology Research” from The Featured Areas Research Center Program within the framework of the Higher Education Sprout Project by the Ministry of Education (MOE) in Taiwan. Also supported in part by the Ministry of Science and Technology, Taiwan, under Grant MOST-107-3017-F-009-002.

TF-WeP-26 Ion-beam Irradiation Induced Surface Chemical and Physical Modification of Polyethylene Glycol Film for Liquid Crystal Alignment*, **In Ho Song**, J Lee, H Jeong, D Seo,* Yonsei University, Republic of Korea

The characteristics of ion beam (IB) irradiated polyethylene glycol (PEG) films were analyzed to determine their potential use as a liquid crystal (LC) alignment layer. The transmittance of the PEG films at various IB intensities was measured to verify the possibility of using it as an alignment layer. Anti-parallel cells with the PEG film were fabricated to examine the LC alignment characteristics. Perfectly dark cross-polarized microscopy images were obtained at an intensity of 700 eV, which indicates uniform LC alignment, and pre-tilt angle measurements supported this finding. X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) analyses were conducted to determine the effect of the IB irradiation on the PEG film on the surface modification. After exposure at an IB intensity of 700 eV where uniform LC alignment was achieved, remarkable chemical composition modification of the PEG film, including the reduction of C-O bonds that affected the uniform LC alignment, was observed via the XPS analysis. Furthermore, the AFM analysis revealed that low kurtosis value was obtained at this IB intensity. Therefore, we are convinced that the PEG films irradiated at this low IB intensity show potential as alternative alignment layer in LC applications.

TF-WeP-27 Ultraviolet Nanoimprint Lithography for Homogeneous Liquid Crystal Alignment using Surface Wrinkling Driven by Ion-beam Irradiation*, **Dong Wook Lee**, J Lee, H Jeong, D Seo,* Yonsei University, Republic of Korea

A simple and controllable surface wrinkling method was used to fabricate a 1-dimensional nanostructure. The structure was transferred to an ultraviolet cured polymer surface through ultraviolet nanoimprint lithography. The transferred 1-dimensional nanostructure of the ultraviolet cured polymer was used as an alignment layer in a liquid crystal display. The anisotropic geometry served as a guide for aligning liquid crystal molecules uniformly without defects. The liquid crystal cell based on the 1-dimensional UV-cured polymer exhibited high thermal stability above 180°C. The proposed 1-dimensional UV-cured polymer has advantages for advanced liquid crystal devices.

TF-WeP-28 Fabrication of Au Atomic Junctions Using Artificial Intelligence Implemented on FPGA*, **Takuya Sakurai**, Y Hirata, K Takebayashi, Y Iwata, J Shirakashi,* Tokyo University of Agriculture & Technology, Japan

Much progress towards artificial intelligence (AI) technique is due to the rapid growth of data size and accessibility in recent years. Thus, AI technique has been applied to many control systems. Meanwhile, feedback-controlled electromigration (FCE) has been employed to create atomic junctions with quantized conductance [1]. Previously, we have proposed ultrafast FCE system using field programmable gate array (FPGA) to adjust quantized conductances of Au atomic junctions [2]. Because of many experimental parameters in FCE procedure, it is difficult to optimize them by rules of thumb in control of quantum states. In this report, we investigated AI-assisted FCE system implemented on FPGA to immediately and precisely fabricate Au atomic junctions.

Au nanowires were fabricated using conventional electron-beam lithography and lift-off process. They were patterned on resist-coated SiO2/Si substrates using electron-beam lithography. Then, electron-beam evaporation of Ti (5 nm) and Au (20 nm) was carried out using a developed resist patterned as template.

AI-assisted FCE system is composed of four engines; learning, evaluation, inference and FCE engines. First, the feature values of conductance quantization obtained from previous experiments were stored in an initial database in learning engine. Then, FCE parameters were evaluated using cost function in evaluation engine. After the evaluation, FCE parameters were optimized by genetic algorithm (GA)-based selection methods in inference engine. Finally, FCE procedure using optimized experimental parameters was applied to Au nanowires in FCE engine. As a result, Au atomic junctions were fabricated by AI-assisted FCE procedure and the conductances of the junctions were successfully quantized at room temperature without catastrophic breaks of the structures. Furthermore, the FCE scheme was performed within an order of millisecond due to the use of FPGA. Therefore, these results imply that Au atomic junctions can be elaborately fabricated with improved controllability of quantized conductance using AI-assisted FCE implemented on FPGA.

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TF-WeP-29 Electromigration-Induced Structural Modification of Series-Parallel-Connected Au Nanogaps*, **Koji Minami**, S Tani, K Sakai, T Sato, M Ito,* Tokyo University of Agriculture & Technology, Japan*; M Yagi,* National Institute of Technology, Ichinoseki College, Japan*; J Shirakashi,* Tokyo University of Agriculture & Technology, Japan

We developed a simple and controllable nanogap fabrication method called “activation.” This method is based on electromigration induced by Fowler-Nordheim (F-N) field emission current passing through the nanogaps. The F-N field emission current plays an important role in triggering the migration of atoms. By performing the activation, gap separations and tunnel resistances of the nanogaps are reduced because of the activated atoms that accumulated at the tips of nanogap electrodes. In this method, by only adjusting the applied current, we are able to control the structural properties of the nanogaps [1]. Previously, simultaneous tuning of the structural properties of series connected Ni nanogaps was achieved by using the activation [2, 3]. In this study, we investigated the application of the activation to the series-parallel-connected Au nanogaps for structurally defined, current-induced modification of nanogaps.

First, 2x1-6x6 series-parallel-connected Au nanogaps with the initial gap separation of 40-70 nm were fabricated with electron-beam lithography and lift-off processes. After the activation, the total resistance of the series-parallel-connected nanogaps became smaller than that before the activation. According to scanning electron microscope images, the current was passed thorough the narrower initial gaps within the series-parallel-connected nanogaps, and the separations of nanogaps were narrowed to less than 10 nm after the activation. Furthermore, we applied the activation to Au nanodots with interdot spacing of 30-50 nm placed between Au nanogap electrodes. As a result, the total resistances and the interdot spacing of Au nanodots were reduced by performing the activation. This tendency is quite similar to that of the series-parallel-connected Au nanogaps. These results clearly indicate that the structural properties of the series-parallel-connected Au nanogaps can be controlled simultaneously and precisely via the activation method. The understandings possibly imply that performing the activation to the series-parallel-connected nanogaps can be applicable to the shortest path problems.

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TF-WeP-30 Oxygen Reduction Reaction Mechanism for N-doped Graphene Nanoribbons*, Haruyuki Matsuyama,* *S Gomi, J Nakamura,* The University of Electro-Communications (UEC-Tokyo), Japan

Recently, much attention has been devoted to the oxygen reduction reaction (ORR) on nitrogen(N)-doped graphene [1]. It has been theoretically revealed that N atoms prefer to be located near the edge of graphene [2,3]. The structure of graphene edge can be mainly classified into two types, armchair and zigzag edges. However, the effect of edge structures on ORR activity has not been fully understood.

We investigated the ORR activity for the N-doped graphene nanoribbons with armchair (N-ACGNRs) and zigzag (N-ZZGNRs) edges using first-principles calculations within the density functional theory. We used the computational hydrogen electrode model [3] to evaluate the maximum electrode potential (U_{max}). ORR mainly proceeds in two pathways: For the two-electron ($2e^-$) pathway, O_2 molecule is reduced to H_2O_2, and for the direct four-electron ($4e^-$) pathway, the final product is H_2O. H_2O_2 for the $2e^-$ pathway might corrode a carbon based electrocatalyst itself, leading to low durability. We also examined the selectivity with respect to these two pathways.

The calculation models are the N-ACGNRs and the N-ZZGNRs, in which a C atom is substituted by a N atom for each doping site from edge to in-plane. The reaction sites are set to C atoms adjacent to the N atom. We calculated the values of U_{max} for each doping site and reaction site for the N-ACGNRs and the N-ZZGNRs. The Umax for N-ACGNR becomes positive for each doping and reaction site. On the other hand, the U_{max} for N-ZGNR has a parity dependence with regard to the nitrogen doping site in the vicinity of the zigzag edges. For the even-numbered doping sites from the edge, the values of U_{max} are larger than 0 V, while for the odd-numbered ones, the values of U_{max} become negative. The reaction selectivity for the $4e^-$ pathway appears only in the vicinity of armchair and zigzag edges. For the models showing the reaction selectivity, the sp^2 configuration of GNR is maintained, even if reaction intermediates are adsorbed on GNR. On the other hand, reaction intermediates adsorb on GNR with sp^3-like configuration for the other models. The mechanism for appearance of the selectivity will be discussed in the presentation.

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TF-WeP-31 The Structure, Oxidation Resistance, Mechanical and Tribological Properties of TiAlSiNO Nanocomposite Coatings for Cutting Tools*, Wang Ryeol Kim,* *S Heo,* Korea Institute of Industrial Technology (KITECH), South Korea*; H Kim,* Korean Institute of Industrial Technology (KITECH), South Korea*; J Kim, I Park,* Korea Institute of Industrial Technology (KITECH), South Korea

Functional graded TiAlSiNO nanocomposite films were deposited onto WC-Co substrate by a filtered arc ion plating system using TiAl and TiSi composite targets under N_2/Ar atmosphere. XRD and XPS analyses revealed that the synthesized TiAlSiNO films were nanocomposite consisting of nanosized (Ti,Al,Si)N crystallites embedded in an amorphous Si_3N_4/SiO_2 matrix. The hardness of the TiAlSiNO films exhibited the maximum hardness values of ∼47GPa at a Si content of ~5.63 at.% due to the microstructural change to a nanocomposite as well as the solid-solution hardening. Besides, TiAlSiNO film with Si content of around 5.63at.% also showed perfect adhesive strength value of 105.3N. These excellent mechanical properties of Ti-Al-Si-N-O films could be help to improve the performance of machining tools and cutting tools with application of the film. Also X-ray diffactometer (XRD) analysis was conducted to investigate the crystallinity and phase transformation of the films. As a result of XRD, TiAl(18at.%)SiNO films showed the great oxidation resistance of 950℃ for 30 min in air. Based on glow discharge optical emission spectroscopy (GD-OES) depth profiles, TiAl(18at.%)SiNO film annealed at 950℃ for 30 min shows formation of aluminum oxide layer on the film surface. On the other hand, TiAl(7.56at.%)SiNO film had a titanium oxide layer on the surface after annealing at 950℃ for 30 min. In this study, TiAlSiNO coatings were applied to insert tools. Their performances were evaluated about cutting-time and cutting-length to Inconel 718 super alloys. Performance of the coated tools were evaluated and compared with different TiAlSiNO coatings onto cemented carbide substrates. Especially, the TiAlSi(5.63at%)N coated tool showed better performance and best tool life.

TF-WeP-32 Influence of Silicon Addition on the Mechanical and Tribological Properties of Zirconium Nitride Coatings Deposited by Hybrid Deposition System*, Sungbo Heo,* *W Kim, J Lee, J Kim, I Park,* Korea Institute of Industrial Technology (KITECH), South Korea

Zr–Si–N coatings with various Si contents were synthesized by a hybrid deposition system combining arc ion plating and d.c. magnetron sputtering techniques. The influence of the Si content on the microstructure, mechanical properties and tribological properties of the Zr–Si–N coatings were investigated. The results showed that as the Si content increased from 0 to 5.8 at.%, the coatings transformed from a columnar ZrN to nanocomposite structure with a nano-sized ZrN crystallites embedded in amorphous Si_3N_4 matrix and further increases of Si content lead to amorphous-like coatings. XPS analysis was applied to ZrN film and Zr–Si(5.8 at.%)–N film respectively. The main peaks at 179.9 and 182.3 eV with a large percentage of area correspond to the ZrN compound. There was also a small contribution from the ZrO_2 oxide phase at 182.16 and 184.59 eV. For the Si 2p region, the silicon binding energy spectrum is also divided into two peaks. The major peak located at 101.8 eV corresponds to Si_3N_4 compound. The maximum hardness (H) of 33 Gpa, Young's modulus € of 265 Gpa, and H/E* value of 0.12 were obtained at Si content of 5.8 at.% in the Zr–Si–N coatings, respectively. The coating with the lowest friction coefficient and the best wear resistance was also obtained at Si content of 5.8 at.%, which was mainly contributed to high value of H/E* and formation of SiO_2 or $Si(OH)_4$ self-lubricating layer due to the interface tribo-chemical reaction.

TF-WeP-33 Coincident Raman and XPS Analysis of 2D-Materials*, Joseph Robinson,* *P Mack,* Thermo Fisher Scientific, UK

Advanced materials present ever-increasing challenges to the analytical scientist. Composite materials built from nanostructures or ultra-thin films, often with complex chemistries present, are now required in a broad range of applications, and achieving full characterization is rarely managed using only one analysis method. To maintain confidence in the results from the utilization of several different methods, it is advantageous to be able to perform experiments on the same platform. Ideally, this should be without having to move the sample between several instruments, removing the need for additional registration or processing to ensure that the data is being collected from the same position.

For surface analysis, it has been common for many years to incorporate related analysis techniques onto the same instrument. For example, X-ray photoelectron spectroscopy (XPS) systems are commonly equipped with UV light sources to facilitate investigation of additional properties of materials via ultra-violet photoelectron spectroscopy (UPS). The ion source that is typically used for sample cleaning and depth profiling can also be used for low energy ion scattering (LEIS or ISS), providing more surface sensitive elemental composition information than can be delivered from XPS alone.

The latest innovation is to extend the range of offered complimentary techniques to include Raman spectroscopy. The focal points are aligned such that data can be acquired from the same point simultaneously, and that the sizes of the analysis areas are comparable in size. Chemical modifications of the material can be easily determined and quantified with XPS. Raman offers a fast way of determining the quality and conformity of the material, and direct compound identification. The greater depth of field of the Raman spectrometer also offers bulk information to complement the surface sensitive XPS data.

In this presentation we will illustrate the strengths of this combined, in-situ approach to surface analysis, illustrated with examples from the analysis of two-dimensional materials, boron nitride and molybdenum disulfide.

TF-WeP-34 Two-Dimensional Doping Layer for Flexible Transparent Conducting Graphene Electrodes with Low Sheet Resistance and High Stability*, Y Seo, H Jang, W Jang, J Lim, Y Jang, T Gu,* ***Dongmok Whang,*** Sungkyunkwan University, Republic of Korea

Graphene, an ultra-thin flexible material with high carrier mobility and transparency, is a promising candidate for flexible transparent conducting electrodes (TCEs). However, its resistance is too high for use as a TCE material by itself. Therefore, fabricating graphene with low sheet resistance and high stability is a significant challenge for practical applications of graphene TCEs. In this study, we proposed a two-dimensional (2D) doping layer, which can stably dope graphene to develop a highly transparent graphene TCE with low sheet resistance. For this purpose, the 2D doping layer is prepared by immobilizing dopant molecules on transparent graphene oxide and simply stacking it with graphene enables efficient and stable charge transfer doping of the graphene. A TCE fabricated by alternately stacking the doping layer and graphene had a high optical transmittance of over 90% at a wavelength of 550 nm and a low sheet resistance of 50 $\Omega\cdot sq^{-1}$. Furthermore, the sheet resistance showed an excellent thermal and mechanical stability with a change of only about 2% in a bending test of 20,000 cycles or at a high temperature of $>200^{o}$C. This result shows that stacking graphene with stable 2D doping layer is a promising approach for graphene-based next generation TCE.

TF-WeP-35 Measurements of Reactive Species in Plasma-Activated Liquids Controlled by Atmospheric Pressure Plasma Operating Parameter*,* ***Hea Min Joh****, T Chung,* Dong-A University, Republic of Korea

Atmospheric pressure helium plasma jetdriven by a low-frequency bipolar pulsed voltage wasemployed for plasma-liquid interactions.Plasma treatment generated the reactive species in gas phase, and these species dissolve into the liquid phase, resulting in the appearance of reactive oxygen and nitrogenspecies (RONS)in liquid. To identify the correlation between the production of RONS in liquids and plasmas, we studiedthe effects of plasma operating parameters on the RONS in gas and liquid phase.The changes of discharge current, optical emission intensities from reactive radicals, gas temperature with the control parameters were measured and compared. The control parameters include applied voltage, pulse withand additive oxygen flowrate.The amountsof O_3 and NO_2 in gas phase weremeasured by gas detector. For quantitative measurement of RONS radicalsin liquidphase, several chemical methodswere performed on plasma-treated HBSS (Hanks' Balanced Salt Solution).Among these RONS, the OH radicals dissolved in the liquidwere monitored indirectly using the fluorescent properties of hydroxyterephthalic acid (HTA) formed by the reaction of terephthalic acid (TA) with OH radicals.The concentrationsof long-living reactive species(H_2O_2, NO_2-, NO_3-, and O_3) in liquidweredetected after plasma treatment usingspectrophotometer.It was observed that the various plasmaoperating parameterscould influence the amount of reactive speciesin liquid.

TF-WeP-36 Ultrafast and Highly-Scalable Organic-Inorganic Hybrid Perovskite Memory Devices for Emerging Memory Applications*,* ***Jang-Sik Lee****, B Hwang,* Pohang University of Science and Technology (POSTECH), Korea

Organic-inorganic hybrid perovskites (OIHPs) have been used as the switching layers in resistive switching memory (RSM) devices due to distinct property of hysteresis in current-voltage (I-V) curves caused by defect migration under electric field [1-3]. For practical memory applications OIHPs are required to be prepared by vacuum deposition with good uniformity. We proposed a high-performance CH3NH3PbI3 (MAPI)-based RSM device utilizing sequential vapor deposition to achieve high-density memory applications [4]. MAPI-based nanoscale RSM and cross-point array structure were fabricated to show the feasibility of OIHP-based memory with high-density data storage. Sequential vapor deposition enabled MAPI layer to be deposited inside the nanotemplates with 250 nm via-hole structures on the silicon wafers. The MAPI-based nanoscale memory showed low operating voltage, good endurance, and long data retention. Additionally, our devices showed sub-microsecond switching speed under ac bias pulses. The memory element of MAPI-based cross-point array structure showed bipolar resistive switching. This work on preparing OIHP-based nanoscale devices and the cross-point array structure will be an important step in the development of OIHPs for high-capacity information storage and for suggesting a novel approach that can be used to apply OIHPs to real memory devices on a large scale. Finally, lead-free, air-stable OIHP-based RSM with ultrafast switching and multilevel data storage capability will be introduced.

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Biomaterial Surfaces & Interfaces
Room Naupaka Salon 6-7 - Session BI-WeE

Biomolecule/Material Interactions and Medical Applications

Moderator: Buddy D. Ratner, University of Washington

5:40pm **BI-WeE-1 Engineered Biointerfaces – Organisation and Functionalisation of Proteins at Surfaces***, **Jenny Malmstrom,*** University of Auckland, New Zealand **INVITED**

In my research group, we are interested in the interface between materials and biological systems – such as proteins and cells. Structured or organised surfaces with nanoscale features are important in a range of fields ranging from energy and computing to controlling cellular adhesion or differentiation. The precise organisation of proteins at surfaces is one route to creating such engineered interfaces. Proteins exist with an enormous structural and chemical versatility and lend themselves well to be functionalized with different moieties. The ability to rationally engineer proteins enables the use of proteins as carefully designed nanometer sized building blocks.

I will present work from our group focussed on using protein-protein interactions to build up higher order protein structures, and our efforts to organize and functionalise these structures. Proteins like Lsmα and peroxiredoxin self-assemble into robust doughnuts whose pore size can be tuned specifically to encapsulate metal complexes or nanoparticles and then assemble further into stacks to create magnetic, electrical or optical nanorods. We are harnessing this potential to create functional arrays of these self-assembling protein rings. We have explored ways of arranging these protein rings, for example through templating using a self-assembling block copolymer, or through specific binding to a patterned surface. Furthermore, the protein core has been used to template the synthesis of small (~4 nm) iron oxide nanoparticles. Throughout all of this work, imaging is an important characterisation tool and I will show how we use AFM (including magnetic force microscopy) and other techniques to understand our systems.

Building on this work, I will also present how we are developing some of these thin block copolymer films as biointerfaces, with the aim to control both protein and cellular interactions at the interface.

6:20pm **BI-WeE-3 Tunable Thermal Transport and Reversible Thermal Conductivity Switching in Topologically Networked Bio-Inspired Materials***, J Tomko,* University of Virginia*; A Pena-Francesh, H Jun,* Pennsylvania State University*; M Tyagi,* National Institute of Standards and Technology*; B Allen, M Demirel,* Pennsylvania State University*;* ***Patrick Hopkins,*** University of Virginia

The dynamic control of thermal transport properties in solids must contend with the fact that phonons are inherently broadband. Thus, efforts to create reversible thermal conductivity switches have resulted in only modest on/off ratios, since only a relatively narrow portion of the phononic spectrum is impacted. Here, we report on the ability to modulate the thermal conductivity of topologically networked materials by nearly a factor of four following hydration, through manipulation of the displacement amplitude of atomic vibrations. By varying the network topology, or crosslinked structure, of squid ring teeth-based bio-polymers through tandem-repetition of DNA sequences, we show that this thermal switching ratio can be directly programmed. This on/off ratio in thermal conductivity switching is over a factor of three larger than the current state-of-the-art thermal switch, offering the possibility of engineering thermally conductive biological materials with dynamic responsivity to heat. More details of this work can be found in the recently published paper, Tomko, J.A., Pena-Francesch, A., Jung, H., Tyagi, M., Allen, B.D., Demirel, M.C., Hopkins, P.E., “Tunable Thermal Transport and Reversible Thermal Conductivity Switching in Topologically-Networked Bio-Inspired Materials,” *Nature Nanotechnology* **DOI: 10.1038/s41565-018-0227-7**.

7:00pm **BI-WeE-5 Design Principles and Potential Applications of Cyclic Peptide Polymer-based Nanomaterials***, **Kenan Fears,*** US Naval Research Laboratory, USA

We present a new class of bioinspired nanomaterials that are stabilized by a combination of covalent and hydrogen bonds. Prior work by others has shown that cyclic peptides can self-assemble to form supramolecular assemblies through backbone-backbone hydrogen bonding. To improve upon this molecular architecture, we develop a synthesis route to polymerize cyclic peptides and form a linear polymer chain that can transition between a rigid nanorod and a “soft” unfolded conformation. For a cyclic peptide polymer containing amine-terminated side chains on each ring, we demonstrate self-assembly can be triggered in aqueous solutions by varying the pH. We measure the elastic modulus of the rigid nanorods to be ca. 50 GPa, which is comparable to our molecular dynamics (MD) prediction (ca. 64 GPa). Our results highlight the uniqueness of our molecular architecture, namely their exemplary toughness (up to 3 GJ m^{-3}), in comparison to other cyclic peptide-based assemblies. Finally, we demonstrate the potential of these novel nanomaterials for biomedical applications, such as wound healing.

7:40pm **BI-WeE-7 Metal Oxides and Bone Healing***, H Nygren,* University of Gothenburg, Göteborg, Sweden*; C Zhang,* Science for Life Laboratory, Stockholm, Sweden*;* ***Per Malmberg,*** Chalmers University of Technology, Sweden

Metal oxides are widely used in implant materials and trace metals are known to deeply influence bone healing. The present study was undertaken to elucidate the mechanisms of the effect of metal ions on bone healing, starting with analyses of the ability of different metal oxides to catalyze the formation of hydroxyapatite (HA) and ending with a global analysis of the transcriptome of bone tissue after implantation of metal ions.

Incubations of MnO and ZnO with cell culture medium followed by analysis with XPS, ToF-SIMS and SEM/EDX showed that these metal oxides are covered with a layer of HA within 12h. Implantation of MnO and ZnO in rat tibia stimulated the formation of callus bone. After 3w of healing of ZnO implants, the bone mineral contained high levels of Zn. This was considered a potential hazard and the use of ZnO was omitted from the study. Sham-operated tibia and bone implanted with MnO were taken to RNA-extraction and global analysis of differently expressed genes at the Science for Life Laboratory in Stockholm (head M. Uhlen). After 4 days of healing, the enrichment analysis showed upregulation of genes reflecting response to cytokines, cytokine regulation and cytokine production in the bones implanted with MnO, compared to sham. Furthermore, genes reflecting leukocyte migration, inflammation and celldeath were upregulated. Analysis of upregulated single genes shows reactions to hypoxia (RGS5), reactions to platelet Ca levels (LHFPL2), genes related to osteogenesis (FetuinB, RUFY4,NFkBIA) and osteoclast differentiation (CPMB6B). The data are still undergoing further analysis.

Manganese has been described as an essential trace metal for bone formation since the mid 1930´s when low levels of Mn in the feed was shown to cause skeletal defects in chicken, rats and rabbits. Mn has been suggested as a trace metal in bone cement based on its effect on biochemical markers of bone metabolism. Manganese is widely used in biomaterials, most extensively as a component of stainless steel.

8:00pm **BI-WeE-8 Thin Films, Coatings and Surface Solutions for Medical Devices***, **Shahram Amini,*** Johnson Matthey Inc.

As medical device manufacturers are pressed to design ever-smaller devices with increasingly long service life, optimizing the performance and profile of each component becomes more crucial. During the past few decades, various medical devices, for instance cardiac rhythm management and neurostimulation devices, have been invented and used in clinical practice to achieve electrical stimulation. These devices function via artificial stimulation of living tissue through transfer of an external electrical signal to an implantable electro-conductive microelectrode across to the membrane of the neural cells or tissue. These electrodes and their surface properties have been a focus for innovation at the Center for Coatings and Surface Solutions (CCSS) to give the next-generation devices a competitive edge via advances in coatings technology that can enable electrodes with better charge exchange capacity, thereby improving accuracy and efficacy of treatment – while also extending the devices’ battery life. In developing these electrodes, the substrate, its surface, and its interface with the electrolytic physiological environment all play important roles in the stimulation process. This presentation will focus on the process development and characterization of coatings that exhibit high electrochemically-active surface areas for implantable stimulation devices. In particular, effect of various electrode surface treatment technologies on microstructural characteristics will be discussed. The results presented in this work demonstrate an unprecedented approach that has facilitated discovery of many unique features in these coatings, and the effect of electrode surface on coating surface and sub-surface features.

8:20pm **BI-WeE-9 Effects of Metal Implants on Bone Healing Analysed by Transcriptomics***, **Håkan Nygren,*** University of Gothenburg, Göteborg, Sweden*; C Zhang, M Arif, M Uhlen,* Science for Life Laboratory, Stockholm, Sweden

Bone fractures affect hundreds of millions people worldwide and are a leading cause of long-term pain and disability. Fractured bone normally heals *ad integrum* through a process undergoing characteristic stages of blood coagulation, inflammation, formation of soft and hard callus and, finally, remodeling to its original structure. In approximately 10% of femur-neck fractures, healing meets with failure, or delay. Common causes of failure to heal are critical size defects, infection, or mobility of the fracture parts. Internal stabilisation of fractures with metal implants is an efficient aid of fracture healing. Tissue engineering of bone healing is efficiently made by implanting metal species like Mg, Sr, Zn and Mn. These metals often have a capacity to catalyze formation of hydroxyapatite in bone tissue (Nygren, Pacsurf 2016) suggesting a possible common pathway for the well documented effect of trace metals on bone healing. In this study we analysed the transcriptomics of fracture healing with and without implanted Mg and Mn after 4 and 7 Days of healing, before mineralization and after completion of the callus bone.

Proteins coded by the most differentially expressed genes during normal fracture healing after 4 Days of healing where regulators of platelet degranulation, upregulators of TGF-beta, regulators of Beta-1 Integrin, IL10 receptor antagonist and ROBO proteins guiding cell movement in embryos.

Proteins most differentially expressed after 7 Days of healing were an enzyme hydrolysing lysine, inhibitors of inflammation, NFkappaB, microtubule associated scaffold protein, angogenic proteins and BMP-2 signalling proteins.

Venn diagrams comparing the up-regulated genes after healing with Mg and Mn after 4 Days of healing showed no overlap between the activated genes in these Groups. After 7 Days of healing, there was an 80% overlap between genes upregulated by Mg and Mn. The data suggest that pathways of bone healing at metal implants differs after 4 Days of healing, before the start of mineralisation, but are more congruent after 7 Days of healing when the callus bone is mineralised and remodelling starts.

8:40pm **BI-WeE-10 Synthesis and Characterization of Reactively Sputtered Platinum Group Metal Oxides for Stimulating and Recording Applications***, G Taylor, N Page, A Marti, R Paladines,* Rowan University*; A Fones,* Johnson Matthey Inc., UK*; S Tint,* Johnson Matthey Inc.*; H Hamilton,* Johnson Matthey Inc., UK*; S Amini,* Johnson Matthey Inc.*; **Jeffrey Hettinger,*** Rowan University

A range of materials have been examined as coatings over the past several decades to improve the performance of implantable devices used in neurostimulation and recording applications. Iridium oxide (IrO_2) has been widely investigated due to its biocompatibility and high charge storage capacity. Modification of the synthesis conditions, as one means of improving the coating performance, led to reports of surface platelets forming at high deposition pressures. This study complements earlier research by extending the range of deposition parameters for the IrO_2 system and investigates the ruthenium oxide (RuO_2) system under the same experimental conditions. The results show that the platelet microstructure in tetragonal IrO_2 is due to the formation of a specific orientation of crystallite. In contrast to previous reports that platelet formation coincided with a decrease in coating performance, it will be shown that the presence of platelets can improve the electrochemical performance of the coatings as measured by cyclic voltammetry in a phosphate buffered saline electrolyte. Furthermore, the platelet microstructure, and thereby the effective surface area, can be systematically controlled by adjusting deposition parameters, including temperature and oxygen partial pressure, used during the reactive sputtering. No such platelet formation has yet been observed in the RuO_2 system.

Thin Films
Room Naupaka Salons 4 - Session TF-WeE

Emerging Topics: Growth and Properties of Electronic Materials, 2D Layers, and Metallic-glass Thin Films

Moderator: Lars Hultman, Linkoping University

5:40pm **TF-WeE-1 Novel Metallic-Glass Nanotube Arrays: Synthesis, Characterization and Applications***, **Jinn P. Chu,*** National Taiwan University of Science and Technology, Taiwan, Republic of China **INVITED**

Thin film metallic glass (TFMG) is a new class of metallic thin film with unique characteristics, including high strength, high ductility, smooth surface, absence of grain boundaries, low coefficient of friction, and corrosion resistance, though their bulk forms are already well-known for properties such as because of their amorphous structure. Thin films prepared by vapor-to-solid deposition are expected to be further from equilibrium than those prepared by liquid-to-solid melting or casting processes. This is expected to further improve the glass forming ability and widen the composition range for amorphization. In this talk, we successfully fabricated the first-ever metallic glass nanotubes (MGNTs) on Si by a simple lithography and sputter deposition process for very large-scale integration. Like biological nanostructured surfaces, MGNTs show some surprising water repelling and attracting properties. Nanotubes are 500-750 nm tall and 500-750 nm in diameter [1]. The MGNT surface becomes hydrophobic and repels water. Upon heating and cooling the array, water can be repelled and attached to the surface [1]. Two examples will be presented in this talk based on modifications of this scheme. First, after modification of biotin, the array acts as a waveguiding layer for an optical sensor. The MGNT sensor waveguide could readily detect the streptavidin by monitoring the shift. With a detection time of 10 min, the detection limit for streptavidin is estimated to be 25 nM. Thus, the arrays may be used as a versatile platform for high-sensitive label-free optical biosensing [2]. Further, the array is prepared on a heating device on Si and, with an applied electric voltage to the heating device underneath, the MGNT surface was heated to generate an extending force from these nanochambers up to ~75°C in order for the array to be functioned as biomimetic artificial suckers for thermally adhesion response in biological systems [3]. As a result, the adhesive forces of the MGNT arrays can be as high as 11.2 N cm^{-2}.

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6:20pm **TF-WeE-3 Growth and Characterization of Atomically-thin MoS_2-$MoSe_2$ Hetero-Junctions Synthesized by Vapor-Phase Chalcogenization***, **Andres De Luna Bugallo,*** CINVESTAV Querétaro México, Mexico*; I Bilgin, D Rubin,* Northeastern University*; K Fujisawa,* Penn State University*; M Terrones,* Pennsylvania State University*; S Kar,* Northeastern University

Junctions between disparate electronic materials have been a focus of fundamental and applied research for over a century, and with the emergence of two dimensional (2D) semiconductors this focus has only intensified. In particular, the electronic and optical properties of 2D hetero-junctions synthesized directly from vapor-phase growth depend on the atomically-sharp interface. In this work, we present an in-depth characterization of vapor phase chalcogenization (VPC) synthesized of 2D molybdenum disulfide/molybdenum diselenide (MoS_2/$MoSe_2$) hetero-junctions exhibiting multiple morphologies. We investigated both, lateral in-plane heterojunctions and vertical out-of-plane heterojunctions with morphologies that range from being atomically-abrupt interfaces with varying degrees of doping, mixing, and alloying. High-resolution microscopy/spectroscopy performed on well-defined regions of these samples show distinguish among these regions, which also exhibit novel physical phenomena. In particular, we demonstrate strong supported-or-suspended sample dependent suppression of certain photoluminescence (PL) and Raman vibrational modes. We also describe atomically-resolved scanning transmission electron microscopy of these hetero-junctions, revealing defects, doping, and formation of different types of Moiré superlattices. This works aims at providing a comprehensive multi-probe high-resolution characterization of TMD heterojunctions.

6:40pm **TF-WeE-4 Band-engineering of $(TiO_2)_{1-x}(TaON)_x$ Thin Films for Photochemical Applications***, **Tetsuya Hasegawa,*** University of Tokyo, Japan

Titanium dioxide (TiO_2) has been extensively studied for photocatalytic applications. Recently, we synthesized epitaxial thin films of anatase tantalum oxynitride (TaON), which has a smaller bandgap and larger refractive index than TiO_2 [1,2]. Alloying of anatase TiO_2 and TaON would enable band structure engineering of TiO_2 in a controller manner. In this study, we have grown thin films of an anatase $(TiO_2)_{1-x}(TaON)_x$ (TTON) solid solution and investigated their optical properties and band alignment. Epitaxial thin films of TTON ($0.1 \le x \le 0.9$) were deposited on $(LaAlO_3)_{0.3}(SrAl_{0.5}Ta_{0.5}O_3)_{0.7}$ substrates by nitrogen plasma-assisted pulsed laser deposition technique. X-ray diffraction confirmed epitaxial growth of phase-pure anatase TTON, of which lattice constants changed with *x* in agreement with Vegard's law. Optical properties and band alignment were examined spectroscopic ellipsometry and X-ray photoelectron spectroscopy, respectively. The bandgap of TTON systematically decreased with increasing *x*, mainly due to upward shift in the valence band maximum through evolution of shallow N 2*p* band. Meanwhile, the position of the conduction band minimum was insensitive to *x*. The band alignment of anatase TTON was found to be suitable for photocatalytic water splitting with visible light. The refractive index of anatase TTON monotonically increased with *x*, possibly originating from the higher covalency of metal-N bonds than that of metal-O bonds.

References

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7:00pm **TF-WeE-5 Exploring Mechanical and Liquid-phase Exfoliation of HOPG through Low-energy Ion Beam Analysis***, **Paolo Branchini,*** INFN RomaTre, Italy*; S De Rosa,* National Institute of Nuclear Physics Roma Tre, Italy*; L Tortora,* INFN RomaTre, Italy*; R Yivlialin, G Bussetti,* Politecnico di Milano, Italy

Among two-dimensional semiconductors, graphene is universally recognized as an emerging material having potentials for a wide range of applications including organic electronics and photonics. Graphene flakes can be produced following different preparation protocols,[1] such as: dry and liquid-phase exfoliation, growth on SiC and metal substrates, CVD, molecular beam epitaxy, atomic layer epitaxy, chemical synthesis etc.. Within the European Graphene flagship program, different analytical techniques [SEM/FIB, TEM, EDS, SPM, XPS, XRD, Raman] are routinely adopted to provide the structural and chemical characterization and to validate the production process.

Here, we propose ToF-SIMS combined with multivariate analysis as validation tool for monitoring the graphene production. In particular, we focused the research on most diffused production methods: (i) the mechanical exfoliation by adhesive tape and (ii) the dispersion of graphene flakes inside an electrochemical bath after the intercalation of ions inside a graphite (HOPG) sample.

The (i) preparation protocol foresees the deposition of graphene onto a silicon wafer, which is then cleaned with acetone, ethanol, and deionized water and dried on a hot plate maintained at 300°C for 1min. The (ii) procedure requires an acid media (e.g. sulphuric or perchloric solutions), purified by bubbling Ar gas inside a separator funnel for several hours. A three-electrode cell is then exploited for inducing ion intercalation in graphite, used as a working electrode, which expands the crystal helping the weakening of the layer-layer interaction.

The high sensitivity of ToF-SIMS technique (few ppm) reveals graphene contamination due to the presence of residual glue coming from the scotch-tape. Furthermore, PCA and K-means cluster analysis were successfully applied to ToF-SIMS high resolution images, showing three different contributions from silicon substrate, residual glue, and graphite/graphene layers. At the same way, results from the graphite mother-crystal, used in the electrochemical approach, also show residual compounds related to the production process such as SO_2^-, SO_3^-, ClO^-, ClO_2, ClO_3^-, ClO_4^-. Dual beam depth profiling experiments showed that these compounds are present not only onto the HOPG surface but also between graphite terraces and inside the nanoprotrusions produced during the intercalation process. These preliminary results contribute to shed light on the chemistry of the intercalation process.

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7:40pm **TF-WeE-7 Altering Cu-Ni Alloy Composition to Control 2D h-BN Growth***, **Boris Feigelson,*** Naval Research Laboratory*; K Sridhara, J Hite, J Wollmershauser,* US Naval Research Laboratory

Atomically thin two dimensional hexagonal boron nitride (2D h-BN) is one of the key materials in the development of new van der Waals heterostructures due to its outstanding properties including an atomically smooth surface, high thermal conductivity, high mechanical strength, chemical inertness and high electrical resistance. Growth of single and multi-layer (2-10 layers) h-BN films of high crystalline quality in controlled manner is still a challenge.

In this work, h-BN films were grown by atmospheric-pressure CVD on metal substrates (Cu, Ni and Cu-Ni alloys). A vertical custom-made CVD reactor was used to grow h-BN films. The design of the vertical reactor allows the simultaneous growth of a few samples of h-BN on different substrates in the same run. Ni-Cu and Cu-Ni alloys were prepared by electroplating Cu on to Ni and Ni on Cu foils, respectively, followed by thermal annealing and polishing [1] to create alloy substrates with increasing Cu or Ni concentrations (at 10 wt.% increments from 10-50 wt.% Cu in Ni and 10-50 wt.% Ni in Cu).

As it was shown in our previous work [2], Fourier transform grazing-incidence infrared reflection absorption spectroscopy (FT-IRRAS) can be used to characterize monolayer and few-layer h-BN films directly on metal substrates. Two sub-bands of the A_{2u}(LO) vibrational mode were found for thin 2D h-BN films in contact with Cu and Ni. The lower-energy A_{2u}(LO)1 sub-band around 819 cm^{-1} is related to 2D h-BN coupled with Cu substrate, while the higher energy A_{2u}(LO)2 sub-band around 824 cm^{-1} is related to decoupled (essentially free standing) h-BN.

The IR-active out-of-plane vibrational mode was exploited to identify and characterize 1-5 layer h-BN on metal substrates, while micro Raman spectroscopy was used to characterize thicker h-BN films. Scanning electron microscope and x-ray photoelectron spectroscopy were used to probe the h-BN crystal size and stoichiometry.

Results on how morphology and thickness of 2D h-BN films depend on Cu-Ni alloy composition will be presented.

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8:00pm **TF-WeE-8 Internal Photoemission Spectroscopy Measurements of Energy Barriers between Metallic Glass Thin Films and ALD Dielectrics***, M Jenkins, **John Conley, Jr.,*** Oregon State University

Metal/insulator/metal (MIM) structures are used as high speed diodes for rectenna based harvesting and sensing of IR radiation, capacitors, resistive memory, and hot-electron transistors. To better control electric fields and improve performance of these devices, there is growing interest in integrating metallic glassy (amorphous) thin films as smooth electrodes with uniform work function. Precise knowledge of metal/insulator barrier heights, ϕ_{Bn}, is critical for predicting, understanding, and optimizing MIM device charge transport and operation. In the simplest model, charge transfer across the interface is neglected, and ϕ_{Bn} should vary with the vacuum work function of the metal, $\Phi_{M,vac}$, so that $\phi_{Bn}=\Phi_{M,vac}-\chi_i$ where χ_i is the insulator electron affinity. In induced gap state theory, charge transfer at intrinsic interface traps which create an interfacial dipole that drives the metal Fermi level, E_{FM}, towards the charge neutral level of the insulator, $E_{CNL,i}$, the energy at which the dominant character of the interface states switches from donor-like to acceptor-like. A metal on an insulator will behave as if it has an effective work function, Φ_{M-eff}, different from $\Phi_{M,vac}$, so that $\Phi_{M,eff}=E_{CNL,i}+S(\Phi_{M,vac}-E_{CNL,i})$.[1] S is the slope that describes how much $\Phi_{M,eff}$ on a given dielectric will change in response to $\Phi_{M,vac}$. Empirically, $S=1/(1+0.1(\varepsilon_{hf}-1)^2$. As the high frequency dielectric constant, ε_{hf}, increases, S decreases and the insulator more effectively "pins" E_{FM} at $E_{CNL,i}$. Finally, actual ϕ_{Bn}'s depend on deposition method and can deviate substantially due to extrinsic interface traps. Thus it is necessary to directly measure ϕ_{Bn} for a given metal-insulator combination.

In this work, we use IPE spectroscopy to measure ϕ_{Bn} of the thin film glassy metals ZrCuAlNi, TaWSi, and TaNiSi in MIM stacks with various insulators deposited via ALD.[2,3] To date, there have been few reports of IPE measurements of MIM structures and only one an amorphous metal.[4] Results are referenced to TaN, Al, and Au barriers on the same devices.

Ta-based metal ϕ_{Bn}'s change with Φ_M for Al_2O_3, but HfO_2 ϕ_{Bn} are relatively constant, likely due to pinning. The asymmetry in the I-V response is qualitatively consistent with the IPE determined ϕ_{Bn}. TaWSi and TaNiSi electrodes showed consistently higher ϕ_{Bn}'s than ZCAN electrodes and comparable performance to TaN. With low roughness and thermal stability approaching 900 °C, TaWSi is a promising electrode for MIM diodes.

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8:20pm **TF-WeE-9 New Insights into the Kinetics of Chemical Vapor Deposition of Two-dimensional hBN Layers on Pd(111)***, **Pedro Arias,*** University of California, Los Angeles*; A Abdulslam,* Colorado School of Mines*; A Ebnonnasir,* University of California, Los Angeles*; C Ciobanu,* Colorado School of Mines*; S Kodambaka,* University of California, Los Angeles

Using in situ variable-temperature scanning tunneling microscopy (VT-STM) and density functional theory (DFT), we investigated the surface structure and growth kinetics of two-dimensional hexagonal boron nitride (hBN) monolayer on Pd(111). STM images of polydomain hBN monolayers, grown via dissociative chemisorption of borazine on Pd(111)/Al_2O_3(0001) thin films, reveal moiré patterns with periodicities between 0.6 nm and 2.8 nm corresponding to four different orientations on Pd(111). We observe tunneling-parameter dependent apparent surface corrugation Δz in the STM images of the hBN domains. Furthermore, for the largest moiré pattern periodicities, we observe a bifurcation behavior in which some domains are nearly flat, and others develop significant hill-and-valley geometric corrugations. We suggest that hBN/Pd can have either mainly geometric or mainly electronic corrugation, depending on the domain orientation.[1] This behavior is unlike any other monolayer hBN-on-metal system.

Using the VT-STM, we investigated the chemical vapor deposition (CVD) kinetics of hBN monolayers on Pd(111). In each experiment, STM images are acquired while exposing Pd(111) to borazine (10^{-7} – 10^{-6} Torr) at temperatures 573 K and 673 K and for times up to 2500 s. The STM images reveal the nucleation and growth of two-dimensional islands on the Pd surfaces. From the images, we measure the areal coverage, island sizes, and island density as a function of time, temperature, and borazine flux. Our STM images reveal an unusual nucleation and growth mode: at lower deposition rate and higher temperature, islands form on terraces; increasing the deposition rate and/or lowering the temperature result in preferential nucleation and growth at the step edges. Interestingly, the attachment of the deposited species is observed on both up and down steps. We attribute this phenomenon to the structure and the highly anisotropic bonding of borazine on Pd(111). Our results provide new insights into the growth dynamics of two-dimensional layered materials.

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8:40pm **TF-WeE-10 Very High Refractive Index Transition Metal Dichalcogenide Photonic Conformal Coatings by Conversion of ALD Metal Oxides***, **Shaul Aloni**, A Schwartzberg, C Chen, C Kastl,* Lawrence Berkeley National Laboratory

Materials for nanophotonic devices ideally combine ease of deposition, very high refractive index, and facile pattern formation through lithographic templating and/or etching. In this work, we present a scalable method for producing high refractive index WS2 layers by chemical conversion of WO3 synthesized via atomic layer deposition (ALD). These conformal nanocrystalline thin films demonstrate a surprisingly high index of refraction (n > 3.9), and structural fidelity compatible with lithographically defined features down to ~10 nm. Although this process yields highly polycrystalline films, the optical constants are in agreement with those reported for single crystal bulk WS2. Subsequently, we demonstrate three photonic structures - first, a two-dimensional hole array made possible by patterning and etching an ALD WO3 thin film before conversion, second, an analogue of the 2D hole array first patterned into fused silica before conformal coating and conversion, and third, a three-dimensional inverse opal photonic crystal made by conformal coating of a self-assembled polystyrene bead template. These results can be trivially extended to other transition metal dichalcogenides, thus opening new opportunities for photonic devices based on high refractive index materials.

Energy Harvesting & Storage
Room Naupaka Salon 6-7 - Session EH-ThM

Batteries

Moderator: Ludvik Martinu, Polytechnique Montréal

8:20am **EH-ThM-2 Real-Time TEM Observation of Electrochemistry and Failure in Battery Materials*, Reza Shahbazian-Yassar,*** University of Illinois at Chicago

Electrodes in rechargeable batteries undergo complex electrochemically-driven phase transformations upon driving Li ions into their structure. Such phase transitions in turn affect the reversibility and stability of the battery. This presentation gives an overview of the PI's research program on in-situ transmission electron microscopy (TEM) of ceramic battery materials. In-situ TEM has been shown to be a very powerful technique in shedding light to some of the mysteries in electrochemical performance of new materials. Various anode materials including SnO$_2$ and MnO$_2$ were subjected to lithiation process and the transport of Li ions was visualized within their atomic structure. For SnO$_2$ nanowires, it was observed that the Li ion transport results in local strain development preferably along (200) or (020) plans and [001] crystallographic directions. The lithiation behavior in the presence of twin boundary defects was completely different compared to pristine state with no twin boundary defect. We showed that twin boundaries in general provide a more accessible pathway for Li ion transport. Anisotropic plastic deformation was also observed along [010] directions of MnO$_2$ nanowires. Sb-based intermetallics which have been proved to be promising anode materials for Li-ion batteries, are also capable of storing of sodium ions. We investigated the microstructural changes and phase evolution of such intermetallic nanowires using in-situ TEM. These alloys also exhibit a new cubic alloying phase that form by intermixing of the ABAB atomic ordering in hexagonal lithiated phase due to Li inclusion in their lattices. Our results indicate that the reaction between these alloys and sodium proceeds through a different pathway during the first compared to the subsequent cycles.

8:40am **EH-ThM-3 Reactive Ion Beam Etching of Piezoelectric ScAlN and LiTaO3 for RF Filter Applications*, Robinson James,*** *Y Pilloux, H Hegde,* Plasma Therm

Etching piezoelectric Scandium Aluminum Nitride (ScAlN) and lithium tantalate (LiTaO3) films with controllable profile angle and very smooth surface is required for next generation Bulk Acoustic Wave (BAW) and Thin Film Surface Acoustic Wave (TF SAW) RF filter applications respectively. First part of the paper reports the facile etching of ScAlN with 15% Scandium concentration by Reactive Ion Beam Etching (RIBE) with very smooth surface of less than 5 nm average roughness and controllable profile angle between 60 to 80 degrees. Recent studies indicate that incorporating high concentration Sc into AlN improves the piezoelectric response of the device by five times and the band width of RF filters also improved. However, etching highly Sc doped ScAlN using traditional RIE and ICP based methods are extremely difficult. Moreover RIE and ICP etching methods exhibit low etch rate and results in rough surfaces when Sc concentration increases more than ~ 8% in ScAlN. Reactive Gas/Ar based RIBE processes were developed with highly controllable profile angle from 60 to 80 degrees, improved etch rate (~ 36 nm/min) and selectivity to photoresist mask (0.7:1), in comparison to conventional IBE. ScAlN selectivity to photoresist was improved significantly when using Reactive Gas/Ar compared to pure Ar based etching. Second part of the paper reports the optimization of LiTaO3 etching with either RIBE or IBE. LiTaO3 etch rate and selectivity were optimized by varying the Reactive gas/ Ar ratio and wafer tilt. LiTaO3 etch rate of ~ 80 nm/min, 1.25: 1 selectivity to PR and a very smooth surface with roughness of ~ 2 nm was achieved. Further improvements in etch rate, selectivity are under investigation. Etching ScAlN and LiTaO3 were characterized using scanning electron microscope (SEM) and white light interferometer (WLI) was used for measuring surface roughness. By varying wafer tilt, Reactive Gas/Ar ratio, beam voltage and current we achieved desired profile angle, etch rate, selectivity and smooth surface. This research has significant importance in fabricating ScAlN based BAW and LiTaO3 based TF SAW RF filters for next generation mobile and wireless applications.

9:00am **EH-ThM-4 Lead-free Epitaxial Ferroelectric Heterostructures for Energy Storage and Harvesting Applications*, Amrit Sharma,*** Center for Materials Research, Norfolk State University

Fast and rapid depletion of natural resources such as fossil fuel and coal is driving researchers to focus continuously on the development of new technologies and exotic materials having high energy density and efficiency for both harvesting and storage of clean and green energy. In United States, nearly 68% of the primary energy produced is wasted as a heat each year. Energy harvesting for low power electronic devices using ferroelectric materials is one of the emerging areas of research because they possess excellent piezoelectric and pyroelectric coefficients. These materials are unique as they only sense time dependent temperature change to generate electric power. Temperature change can be obtained through different ambient sources such as waste-heat, solar radiation etc. We have grown lead free BaZr$_{0.2}$Ti$_{0.8}$O$_3$ (BZT)/ Ba$_{0.7}$Ca$_{0.3}$TiO$_3$ (BCT) multi-layer hetero structures and studied the structural, dielectric, ferroelectric, pyroelectric and energy density characteristics. The BZT/BCT multiplayer epitaxial hetero-structures were grown on La Sr MnO (LSMO) buffered SrTiO (STO) single crystal substrate by optimized pulsed laser deposition technique. The ferroelectric phase transitions have been probed above room temperature with relaxor behavior. These heterostructures show large polarization change and high energy density characteristics due to interface effect even at low applied field and small temperature fluctuation which may be useful for both high energy storage density and thermal harvesting applications.

9:20am **EH-ThM-5 Direct Electrodeposition of High-Performance Li-ion Battery Electrodes*, Paul Braun,*** University of Illinois at Urbana-Champaign, USA **INVITED**

Lithium-ion battery electrodes are nearly universally formed via tape casting of a slurry containing a mixture of active material, binder, and conductive carbon. However, the electrochemical and mechanical properties of slurry cast electrodes are often limited by weak interconnections between particles and between the particles and the substrate. We suggest conformal electrodeposition of high-quality electrode materials would provide opportunities to enhance battery performance (energy density, power density, and flexibility) and broaden the scope of available electrode form factors (size, shape, porosity, and 3D integration). We have now made considerable advances in the direct electrodeposition at modest temperatures of high performance tin-based Li-ion anodes and LiCoO$_2$, NaCoO$_2$, LiMn$_2$O$_4$, and Al-doped LiCoO$_2$-based Li-ion cathodes. The electrolytically active materials were formed either as solid films, or where significant volume changes upon cycling are present, via a templating process, as a 3D mesostructured film. The capacities are near-theoretical, and in the case of the electroplated oxides, the crystallinities and electrochemical capacities of the oxides are comparable to powders synthesized at much higher temperatures (700 ~ 1000°C). The electrodeposition method significantly broadens the scope of battery form factors and functionalities, enabling a variety of highly desirable battery properties including microbatteries, and high energy, high power, and flexible designs.

Plasma Processing
Room Naupaka Salon 5 - Session PS-ThM

Plasma Processing

Moderator: Martin Nieto-Perez, CICATA Queretaro

8:00am **PS-ThM-1 Plasma Surface Modification: Optimizing the Positives of Plasma-Materials Interactions*, Ellen Fisher,*** Colorado State University **INVITED**

Plasma processing represents a powerful approach to modification of a range of substrates utilizing an array of chemistries and morphologies. Unfortunately, plasmas are often given a bad rap with respect to the level of reproducibility achievable as well as the uniformity of any given treatment. Nevertheless, new applications for plasmas continue to be developed and they are employed in a vast array of industries to produce high impact, high value products. One strategy for increasing the robustness of plasma surface modification processes lies in increasing our understanding of the fundamental chemistry of the gas phase chemistry in plasmas, the resulting film chemistry and perhaps most importantly, the gas-surface interface. This talk will focus on recent work in our laboratory that explores not only the impact of the plasma on the surface, but also the effect of the substrate on the plasma chemistry. Data on systems used for plasma assisted catalysis (PAC) and plasma modification of nanostructured sensor materials will be presented. As one example, we have combined a range of spectroscopy techniques, materials characterization tools, and plasma-surface interface studies to reveal that the presence of a catalytic substrate in the plasma system results in significant changes in the plasma chemistry, most notably affecting the internal temperatures (vibrational, rotational) of various plasma species. Changes in plasma composition as well as substrate surface chemistry and morphology were also observed.

Connections between these results and other trends we observe at the plasma-surface interface will be discussed.

8:40am **PS-ThM-3 Super-reactive Haloester Surface Initiator for ARGET ATRP Readily Prepared by RF Glow Discharge Plasma***, **Marvin Mecwan**, B Ratner,* University of Washington

Introduction: Surface initiated activators regenerated by electron transfer atomic transfer radical polymerization or SI ARGET ATRP is a technique that has become a powerful tool for the preparation of functional surfaces and interfaces to match the desired needs of a specific biomedical application. Glow discharge plasma polymerization has historically been used to create uniform thin polymer films that are strongly bond to surfaces. In this research, we explore ARGET ATRP surface initiators that were prepared using a novel, robust and easy synthesis method using plasma polymerization of haloesters, specifically: methyl-3-bromopropionate (M3BP), methyl-2-chloropropionate (M2CP), and ethyl-2-fluoropropionate (E2FP). Once prepared, we used the plasma polymerized haloester surface as a surface initiator for SI ARGET ATRP synthesis of HEMA as proof of concept.

Methods: Cleaned glass discs were Ar etched (40W for 10 min), followed by a CH4 layer (80W for 5 min). The monomer of choice—M3BP, M2CP or E2FP—was introduced into the reactor and plasma deposition was carried out at 150mT pressure; 80W for 1 min (adhesion), 10W for 10 mins (deposition). Plasma-treated samples were washed in methanol and ESCA was used to assess coating composition before and after washing. To grow HEMA brushes on plasma polymerized haloester surfaces, a solution prepared from HEMA, methanol, CuBr2/TPMA, and L-ascorbic acid was pipetted onto the plasma polymerized substrates and allowed to polymerize for 5, 15, 30, 60 and 120mins. ESCA, TofSIMS and ellipsometry were used to analyze the surfaces after ARGET ATRP of HEMA. Clean glass discs were used as negative controls.

Results and Conclusions: RF glow discharge plasma is a robust technique that is able to create a surface coatings that is rich in halogen species and does not delaminates; hence it can be used as a surface initiator for ARGET ATRP. Of all plasma polymerized surface coatings, M3BP showed the highest halogen content and was able to grow HEMA polymer brushes on its surface via ARGET ATRP in as fast as 15 mins. Surprisingly, E2FP, a fluoroester, was also able to grow HEMA polymer brushes despite fluorine being a poor leaving group for ARGET ATRP. The versatility of RF glow discharge plasma offers a clear advantage over other techniques previously used to deposit ARGET ATRP surface initiators.

9:20am **PS-ThM-5 Practical Applications of Plasmas in Microelectronics***, **David Ruzic**, E Barlaz, J Mettler, G Panici, D Qerimi,* University of Illinois at Urbana-Champaign **INVITED**

After presenting a brief overview of the uses of plasmas to make microelectronics, the talk will focus in on metal surface wave plasmas (MSWP). These plasmas have characteristics which make them ideal for many applications. They are microwave driven, and can be launched from a number of antenna or window-like structures. If the plasma density is above cut-off, the waves are completely absorbed in the plasma sheath, spreading out along the surfaces adjacent to the launcher. In this way, a plasma can be made which hugs surfaces. This is ideal for processing of that surface. For instance, when trying to etch Sn from an EUV mirror, making a H plasma right along the mirror surface creates the active radicals which do the etching directly where they are needed.

There is a second advantage of MSWP for processing. While the first couple of mm near the surface are immersed in a higher temperature (4 eV) and density (1e12 cm^{-3}) plasma, the region many cm above the surface contains a cold (1 eV) plasma which is still fairly dense (1e11 cm^{-3}). The two distinct plasma regions created by the same source can be quite useful. If one wants to “crack’ the gas used for atomic-layer processing, pass it through the surface and the dense plasma. If the desire is to not break up the molecules, inject it down stream. The advantages of having a plasma in contact with the substrate are retained in both cases. This talk will show examples of using such plasmas for both etching and deposition.

10:20am **PS-ThM-8 From Atomic- to macro- via Nano-scales: Plasma and Ion Effects in Surface *Structuring*, *Kostya (Ken) Ostrikov*,** Queensland University of Technology, Australia **INVITED**

This presentation critically examines the effects of ions and plasmas on the formation of thin films, microscopic and nanoscale structures on the surface. Nanoscale localization of energy and matter plays a critical role in the mechanisms of ion/plasma-surface interactions that lead to the surface structuring. Examples of localization of energy and matter and plasma-specific effects in nanoscales creates specific and unique conditions not common at larger scales. Importantly, the effects of interactions of ions and other species at atomic scales (e.g., atomic bond scission, vacancy or defect creation or elimination) are intimately related to self-organization and texturing of the surface features and nanostructures at nanoscale and microscopic scales. One typical example is the formation of self-organized arrays of nanostructures on plasma exposed surfaces. Specific driving forces that lead to the creation of the textures and structures owe to the unique features of the plasma environment, prominently related to charges, electric fields, as well as mobility and reactivity of plasma-generated species. Another example is the possibility to manipulate atomic bonds in nanoporous materials to control nanopore sizes and modify the plasticity of solid materials. In particular, anodized aluminium oxide (AAO) which is normally brittle under normal conditions, can become superplastic subjected to irradiation by energetic ion beams. Examples are provided where interactions at the plasma interface lead to interesting synergistic effects. These interactions lead to several applications in nanoscale synthesis, fabrication and processing, catalytic gas conversion and biomass reforming, new sustainable industrial processes based on green chemistry. Selected examples are related to plasma-catalysis, sustainable, green-chemistry based nanomaterials and chemical processing, as well as exotic high-energy-density physical effects during nano-plasma generation using intense radiation.

11:00am **PS-ThM-10 Atmospheric Plasma Synthesis of Nanoparticulates at Low Temperature and Roll-to-Roll Binder-Free Coating on Polyethylene Separator for Lithium Ion Battery with Improved Performances***, **Jing Zhang**,* Donghua University, China

The roll-to-roll atmospheric pressure plasma synthesis and coating of nanoparticulates at low temperature is the most prominent green technique to fabricate thin film on polymer substrates. It can provide a unique environment for chemical reactions and film growth, which is distinct from the ordinary condensed chemical reaction driven by single hot source. All the reactions are far from chemical equilibrium and take place at low gas temperature. Its vital role have been more and more recongnized in flexible fiber optoelectronic/electronic devices, intelligent wearable technology, lightweight fiber compositese and organic/inorganic functional composite membrane etc..

In the present study, different kinds of non-thermal reactive plasmas of HMDSO/Ar/O2 and TiCl4/Ar/O2 have applied to obtain stable discharge at atmospheric pressure and low temperature. The gas phase dissociation and nucleation process, combination of discharge modes, plasma parameter influences on the TiO2 and SiOxCyHz films have been investigated by optical emission spectrum(OES), field scanning electron microscope (FESEM), X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) etc.. Polyethylene (PE) separator for lithium-ion batteries has been tested to move through a home-made roll to roll plasma reactor and a thin film composed of well limited nanoparticulates (average size is around 100 nm) is directly deposited on its top and internal fiber surface. The nanoparticulates are tightly bound on porous PE separator top and inner surface without any other organic binders. The coated PE separator exhibits improved thermal stability, wettability to electrolyte and electrolyte uptake. LiFePO4 cells assembled with the coated PE separator display better conductivity and cycling performance. To the best of our knowledge, this is the first report on atmospheric plasma roll to roll coating of nanoparticulate film on polyolefin separators for LIBs compatible with its present online manufacture process.

11:20am **PS-ThM-11 Thermo-Corrosive and Mechanical Properties of ZrO_2 based Thermal Barrier Coatings***, **Byung-Koog Jang**,* Kyushu University*; H Kim,* Korea Institute of Ceramic Engineering and Technology

Thermal barrier coatings (TBCs) have received a large attention because they increase the thermal efficiency of gas turbine engines by increasing the gas turbine inlet temperature and reducing the amount of cooling air required for the hot section components. Electron beam-physical vapor deposition (EB-PVD) or plasma spray coatings is a widely used technique for depositing thermal barrier coatings (TBCs) on metal substrates for high temperature applications, such as gas turbines, in order to improve the thermal efficiency. High temperature capability of TBCs used in a gas turbine is often degraded by deposits of calcium-magnesium-alumino-silicate (CMAS). The CMAS melts are produced when siliceous minerals (volcanic ash, dust and sand) are ingested with the intake air and deposited on the hot surface of TBCs.

This work describes the thermal conductivity and corrosive properties of 2~8mol%Y_2O_3-stabilized ZrO_2 (YSZ) coatings by EB-PVD and plasma sprayed coatings. The hot corrosion between YSZ coatings and volcanic ash was examined by isothermal heating at 1200°C in air between 10 min and 100hrs. The thickness of corrosive region at top surface of TBCs by the reaction between YSZ coating and volcanic ash was increased with increasing the oxidation time. In addition, the mechanical properties of YSZ TBCs were evaluated by nano indentation.

Thin Films
Room Naupaka Salons 4 - Session TF-ThM
Nanostructured Surfaces and Thin Films: Synthesis and Characterization III

8:00am **TF-ThM-1 Interface and Surface Control of MoS2-based Nanoelectronic Devices with Organic Treatment***, **Takhee Lee,*** Seoul National University, Republic of Korea

Transition metal dichalcogenide (TMD) two-dimensional (2D) atomic layered materials have recently drawn considerable attention as promising semiconductors for future ultrathin layered nanoelectronic device applications. Unlike graphene, TMD materials have a semiconductor band gap, for example, molybdenum disulfide (MoS_2) that has been widely studied is known to have a direct band gap of ~1.9 eV as a single MoS_2 layer and an indirect band gap of ~1.2 eV as a bulk MoS_2 crystal.

In this talk, I will present our group research works on MoS_2-based nanoelectronic devices. In particular, I explain the following topics on the electrical properties of MoS_2 FETs; the effect by the environments such as oxygen and water [1], gate bias stress-dependent device instability [2], interface control by high energetic proton beam irradiation [3], surface treatment by molecules for sulfur vacancy passivation of MoS_2 [4], and hybrid devices of organic materials and MoS_2 [5].

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[4] K. Cho et al., ACS Nano, 9, 8044 (2015); K. Cho et al. Adv. Mater. 30, 1705540 (2018).

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8:40am **TF-ThM-3 Epitaxial $GdFe_{0.8}Ni_{0.2}O_3$ Multiferroic Thin Films Grown Device Using Operando X-ray Technique***, **Shu-Jui Chang**, M Chung,* National Chiao Tung University, Republic of China*; Y Liu, H Lee,* National Synchrotron Radiation Research Center*; Y Tseng,* National Chiao Tung University, Republic of China

Complex oxides have been extensively investigated due to complicated structural and electronic orbitals. The physical properties of these oxides may vary with growth mechanism. Among all the growing methods, radio frequency (RF) sputtering possesses advantages of good stoichiometry, great reproducibility and less pricy. This work demonstrates the fabrication of epitaxial $GdFe_{0.8}Ni_{0.2}O_3$ thin Film (abbreviated as GFNO) by RF sputtering, analysis of fundamental physical properties and the application in the research in ferromagnetic and multiferroic layer heterostructure interface with in-situ spectroscopy technique. The epitaxial nature properties of thin film were examined by synchrotron radiation high resolution X-ray scattering at NSRRC. In addition to structure, the analysis on ferroelectricity (polarization and leakage), magnetism, electronic configuration and valence state have been also conducted with the result of room-temperature ferroelectricity and ferrimagnetism of GFNO thin film. Using in-situ XAS, XMCD and MOKE analysis have been conducted to investigate the effect of the electric field on the Co and GFNO interface. The native cobalt oxide in the interface has been found to transfer into metallic state due to the enhancement in the intensity of XAS absorption peak. Meanwhile, the intensity of XMCD also increases, indicating that the spin moment has also increases. In MOKE analysis, the coercivity of cobalt declines with rising applied electric filed which comes from the increase in metallic state cobalt. This work was financially supported by the “Center for the Semiconductor Technology Research” from The Featured Areas Research Center Program within the framework of the Higher Education Sprout Project by the Ministry of Education (MOE) in Taiwan. Also supported in part by the Ministry of Science and Technology, Taiwan, under Grant MOST-107-3017-F-009-002.

9:00am **TF-ThM-4 Effect of the Ultrasonic Treatment on the Si-SiO_2 System Defects Structure***, **Daniel Kropman,*** Tallinn University, Estonia*; V Seeman,* Tartu University, Estonia*; A Medvids,* Riga Technical University, Latvia*; P Onufrievs,* Riga Technicacal University, Latvia

The effect of ultrasonic treatment (UST) on the defect structure of the Si–SiO_2 system by means of electron spin resonance(ESR),selective etching, MOS capacitance technique and secondary ions mass-spectroscopy is presented. The non-monotonous dependence of the defect densities on the US wave intensity has been observed. The influence of the UST frequency on the ESR signal intensity of the defect centres depended on the defects type and may be caused by vibration energy dissipation, which are a function of defect centres type. In the ESR spectra of Si samples a signal with g=1.9996 (Pa centres) connected with vacancy complexes is observed. After UST appears another signal with g=2.0055 (broken bonds of Si atoms). The influence of the US frequency and sample orientation on the ESR signal intensity varies for different centres. The frequency and orientation dependence of the ESR signal with g=l.9996 and the lack of this dependence for the centres with g=2.0055 show that vibration energy dissipation depends on the type of defect centers. Defect density at the interface grows with an increase of US wave intencity or changes nonmonotonously depending on the oxide thickness and crystallographic orientation. In the samples with thick oxide/0,6 mkm there is a maximum in the dependence of the charge carriers lifetime on the US wave amplitude and in the samples with thin oxides /0,3 mkm/ there is a minimum. This shows that the structural defects form electrically active centres and their density can be varied by US. The density of point defects and absorbed impurities at the Si–SiO_2 interface can be reduced and its electrical parameters improved by an appropriate choice of the UST and oxidation condition. US is widely used not only for materials treatment but in medicine as well (cancer treatment).

References:

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9:40am **TF-ThM-6 Charge Induced Disorder Controls the Thermal Conductivity of Entropy Stabilized Oxides***, **Jeffrey Braun**, C Rost,* University of Virginia*; M Lim,* North Carolina State University*; A Giri, D Olson,* University of Virginia*; G Kotsonis,* Pennsylvania State University*; G Stan,* National Institute of Standards and Technology*; D Brenner,* North Carolina State University*; J Maria,* Pennsylvania State University*; P Hopkins,* University of Virginia

Manipulating a crystalline material's configurational entropy though the introduction of unique atomic species can produce novel materials with desirable mechanical and electrical properties. From a thermal transport perspective, large differences between elemental properties such as mass and interatomic force can reduce the rate at which phonons carry heat and thus reduce the thermal conductivity. Recent advances in materials synthesis have enabled the fabrication of entropy-stabilized ceramics, opening the door for understanding the implications of extreme disorder on thermal transport. Measuring the structural, mechanical, and thermal properties of single-crystal entropy stabilized oxides, we show that local ionic charge disorder can effectively reduce thermal conductivity without compromising mechanical stiffness. These materials demonstrate similar thermal conductivities to their amorphous counterparts, in agreement with the theoretical minimum limit, resulting in this class of material possessing the highest ratio of elastic modulus to thermal conductivity of any isotropic crystal.

10:20am **TF-ThM-8 Thermal Boundary Conductance Across Heteroepitaxial ZnO/GaN Interfaces: Experimental Assessment of the Phonon Gas Model**, ***John Gaskins,*** University of Virginia*; G Kotsonis,* Pennsylvania State University*; A Giri,* University of Virginia*; S Ju,* University of Tokyo, Japan*; A Rohskopf,* Massachusetts Institute of Technology*; Y Wang, T Bai,* University of California, Los Angeles*; E Sachet, C Shelton,* North Carolina State University*; Z Liu,* University of Notre Dame*; Z Cheng,* Georgia Institute of Technology*; B Foley,* Pennsylvania State University*; S Graham,* Georgia Institute of Technology*; T Luo,* University of Notre Dame*; A Henry,* Massachusetts Institute of Technology*; M Goorsky,* University of California, Los Angeles*; J Shiomi,* University of Tokyo, Japan*; J Maria,* Pennsylvania State University*; P Hopkins,* University of Virginia

We present experimental measurements of the thermal boundary conductance (TBC) from 77 − 500 K across isolated heteroepitaxially grown ZnO films on GaN substrates. This data provides an assessment of the underlying assumptions driving phonon gas based models, such as the diffuse mismatch model (DMM), and atomistic Green's function (AGF) formalisms used to predict TBC. Our measurements, when compared to previous experimental data, suggest that TBC can be influenced by long wavelength, zone center modes in a material on one side of the interface as opposed to the "vibrational mismatch" concept assumed in the DMM; this disagreement is pronounced at high temperatures. At room temperature, we measure the ZnO/GaN TBC as 490[+150, −110] MW m^{-2} K^{-1}. The disagreement among the DMM and A GF, and the experimental data at these elevated temperatures, suggests a non-negligible contribution from other types of modes that are not accounted for in the fundamental assumptions of these harmonic based formalisms, which may rely on anharmonicity . Given the high quality of these ZnO/GaN interfaces, these results provide an invaluable, critical, and quantitative assessment of the accuracy of assumptions in the current state of the art computational approaches used to predict phonon TBC across interfaces.

10:40am **TF-ThM-9 Studies on Hot-wall Deposited Cadmium Sulphide (CdS) Thin Films for Buffer Layers in Thin Film Solar Cell**, ***Balaji Gururajan,*** *B Rangasamy, P Sankaran, P Nagarajan, S Kaliappan, K Dhonan,* PSG College of Technology, India*; V Asokan,* Chalmers University of Technology, Sweden*; M Natarajan,* Coimbatore Institute of Technology, India*; D Velauthapillai,* Western Norway University of Applied Sciences, Norway

Cadmium Sulphide (CdS) thin films were deposited onto well-cleaned soda lime glass substrates using hot wall deposition technique at room temperature. The structure of the as-deposited CdS thin films was found to be hexagonal and oriented along <0 0 2> direction. The CdS films were then annealed to 300 ^{o}C and crystallinity of the films was found to improve with the presence of additional diffraction peaks along <0 0 2>, <1 0 1>, <1 0 2>, <1 1 2> directions. Raman Spectroscopy of the annealed films confirmed the hexagonal structure with a shift observed at 312 cm^{-1}. Selected area electron diffraction (SAED) pattern acquired from transmission electron microscopy analysis substantiated the hexagonal phase formation. X-ray photoelectron spectroscopy (XPS) confirmed the stochiometric nature of CdS thin films with Cd:S atomic ratio of 1. Field emission scanning electron microscopy (FESEM) images revealed smooth morphology of the CdS films with distinctive grains. Atomic force microscopy (AFM) results indicated a surface roughness of 4.47 nm. Transmission spectra of the films were studied and the transparency was found to be above 80%. The optical band gap was found to be around 2.4 eV in accordance with the reported values. The results obtained clearly show that device quality CdS buffer layers can be effectively deposited using Hot-wall deposition.

11:00am **TF-ThM-10 Intrinsec Photoluminiscent Properties of Crystalline and Amorphous $Cd_2V_2O_7$**, ***Erika Cervantes Juárez****, R Lozada Morales, A Meza Rocha, R Licona Ibarra,* BUAP, Mexico

$Cd_2V_2O_7$ compounds in crystalline and amorphous phases were fabricated by the melt-quenching process. Characterizations such as X-ray diffraction, Raman spectroscopy and photoluminescence were performed. X-ray diffraction patterns of the crystalline sample showed peaks associated with a pure $Cd_2V_2O_7$ monoclinic structure, in agreement with the Raman vibrational spectrum. In the case of the amorphous sample, X-ray diffraction patterns only exhibited a broad band, typical of a glassy structure, whereas its Raman spectrum displayed two broad vibrational modes centered at 350 and 850 cm^{-1}, attributed to stretching vibrations of VO_3 groups. In spite of the structural differences, both samples presented similar photoluminescence features, consisting of a wide band in the 375–525 nm range with two peaks at 411 and 432 nm, associated respectively with the $^3T2 \rightarrow {}^1A1$ and $^3T1 \rightarrow {}^1A1$ electronic transitions in the VO_4 tetrahedron, under 340 nm excitation. Thus, blue light emission with CIE1931 chromaticity coordinates x~ 0.200 and y~ 0.145, and color purity of 62–63%, is achieved from the crystalline and amorphous Cd2V2O7 compounds. The emission decay time profiles were well fitted to a bi-exponential function from which the calculated average lifetime values resulted to be 112 ± 13 and 99 ± 4 ns for the crystalline and amorphous $Cd_2V_2O_7$ samples, respectively. Theoretical calculations based on the density of electronic states revealed that the photoluminescence arises through charge transference processes from *3d* orbitals of four-fold coordinated vanadiums to *2p* orbitals of three-fold coordinated oxygens in the VO_4 tetrahedron, being the basic unit of $Cd_2V_2O_7$ in crystalline and amorphous phases.

11:20am **TF-ThM-11 The Effect of Tin Impurities on CdTe Thin Films Solar Cell**, *J Ríos-González,* CINVESTAV-Unidad Mérida, Mexico*; R Mis-Fernández, I Rimmaudo, E Camacho-Espinosa,* ***Juan Luis Peña,*** CINVESTAV-Unidad Mérida, Mexico, México

The doping of CdTe has been investigated with different materials such as Sb, As, Mg, Se, Bi. Sn-doped CdTe is a promising intermediate band photovoltaic material, therefore the optoelectronic and structural properties have been investigated in this work. Tin was co-sublimated with CdTe films by close-spaced sublimation (CSS) process in Ar environment to avoid Sn oxidation. CdTe:Sn was deposited on a superstrate structure, glass/ITO/ZnO/CdS, and Cu/Mo bi-layer was used as back contact. The amount of tin doping was kept constant. Well shaped and uniform grains were found by Field Emission Scanning Electron Microscopy (FE-SEM) analysis (about ~ 3 µm). Also it was observed a morphological changes between as-deposited CdTe and Sn-doping CdTe. Energy Dispersive X-ray Spectroscopy (EDS) and X-ray Photoelectron Spectroscopy (XPS) showed presence of tin in the CdTe films. Xrays Diffraction (XRD) revealed peaks corresponding to the SnTe compound, as well as CdTe peaks strongly orientated along the (220) and (311) directions. The CdTe:Sn and as-deposited films showed a band gap of 1.49 eV. The measured efficiency of CdTe:Sn solar cell was 5.4%.

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