

Thin Films

Room Makai - Session TF-MoM

Advances/Innovation in Synthesis & Characterization

Moderator: Franz Himpsel, University of Wisconsin Madison, USA

8:00am **TF-MoM1 ToF-SIMS Depth Profiling of Full Organic/inorganic Hybrid Devices with Low-Energy Cesium Ions**, *Céline Noël*, University of Namur, Belgium; *L. El Fissi, L.A. Francis*, Université Catholique de Louvain; *L. Houssiau*, University of Namur, Belgium

In the last few years, growing attention has been brought to devices based on hybrid (organic/inorganic) multilayered materials as they allow for highly versatile properties, such as tunable optical and electronic features, malleability, transparency and cost-efficiency that could find applications in a large variety of devices such as OPVs, OLEDs, sensors, microfluidics, fuel cells, etc. . Forthcoming technological advances will require detailed knowledge of layers and interfaces composition and morphology in order to optimize device efficiency, stability, processing conditions.

ToF-SIMS is a well-suited technique to obtain key information such as the in-depth molecular composition of each layer and diffusion at the interfaces. However, for hybrid materials, depth profiling remains challenging as ion sources which are efficient on organic materials are generally not efficient on inorganic ones. Numerous dynamic-SIMS studies of interfacial migration between organic/inorganic layers have been reported, but no molecular signal could be monitored. Recently, low-energy (500 eV) Cs⁺ ions were shown to possibly offer a reliable solution for depth-profiling hybrid systems [1]. Using this novel approach, the present work presents molecular depth-profiling on complex OLEDs interfaced materials showing that each layer, until the substrate, could be successfully identified by its specific molecular signal within a reasonable sputtering time.

In parallel, oxide/polymer hybrid materials were investigated with future applications in microfluidics, BioMEMS and lab-on-chip devices. Samples consisted of TiO₂ or Al₂O₃ coating on three different polymers, namely cyclic olefin copolymer (COC), polyimide (PI) and SU-8 (a negative photoresist). Again, all samples were easily depth profiled by low-energy Cs⁺, with characteristic molecular fragments monitored on each polymer even after the oxide layer is sputtered. This again proves that low-energy Cs⁺ is an efficient solution to depth profile hybrid materials. We also compared metal diffusion in different oxides coating and polymers. Issues like homogeneity, contamination or non-stoichiometry near the interface could be addressed by ToF-SIMS analyses; matrix effects and ion beam induced modifications were discussed based on complementary XPS measurements.

With the development of new technologies, an increasing number of applications are expected to require in-depth molecular information of organic/inorganic materials. The present work shows how ToF-SIMS can answer this demand, opening the way for the characterization of such novel applied materials.

[1] C. Noël and L. Houssiau, *J Am Soc Mass Spectrom*, 2016. 27(5): p. 908-16.

8:20am **TF-MoM2 Amplitude Contrast High Resolution Electron Microscopy of A-site Associated Oxygen Octahedral Rotations in Artificial Perovskite Superlattices**, *Dean Miller, J.G. Wen*, Argonne National Laboratory, USA; *X. Wu*, Temple University, USA

Artificially structured perovskite superlattices offer rich opportunities for novel ferroelectricity. We have developed a new high-resolution TEM imaging technique that allows the direct observation of A-site associated oxygen octahedral rotations in perovskite oxide superlattices that reveals the underlying mechanisms of enhance ferroelectricity in complex heterostructures. By combining the amplitude-contrast high-resolution electron microscopy and DFT calculations, we show that a highly polar CaTiO₃ phase with a BiFeO₃-like structure can be stabilized in (CaTiO₃)_n/(BaTiO₃)_n superlattice. Amplitude contrast imaging (ACI) relies on both spherical and chromatic aberration correction for TEM imaging. Under ACI conditions, atomic resolution channeling contrast can be realized, allowing one to obtain directly interpretable high-resolution electron microscopic images with discrimination between light and heavy atomic columns. Using this imaging approach, we were able to image the atomic structure in a BaTiO₃/CaTiO₃ superlattice with high spatial accuracy and discrimination between Ba and Ca columns, providing direct visualization of

the Ca and Ba associated oxygen octahedral rotations. Combined with the first-principles calculations, we found that a highly polar metastable "interface phase" of CaTiO₃ with a structure of BiFeO₃ is stabilized by the mechanical and electrical boundary conditions of the BaTiO₃/CaTiO₃ superlattice. Under this new mechanism, a large number of perovskites with the CaTiO₃ type structure will become good candidates for novel highly-polar multiferroic materials.

8:40am **TF-MoM3 Controlled Growth of Transition-Metal Nitride Alloy Films via Hybrid HIPIMS/Magnetron Co-Sputtering using Synchronized Metal-Ion Irradiation**, *Grzegorz Greczynski, J. Lu, O. Tengstrand*, Linköping University, Sweden; *I. Petrov, J.E. Greene*, Linköping University, Sweden, University of Illinois at Urbana-Champaign; *W. Kölker, S. Bolz, C. Schiffers, O. Lemmer*, CemeCon AG, Germany; *L. Hultman*, Linköping University, Sweden

INVITED

Growth of thin films by physical vapor deposition (PVD) typically requires elevated substrate temperatures and/or ion irradiation to ensure high adatom mobilities necessary for film densification. However, obtaining densification via high incident gas-ion energies extracts a steep price in the form of residual ion-induced compressive stress resulting from both recoil implantation of surface atoms and trapping of rare-gas ions in the lattice. Our solution for these issues employs high-power pulsed magnetron sputtering (HIPIMS) owing to the high ionization degree of sputter-ejected metal atoms, and the time separation of metal- and gas-ion fluxes incident at the substrate. The former implies that ion fluxes originating from elemental targets operated in HIPIMS are distinctly different from those obtained during dc magnetron sputtering (DCMS). The latter feature allows us to suppress the role of gas-ion irradiation, by synchronizing the pulsed substrate bias with the metal-rich-plasma portion of the HIPIMS pulse.¹

We carry out experiments in a hybrid configuration with one target powered by HIPIMS and the other operated in DCMS mode (HIPIMS/DCMS).^{2,3} This allows us to probe the roles of intense metal-ion fluxes from HIPIMS-powered targets on film growth kinetics, microstructure, and physical properties over a wide range of transition metal nitride M₁M₂N alloy compositions. Model materials systems include TiAlN, TiSiN, TiTa_nN, and TiAlTa_nN. In a series of extensive experiments, we established that the essential factors determining film growth pathways include (i) the average metal-ion momentum transfer per deposited atom, (ii) metal-ion charge state, and (iii) mass of metal ion assisting the growth.⁴

Based on the above results, a new PVD approach is proposed which relies on the hybrid concept to grow dense, hard, and stress-free thin films with no external heating.⁵ TiTa_nN and TiAlTa_nN film densification is achieved by pulsed synchronized bombardment with Ta⁺/Ta²⁺ metal ions which are film constituents; this, in turn, minimizes film stress. The preliminary results are very promising. For example, with as little as 8 mol% of TaN, fully-dense TiTa_nN alloys with high hardness and low residual stress can be obtained at temperatures T_s < 150 °C (due to plasma heating). This novel approach expands the PVD process envelope to allow the use of temperature-sensitive substrates, including plastics.

[1] G. Greczynski, J. Lu, J. Jensen, I. Petrov, J.E. Greene, S. Bolz, W. Kölker, Ch. Schiffers, O. Lemmer and L. Hultman, *JVSTA* 30 (2012) 061504-1

[2] G. Greczynski, J. Lu, M. Johansson, J. Jensen, I. Petrov, J.E. Greene, and L. Hultman, *Surf. Coat. Technol.* 206 (2012) 4202.

[3] G. Greczynski, J. Lu, M. Johansson, J. Jensen, I. Petrov, J.E. Greene, and L. Hultman, *Vacuum* 86 (2012) 1036

[4] G. Greczynski, J. Lu, J. Jensen, I. Petrov, J.E. Greene, S. Bolz, W. Kölker, Ch. Schiffers, O. Lemmer and L. Hultman, *Thin Solid Films*, 556 (2014) 87

[5] G. Greczynski, J. Lu, I. Petrov, J.E. Greene, S. Bolz, W. Kölker, Ch. Schiffers, O. Lemmer and L. Hultman, *JVSTA* 32 (2014) 041515

9:20am **TF-MoM5 Evaluation of Perturbation Induced by Ionic Clusters Bombardment: XPS and Electrochemical Coupled Approach**, *Arnaud Etcheberry*, Paris Saclay University, France

Evaluation of perturbation induced by ionic clusters bombardment: XPS and Electrochemical coupled approach.

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The XPS profiling is a key technique to provide quantitative compositional profiles of ultra thin and thin films. XPS profiling needs ion guns etching which can induce perturbations of the XPS probed films. It is particularly

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true when fragile films are submitted to the etching procedure as for example organic films, oxide etc. Rational evaluation of the exact nature of the perturbation is an very important question which needs accurate approach to compare different etching procedure and to propose calibrated etching strategy. In this paper we treat the evaluation of perturbation induced by ionic argon cluster gun which is a very interesting method to provide very different conditions to perform XPS profiling as soon as possible close to the actual compositional profile. To perform that we use as supporting material InP a well known semiconductor for which problem of preferential etching is well documented. We chose to combine on same samples (n,p & undoped) XPS, UPS and electrochemical characterizations to evaluate the impact of a ionic or ionic cluster bombardment on the responses of the surface. We show that modifying the size of the cluster, the energy, the angle we induced very important modulation of the perturbations. The interesting feature of our proposal is that XPS modification: position of Peak Energy, valence band, fwhm, atomic ratio are related to the electric ones: capacitive response, I-V toward electrochemical processes, anodic dissolution. This coupling approach gives rise to a set of experimental data which are used as calibration information to provide adapted perturbation by an ion cluster bombardment. Moreover electrochemical diode has the advantage to be easily broken so it is compatible with XPS, Electrochemistry sequences which allows very fast experimental cycles. For example perturbation induced by ionic bombardment can be eliminated by dissolution of the semiconductor induced by chemical etching or by anodic oxidation. Both provide quantitative evaluation of the depth of the perturbed zone before a complete recovering of the initial XPS or electrochemical responses. We propose in this paper to detail several facets of this interfacial chemistry study

9:40am **TF-MoM6 TOF-SIMS Parallel Imaging MS/MS - Making Data Interpretation Easier**, *John Newman, S.R. Bryan, G.L. Fisher, P.E. Larson, J.S. Hammond*, Physical Electronics, USA; *R.M.A. Heeren*, Maastricht University; *S. Iida, H. Chang, T. Miyayama*, Ulvac-PHI

Over the last quarter century Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) has been successfully used to characterize the molecular composition of the outermost layers of solid surfaces. However, even with mass resolutions greater than 15,000 $m/\Delta m$ and mass accuracies better than 10 ppm, making definitive chemical assignments of higher mass peaks above $\sim 200 m/z$ has continued to be a challenge. This problem has become even more pronounced with the advent of cluster beams (e.g. Au₃, Bi₃, C₆₀ and Ar gas cluster) which provide substantially improved yields for higher mass fragment ions. To overcome this shortcoming, Physical Electronics has developed a revolutionary TOF-SIMS tandem mass spec method specifically designed to unambiguously identify the composition of higher mass secondary ions [1]. The method allows for MS/MS spectra (MS²) of select secondary ions of interest (precursor ions) to be acquired in parallel with conventional TOF-SIMS spectra (MS¹); both being simultaneously generated from the same analytical volume. The precursor ion, defined by a 1 Da selection window, is deflected from the MS¹ secondary ion stream into an argon filled high energy (1.5 keV) collision-induced-dissociation (CID) cell. In the CID cell, the precursor ions collide with argon atoms which results in partial fragmentation of the precursor ions. The precursor and its fragment ions are then accelerated into a linear TOF analyzer and recorded by a pulse-counting detector. In both the MS¹ and MS² data, a full mass spectrum is collected for each image pixel, with spatial resolutions in the tenths of a micrometer. As the MS² spectra are predominantly generated from single molecular ions, they are much cleaner and simpler than conventional MS¹ spectra which usually contain secondary ions from multiple chemical species. The MS/MS fragmentation spectrum (MS²) is used to identify the composition of the precursor ion by either identification of the fragmented ions and/or comparison to spectra contained in on-line databases. Applications of this new method will be shown for a variety of materials including polymers, pharmaceuticals, tissue cross sections, and other organics.

References

[1] P.E. Larson, J.S. Hammond, R.M.A. Heeren and G.L. Fisher, Method and Apparatus to Provide Parallel Acquisition of MS/MS Data, U.S. Patent 20150090874, April 2015

10:20am **TF-MoM8 Atomic Layer Deposition of Thin VO₂ Films to Enable Smart, Functional Coatings**, *Virginia Wheeler, B.P. Downey, M. Currie, M. Tadjer, A. Kozen*, US Naval Research Laboratory, USA; *R. Bell, M. Thompson*, Cornell University, USA; *D.J. Meyer, F.J. Kub, C. Eddy Jr.*, US Naval Research Laboratory, USA

VO₂ is a phase change material that exhibits significant changes in thermal emittance, optical transmittance and reflectance, and intrinsic electrical properties due to a metal-insulator phase transition (MIT) at a critical temperature (T_c). Electrical and optical properties across the MIT are strongly reliant on microstructural characteristics which are dependent on deposition technique. While several different methods have been explored to deposit VO₂ films, atomic layer deposition (ALD) provides a way to obtain large area film uniformity, abrupt interfaces and angstrom-scale control of thickness conformally across planar and high surface area nanostructures. Thus, this method could be used to integrate VO₂ films into complex electronic and optical devices for additional functionality. Moreover, as-deposited films are amorphous which can be subsequently annealed to tailor the crystallinity and thus the MIT properties. Here, we will show the properties of amorphous and crystalline ALD VO₂ films and discuss their integration with other materials to achieve functional optical and electrical coatings.

Amorphous ALD VO₂ films were deposited at 150°C using TEMAV and ozone precursors. XPS revealed that beneath ~ 1 nm of atmospheric contamination, there was no residual carbon impurities and only a single VO₂ peak was evident. Electrical measurements showed an exponential change in resistance of ten orders of magnitude from 77-500K, though no characteristic sharp transition was detected. This resulted in an average activation energy of -0.20eV and temperature coefficient of resistance of 2.39% at 310K.

To realize sharp MIT transitions, ALD VO₂ films were crystallized with an optimized ex-situ anneal at 650°C in 1.5x10⁻⁵ Torr of oxygen for 1-4hrs depending on film thickness. Electrical measurements showed that the R_{off}/R_{on} ratio increased from 3.4 to 7083 as VO₂ thickness increased from 12 to 92nm. The T_c also increased with increasing thickness, while all films exhibited relatively low hysteresis (<8°C). Temperature dependent near-IR measurements also show an increase in the change in reflectivity (up to 80%) and decrease in transmission (up to 60%) with film thickness.

ALD is a preferred method to deposit on soft materials due to its low deposition temperature. However, for VO₂ films, this benefit is negated by the higher anneal temperatures required for crystallization. To overcome this problem, laser annealing was investigated as an alternative crystallization approach. Initial results show that by varying the laser power one can tailor the local temperature within the VO₂ film to attain the required crystallinity without affecting the underlying substrate.

11:00am **TF-MoM10 PACSURF 2016 PLENARY LECTURE: Detecting the Invisible with Electron Beams: The Hidden Secrets of Nanocrystals, Interfaces and Surfaces at Atomic Resolution**, *Christian Kisielowski*, Lawrence Berkeley National Laboratory

INVITED

As heterogeneous materials scale below 10 nm, a suitable combination of single digit nanocrystals with their rich variety of tunable surfaces and interfaces allows tailoring unprecedented materials with novel structure-function relationships. The design of new catalysts [1] or investigations of polymers at atomic resolution [2] may serve as examples. This contribution describes research that aims at exploiting the emerging ability to analyze and understand such materials by directly determining their atom arrangement in three-dimensions using aberration-corrected transmission electron microscopy [3]. Attempts to unravel the atomic structure of such nanoscale composites in this manner must explicitly address their pronounced sensitivity to the probing radiation that can unintentionally alter their pristine structure, often beyond recognition. We address this challenge by applying low dose-rate in-line holography [4], which allows operating electron microscopes with dose rates as low as 5-10 e/Å²s that help maintaining structural integrity at atomic resolution to an unexplored end. The approach mimics best practices in biological research but achieves atomic resolution with single atom sensitivity by the acquisition of large image series. In essence, the method captures series of entirely noise dominated single images that are reconstructed to obtain electron exit wave functions of the radiation sensitive matter with unprecedented contrast and resolution. We observe a variety of previously unknown atom configurations in surface proximity of CoOx nanocrystals and coatings that are hidden behind unusually broadened diffraction patterns but become visible in real space images because the phase problem is solved. The observed structures are drastically altered by an exposure of the material

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to water vapor or other gases, which is investigated at atomic resolution in environmental electron microscopy. It is shown for Rh/W catalysts that electron beam-induced atom dynamics can be entirely suppressed even for atom clusters made from less than 10 atoms. Resultantly, chemical compositions can be determined by contrast measurements alone and functional processes can be triggered and tracked in real time at atomic resolution.

[1] J. A. Haber et al., Multiphase Nanostructure of a Quinary Metal Oxide Electrocatalyst Reveals a New Direction for OER Electrocatalyst Design, *Advanced Energy Materials* 5 (2015) 1402307

[2] D. Lolla et al., Polyvinylidene fluoride molecules in nanofibers, imaged at atomic scale by aberration corrected electron microscopy, *Nanoscale* 8 (2016) 120 - 128

[3] F.R. Chen et al., In-line three-dimensional holography of nanocrystalline objects at atomic resolution, *Nature Commun.* 7:10603 doi: 10.1038/ncomms10603 (2016)

[4] C. Kisielowski, Observing atoms at work by controlling beam-sample interactions, *Advanced Materials* 27 (2015) 5838-5844

Thin Films

Room Makai - Session TF-MoE

Nanostructured Surfaces & Thin Films I

Moderator: Joe Greene, Linköping University, Sweden, University of Illinois at Urbana-Champaign

5:40pm TF-MoE1 Reducing Losses In Magnetic Thin Films by Surface Patterning, Goran Rasic, BV. Vlahovic, North Carolina Central University, USA; J. Schwartz, North Carolina State University, USA

As technology advances the demand for smaller and faster devices with reduced power losses becomes increasingly important. For high-frequency devices, such as antenna and sensors, two loss mechanisms are relevant, electrical and magnetic. Electrical losses are reduced by forming laminate structures and/or choosing materials with high electrical resistivity. Magnetic losses, however, arise from the magnetic hysteresis of the material, and thus are intrinsic. At frequencies above 1 GHz, these losses become immense. To reduce magnetic losses, the hysteresis losses must be reduced without losing desirable magnetic properties; reduced coercivity is needed, while retaining high saturation magnetization.

Textured nickel ferrite (NiFe_2O_4) thin films were deposited onto a c-plane sapphire substrate using chemical solution deposition. Surface of the films was patterned with a polydimethylsiloxane (PDMS) stamp using a modified nanoimprint lithography technique. A series of pattern masters with periods ranging from 500 nm to 1500 nm was used for patterning. In addition, samples with different thicknesses were prepared. Atomic force microscopy showed that the pattern was faithfully copied from the pattern masters to the thin films. X-Ray diffraction revealed all samples to be textured single phase inverse spinel nickel ferrite with preferential orientation along the $\langle 111 \rangle$ easy axis direction. Magnetic measurements showed the magnetic field response in the patterned samples to be unchanged as compared to plain samples, indicating there was no loss in magnetic properties. Similarly, the patterned samples showed appreciable and consistent saturation magnetization values. The coercivity of all samples showed significant reduction as compared to the plain samples. In addition, two distinct regimes were identified. For the out-of-plane measurements, the coercivity reduction increases with increasing feature size, whereas for the in-plane measurements the opposite is observed. These polar trends for the in-plane and out-of-plane measurements allow us to further fine tune the material for specific applications by not only controlling the feature size but also the orientation of the film with respect to the field. Finally, the origin of the coercivity reduction was shown to be the surface morphology anisotropy by MFM measurements. Magnetic domains were shown to be strongly affected by the surface features and oppositely oriented, reducing magnetostatic energy and leading to coercivity reduction. These results, in combination with the theoretical investigation, confirmed the origin of the coercivity reduction to be a direct consequence of altered surface topography.

6:00pm TF-MoE2 Orientational Control of Polar Molecules in Macroporous Systems and their Dielectric Properties, Ryosuke Yamamoto, N. Kimizuka, Kyushu University, Japan

Organic ferroelectric materials have been attracting much interest as a new family of memory materials that operate under lower electric field. However to date, most of the reported organic ferroelectric materials are solid and they show dielectric hysteresis only in the presence of high electric field. Accordingly, there is a compelling need for new dielectric materials working at a lower electric field and ambient temperature. In this light, we have focused on supramolecular gels as organic soft dielectric materials. Gelator molecules were dissolved in solvents with large dipole moment such as nitrobenzene by heating and succeeding cooling of the mixture afforded organogels. In the electron microscopes (SEM, TEM) observations, extended nanofibrous aggregates were abundantly observed for the dried gel. In this gel, polar solvent molecules are confined and their molecular motion are expected to be limited since they interact with fibrous gel networks which contain extended hydrogen bonding networks. Thus, the dielectric properties of these supramolecular gels were investigated systematically. The gels showed increase in the magnitude of polarization with distinctive polarization-electric field hysteresis loop, though such hysteresis was not observed for the polar solvents without gelators. In addition, in contrast to the gels formed with polar solvents, gels formed with non-polar solvents didn't show the hysteresis loop. From these findings, confinement of polar solvent molecules in the

suramolecular gel fiber networks play an important role to control mobility of solvent molecules, thus leading to orientational polarization.

To better understand this confinement effect and to generalize the approach, we employed porous polymer films with controlled pore-size as matrixes. Dielectric properties of polar molecules introduced into these porous polymer systems were investigated, which show similar hysteresis. We also found that polar molecules trapped in the different pore-sized polymer films showed distinct phase transition and dielectric behaviors. From these observations, it is suggested that polar molecules in the pores exert interactions with the pore surfaces and accordingly, their orientation is maintained even after cutting off the electric field. Furthermore, this system works at low electric fields. We believe that our approach would provide a new concept to design soft ferroelectrics.

7:00pm TF-MoE5 Atomic Layer Deposition of Al_2O_3 films on Various Two-Dimensional Materials, Taejin Park, Samsung Electronics, Republic of Korea; H.J. Kim, M. Lim, W.S. Ahn, S.H. Choi, Sungkyunkwan University, Korea, Republic of Korea; J.B. Kim, J. Uh, B.S. Kim, Y.S. Hwang, H.S. Hong, Samsung Electronics, Republic of Korea; S.J. Jeong, S.J. Park, Samsung Advanced Institute of Technology, Republic of Korea; Y.S. Kim, H.S. Kim, Sungkyunkwan University, Korea, Republic of Korea

The atomic layer deposition (ALD) of high- k films usually fails on two dimensional (2D) materials due to the absence of dangling bonds on their surface, which only allows physisorption of a precursor that can be easily detached *via* thermal desorption [1].

In this presentation, the surface coverage of the ALD- Al_2O_3 films on various 2D flakes (MoS_2 , WS_2 , WSe_2 , and h -BN) was examined as a function of the substrate temperature to extract the adsorption energy (E_{ads}) of a trimethyl-aluminum (TMA) precursor. The film coverage exhibited a strong dependence on the ALD temperature and the 2D substrate. The E_{ads} values of TMA on various 2D material surfaces were experimentally determined using the measured film coverage after 10-cycled ALD at different temperatures. The E_{ads} values were in the range of 0.05-0.26 eV, which corresponded to the values for van der Waals physisorption and could be well explained by different induced dipole polarizability of 2D materials.

[1] H. Liu *et al.*, Appl. Phys. Lett. **100**, 152115 (2012).

7:40pm TF-MoE7 Initial stage Growth Mode of ALD deposited Al_2O_3 on Tungsten Nano-powder, Kedar Manandhar, J.A. Wollmershauser, B.N. Feigelson, U.S. Naval Research Laboratory, USA

Powders with particle size ≤ 100 nm typically possess unique physical, chemical, opto-electronic, mechanical and catalytic properties compared to bigger size particle powder and their bulk counterpart and are increasingly being used in commercial systems. However a path to exploit these size specific properties of nano-powders is not always straight forward since they are often in danger of being deteriorated from the environments in which they are intended to be used. To enable these powders to withstand working environments, the surface of powders are commonly engineered via coating with films of thickness varying few monolayer to thousands of monolayers. For many cases a continuous ultrathin shell is desired. In the applications where a continuous ultrathin films is desired, understandings about growth mode, in the early stage of growth is very important since it defines how the material is arranged on the surface.

When it comes to the need of a thin metal-oxide film as protective layer or active surface, aluminum oxide is the material of choice for at least two reasons, (i) ALD chemistry of alumina from trimethylaluminum/ water is well studied (ii) relative easiness of forming a continuous film with alumina. To understand film morphology of alumina in the early stage of growth, we selected tungsten powder as substrate because this substrate/ film material combination eases for core-shell analysis by transmission electron microscopy (TEM) as TEM micrographs show a high contrast between core and shell for easy and more accurate determine of films thickness ranging from ultrathin to thin[1]. Alumina films resulting from 1 to 20 ALD cycles were grown on W-nanopowders with an average particle size of 50 nm using rotary reactor ALD. The results for alumina deposition at ~ 110 °C demonstrated stoichiometric and continuous but non-uniformly thick films in the beginning with varying growth per cycle (GPC) as a function of number of cycles. The as prepared samples were investigated with x-ray photoelectron spectroscopy, scanning and transmission electron microscopy. Film surface morphology and GPC as a function of ALD cycle for early stage growth will be presented and discussed.

1. Manandhar, K., et al., Growth per cycle of alumina atomic layer deposition on nano- and micro-powders. *Journal of Vacuum Science & Technology A*, 2016. 34(2): p. 021519.

Work is supported by NRL Base Program and DARPA

8:00pm TF-MoE8 Crystal Growth Simulation of ZnO Thin Film on α -Al₂O₃ Substrate by Molecular Dynamics Simulation, Shunsuke Kawagishi, J. Xu, Y. Ootani, T. Nishimatsu, Y. Higuchi, N. Ozawa, M. Kubo, Tohoku University, Japan

A ZnO thin-film semiconductor is used as light emitting devices and quantum hall effect devices because of its broad wide band gap of 3.2 eV and large exciton binding energy of 60 meV. In the previous research, optical properties of the ZnO thin film depend on the crystal orientation and quality [1]. Therefore, in order to obtain the high-quality thin film, it is necessary to understand crystal growth process such as physical vapor deposition. However, it is difficult to observe the crystal growth process at atomic scale by experiments. In this study, to elucidate the crystal growth process of ZnO, we performed crystal growth simulation of a ZnO thin film on an α -Al₂O₃ substrate by our molecular dynamics simulator and analyzed crystal quality of the formed ZnO thin film.

At first, to investigate crystal growth process of the ZnO thin film, we irradiated ZnO molecules on an α -Al₂O₃(0001) substrate at a velocity of 900 m/s at 700, 900, and 1200 K. The ZnO thin films are formed on the substrate at 700, 900, and 1200 K. Next, to evaluate crystal quality of the formed ZnO thin films, we analyzed radial distribution function of the formed thin films. The first and second peaks of the radial distribution function at 1200 K are sharper than those at 700 and 900 K. This indicates that crystallinity of the formed thin film at 1200K is higher than that at 700 and 900 K. Our simulation result is in good agreement with the experimental result in which crystal quality is improved by increasing the substrate temperature [2]. Next, we investigated the atomic behavior in the growth process. At only 1200 K, some of the irradiated ZnO molecules dissociate on the thin film. Then, the Zn and O atoms diffuse into the formed thin film. Finally, 6-membered rings are formed by diffusion of the Zn and O atoms in the formed thin film. This indicates that atomic mobility of the Zn and O atoms on the substrate is promoted due to raising substrate temperature and this high mobility of the Zn and O atoms contributes to the quality of the formed thin film. Thus, we succeeded in crystal growth simulation of a ZnO thin film on an α -Al₂O₃ substrate and found difference in the growth process of the thin film at 700, 900, and 1200 K.

[1] S. Dutta et al., *Progress in Materials Science*, 54, 89-136 (2009).

[2] A. El-shaer et al., *Superlattices and Microstructures*, 38, 265-271 (2005).

8:20pm TF-MoE9 Nucleation and Aggregation of Nanoparticles during Atomic Layer Deposition on High-Surface-Area Substrates, Fabio Grillo, H. Van Bui, Delft University of Technology, The Netherlands; J.R. van Ommen, Delft University of Technology, The Netherlands

Atomic layer deposition (ALD) is proving to be an attractive technique for depositing nanoparticles (NPs) in a controlled fashion. By relying on self-limiting surface reactions, ALD lends itself to the decoration of high-surface-area substrates with NPs for various applications such as enhanced catalysts and batteries. However, the mechanisms underlying the nucleation and growth of NPs during ALD are still poorly understood. Understanding the evolution of the particle size distribution of NPs during ALD is essential for fabricating supported NPs with predictable morphology and functionality. ALD growth is generally explained in terms of self-limited layer-by-layer growth, and although such picture applies to the deposition of a variety of metal oxides, especially at low temperature, it does not apply to the nucleation and growth of metal NPs. In fact, the evolution of the particle size distribution (PSD) of NPs is governed by kinetic processes such as surface diffusion, aggregation and coalescence. Here, we study the evolution of the PSD of Pt and Pd NPs deposited in time scales relevant to thermal ALD based on oxidative chemistries on high-surface-area substrates. To unravel the relevant processes underlying the evolution of the shape of the PSD, we devise a kinetic model based on the Smoluchowski equation that incorporates the generation of adatoms on both the substrate and the pre-existing NPs due to surface reactions, surface diffusion, adatom capture and NP aggregation. In doing so, we show that, during the first cycles, NP growth proceeds mostly due to NP diffusion and coalescence. The evolution of the PSD during dedicated sintering experiments of the ALD-grown NPs suggests that NPs aggregation takes place mostly during the oxygen exposure. In fact, the oxygen exposure not only regenerates the active surface for the subsequent precursor exposure but also mediates the metal-support interaction.

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Finally, we show that by varying the deposition temperature, while adjusting the exposure times to retain saturation conditions, the determining mechanism for NPs growth shifts from accretion due single-atom capture, at low temperatures ($T < 100$ °C), to NPs diffusion and coalescence at high temperatures ($T > 150$ °C). The insights obtained in this study open up new avenues to the rational design of novel composite materials based on supported metals NPs.

8:40pm TF-MoE10 Tight-Binding Quantum Chemical Molecular Dynamics Simulation on Water Lubrication Mechanism of Silicon Nitride, Jun Chida, N. Takahashi, Y. Wang, Y. Ootani, T. Nishimatsu, Y. Higuchi, N. Ozawa, K. Adachi, M. Kubo, Tohoku University, Japan

Silicon nitride (Si₃N₄) is used as a low friction material under water lubrication. It is suggested that the low friction is caused by the SiO₂·n(H₂O) (silica gel) layer generated by chemical reactions between the Si₃N₄ and the water at a friction interface [1]. Thus, the understanding of formation mechanisms of the silica gel is required to improve the friction properties. However, it is difficult to directly observe the chemical reaction dynamics at atomic scale by experiments. In this work, we investigated the formation mechanism of the silica gel by our tight-binding quantum chemical molecule dynamics simulator [2].

We performed the sliding simulation of Si₃N₄ under water lubrication. The simulation model consists of two amorphous Si₃N₄ substrates and H₂O molecules. The top of the upper substrate was slid by 100 m/s with a load of 3 GPa. The Si atoms and the N atoms on the surfaces were terminated by OH groups and H atoms, respectively.

First, we employed the flat substrate model. During the friction simulation, an H atom of a Si-OH bond on the Si₃N₄ surface transferred to a nearby N atom. Then, the O atom of the Si-O bond approached another Si atom in the surface, and a Si-O-Si bond was generated. The Si-OH groups changed to the Si-O-Si groups at the friction interface. This process leads to the formation of Si-O-Si bond network which is the main component of the silica gel.

Next, in order to reveal the influence of surface roughness on the formation mechanism of the silica gel, we employed the Si₃N₄ substrates with a rough surface. During the friction simulation, the Si-O-Si bonds were generated on the surface of the convex parts, as observed in the simulation with the flat substrates. When the two convex parts collided, the chemical bonds were generated between the two substrates. Then, the convex part of the lower substrate combined with the upper substrate was scraped off. H₂O molecules dissociated and adsorbed on a newly generated surface to saturate the dangling bonds. Finally, the flat Si-O-Si chain was formed on the surface. This result indicates that the collision of the convex parts leads to the formation of the flat Si-O-Si bond network.

In this work, we found that the Si-O-Si network, which is the main component of silica gel, is generated at the friction interface of Si₃N₄ by the chemical reaction of the Si-OH groups and the collision of the convex parts. Remarkably, the flat Si-O-Si network was formed after the scraping the convex parts.

[1] M. Chen et al., *Tribol. Lett.* 11 (2001) 23.

[2] K. Hayashi, M. Kubo et al., *J. Phys. Chem. C*, 115, 22981-22986 (2011).

Thin Films

Room Makai - Session TF-TuM

Nanostructured Surfaces & Thin Films II

Moderator: Sumit Agarwal, Colorado School of Mines, USA

8:00am **TF-TuM1 Ways to Increase the Strength of Langmuir Monolayers of Particles at Air/aqueous Interfaces**, *Cathy McNamee*, Shinshu University, Japan; *S. Fujii*, Osaka Institute of Technology, Japan; *S. Yusa*, University of Hyogo, Japan; *M. Kappl*, MPIP, Germany

The use of Langmuir monolayers of polymer particles stabilized at air/liquid surfaces in medical and industrial applications are affected by their physical properties, e.g., stiffness (deformability), their resistance against breakage upon impact of other materials, and their adhesion to other surfaces. We previously studied the physical properties of a Langmuir monolayer of polystyrene particles loaded with poly(*N,N*-dimethylaminoethyl methacrylate) (particle abbreviation: "PDMA_PS") at air/aqueous interfaces by using the Monolayer Particle Interaction Apparatus [1]. A particle was attached to an Atomic Force Microscope cantilever (probe), which acted as the colliding material. The probe was brought from the bulk water to the monolayer of PDMA_PS particles at the air/water interface and then returned back into the bulk water, during which time the forces between the probe and the monolayer were measured. A monolayer of PDMA_PS particles at the air/water interface was seen from the force-distance curves to give a low stiffness, a result explained by the induced movement of the particles in the monolayer at the air/water interface by the probe, when the probe was brought into contact with the monolayer from the bulk water.

In this study, we aimed to create a Langmuir monolayer of polymer particles at an air/water interface that showed a high stiffness, even after the collision of a probe or another material. This was achieved by adding a poly(2-hydroxyethyl methacrylate) ("PHEMA") polymer to a Langmuir monolayer of PDMA_PS particles at an air/water interface. The mixed PHEMA- PDMA_PS monolayer gave a polymer-like monolayer at low surface pressures and a particle-like monolayer at high surface pressures. The PDMA_PS particles formed small aggregates that were dispersed throughout the PHEMA monolayer at low surface pressures, a result suggesting that the particles were trapped in the PHEMA network. The stiffness of the mixed monolayer was independent of the surface pressure, but increased as the ratio of PHEMA in the mixed monolayer increased. The stiffness increase was explained by the PDMA_PS particles being embedded in the PHEMA polymer network, which inhibited the movement of the PDMA_PS particles by the probe. A PHEMA polymer monolayer containing a small amount of PDMA_PS particles gave a stiffer film than a pure PHEMA polymer monolayer. It was therefore concluded that the stiffness of a particle monolayer could be changed by adding a polymer to a Langmuir monolayer of particles.

[1] McNamee, C.E.; Fujii, S.; Yusa, S.; Azakami, Y.; Butt, H.-J.; Kappl, M. *Colloid Surf. B-Biointerfaces*, **2015**, *470*, 322-332.

8:20am **TF-TuM2 Carbon Incorporation into the Si(111)-7x7 Surface**, *E. Seo*, *D. Eom*, Korea Research Institute of Standards and Science (KRISS), Republic of Korea; *J.-M. Hyun*, *H. Kim*, Sookmyung Women's University, Republic of Korea; *Ja-Yong Koo*, Korea Research Institute of Standards and Science (KRISS), Republic of Korea

Carbon incorporation into Si wafer has attracted much attention due to the important role of carbon in developing high-performance, Si-based devices. The isovalent C atoms may induce systematic surface strains for building nanostructures on Si wafer without the doping effects. However, the extremely low solubility of C atoms in bulk Si (below 0.001%) has been considered as an obstacle to C incorporation into Si surface.

C atoms can be incorporated into the 4th delta-layer (0.4 nm deep) under the Si(001) surface upto the density of 0.125 monolayer with the c(4x4) surface reconstruction.

We investigated the incorporation of C atoms into Si(111)-7x7 surface by using scanning tunneling microscopy. The C atoms are extracted by thermal dissociation of CO molecules adsorbed on the Si(111)-7x7 surface. Previous studies negate adsorption of CO molecules on this surface even at low temperatures near 10 K. However, we find that every surface dangling bond on the Si(111)-7x7 surface can bind strongly with the C atom of a CO molecule even at temperatures higher than room temperature. Especially

CO molecules bind with Si adatoms in three configurations; one <on-top> and two <back-bond inserted> structures.

By thermal annealing, C atoms are incorporated under the Si adatoms of Si(111)-7x7 surface. The maximum density of incorporated C atoms on Si(111)-7x7 is low compared with that on Si(001)-2x1. At high density, C atoms are swept away from the 7x7 reconstructed surface due to the excessive surface stress, forming irregular SiC phases along the step edge.

Regular and uniform C-incorporated Si(111)- $\sqrt{3}\times\sqrt{3}$ reconstruction is not formed on this Si wafer surface.

8:40am **TF-TuM3 Optical, Electronic and Structural Properties of Eu and Gd bis-phthalocyanines Thin Films for Optoelectronics**, *E. Maresova*, *Michal Novotny*, Institute of Physics of the Czech Academy of Sciences, Czech Republic; *P. Fitl*, *J. Vlcek*, University of Chemistry and Technology Prague, Czech Republic; *M. Vondracek*, *P. Hubik*, *L. Fekete*, Institute of Physics of the Czech Academy of Sciences, Czech Republic; *M. Vrnata*, University of Chemistry and Technology Prague, Czech Republic; *J. Bulir*, Institute of Physics of the Czech Academy of Sciences, Czech Republic; *B. Paruzel*, *J. Pflieger*, Institute of Macromolecular Chemistry of the Czech Academy of Sciences, Czech Republic; *R. Słota*, Faculty of Chemistry, Opole University, Poland; *J. Sebera*, Institute of Physics of the Czech Academy of Sciences, Czech Republic; *I. Pis*, Elettra - Sincrotrone Trieste S.C.p.A., Italy; *I. Kratochvilova*, *J. Lancok*, Institute of Physics of the Czech Academy of Sciences, Czech Republic

Phthalocyanines (Pcs) exhibit unique properties, i.e. semiconductivity, photoconductivity, chemical stability and optical absorption in the UV-VIS-NIR region. These properties make the Pcs suitable candidates for optoelectronic devices, small molecular organic solar cells, laser printers or chemiresistive gas sensors. Pcs belong in the most efficient class of organic semiconductors for solid state photovoltaic conversion. Metal 'mono'-Pc compounds, i.e. ZnPcs, CuPcs, are most commonly utilized. Lanthanide bis-phthalocyanines (LnPc₂) based on two macrocycles coordinated by the rare earth metal offer additional possibilities since their arrangement allows changing the distribution of electronic density within the cores of the particular phthalocyanine moieties whereas the molecular structure of the sandwich complex remains intact.

Bis-phthalocyanine thin films of GdPc₂ and EuPc₂ were grown by vacuum evaporation from effusion cell. The optical properties were characterized by spectrophotometry and spectral ellipsometry. The spectra exhibited well pronounced Q, B, N and C bands and a band around 460 nm that could be attributed to radical band (X band) – transition [2e_g(π)-2a_{1u}(π)] suggesting Ln³⁺Pc₂. Relatively high values of conductivity (1.3·10⁻⁵ S.cm⁻¹ for EuPc₂ and 6.1·10⁻⁵ S.cm⁻¹ for GdPc₂) were obtained in open air at room temperature with interdigital surface Au electrodes arrangement. The conductivity was found to be sensitive to the thermal annealing and ambient conditions. Electronic structure was analyzed by XPS, resonant PES and NEXAFS. Well pronounced individual components of core level spectra of C 1s, N 1s, Eu 4d and Gd 4d and resonating lanthanide 4f levels in valence band were obtained and analyzed. The analyses confirmed Ln³⁺ ionic state. NEXAFS measurement supported by density functional theory calculations revealed rather inclined orientation of LnPc₂ molecules on the substrate. The molecular orientation could be manipulated by deposition pressure and depends on the film thickness. Morphology was studied by SEM and AFM. The surface roughness was found to be lower than 1 nm. FTIR characterization suggested low deterioration of LnPc₂ in the films.

The obtained results suggest both GdPc₂ and EuPc₂ as promising candidates for application in photovoltaics.

9:00am **TF-TuM4 Defect-induced Localized States on Nitride-Based HEMT and Their Influence on the Radiative Recombination Processes**, *Manolo Ramirez López*, Instituto Politécnico Nacional, Mexico; *L. Janicki*, *R. Kudrawiec*, *M. Baranowski*, *J. Misiewicz*, Institute of Physics, Wrocław University of Technology, Poland; *M. Zhao*, *K. Kai Cheng*, IMEC, Belgium

Intensive efforts have been made to improve electrical performance of GaN-based HEMT transistors but it has not been identified factors that limit the breakdown voltage, electrical mobility and lead to the early device failure[1]. Incorporation of impurities, point defects, dislocations and grain boundaries formed at semiconductor layers of the device are good candidates to explain their electrical limitations. This work was focused to study the effect of non-intentional carbon concentration on optical recombination processes in AlGaIn buffer layer and GaN channel of HEMT transistors grown by MOCVD technique. Samples were grown by changing growth temperature from 950 to 1040 °C, which reduced carbon concentration from 8x10¹⁹ to 5x10¹⁷ atoms/cm³ (measured by SIMS). Low temperature photoluminescence (PL) spectra of AlGaIn buffer layers where

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show yellow band (YL), blue band (BL) and near band emissions (NBE), whose relative intensities are well related with dislocation density and carbon incorporation. Optical quenching phenomena on YL, BL and NBE was observed as temperature increases and NBE peak position suffers a redshift as carbon concentration decreases [2]. In samples with high carbon concentration (8×10^{19} and 2×10^{19} atoms/cm³) only carrier redistribution within localized state was observed, while for samples with lowest carbon concentration (5×10^{17} to 3×10^{18} atoms/cm³) two optical quenching process were identified (carrier redistribution and delocalization). Carrier delocalization was confirmed by yellow-band intensity increase when this process was thermally activated at 150 K. Results are explained in terms of carbon-generated localized states with different depth and aluminum fluctuations within AlGaIn buffer layers. High-resolution PL spectra of C-doped layers show free A exciton and acceptor bound-exciton whose intensities are correlated with crystal quality and carbon concentration. Complementary analysis will be presented for GaN channel of HEMT transistors.

[1] E. Zanoni, M. Meghini, A. Chini, D. Marcon and G. Meneghesso, IEEE Transactions On Electron Devices, **60**, 10 (2013).

[2] M. A. Reshchikov, D. O. Demchenko, A. Usikov, H. Helava, and Yu. Makarov, Phys. Rev. B **90**, 235203 (2014).

This work was performed within the grant of the National Science Center (NCS) (OPUS 5 No. 2013/09/B/st7/02395), and supported by SIP-IPN project No. 20160610. The authors acknowledge to CONACYT for financial support through postdoctoral scholarship No. 265970.

9:20am TF-TuM5 Comparative Study of the Ni-Silicide Films formed on Si and Strained Si:P, Seongheum Choi, J. Kim, J. Choi, S. Cho, Sungkyunkwan University, Korea, Republic of Korea; M. Lee, E. Ko, Yonsei University, Korea; I. Rho, C.H. Kim, SK Hynix Inc.; D.-H. Ko, Yonsei University, Korea; H.S. Kim, Sungkyunkwan University, Korea, Republic of Korea

The epitaxially-grown strained Si:P film can be used as an uni-axial stressor and/or a low resistance contact material in the n-channel metal-oxide-semiconductor field-effect transistors (NMOSFETs) [1]. Because an additional silicidation process is expected on top of the strained Si:P layer, there have been a few attempts to synthesize metal-silicide films, such as Ti- and Ni-silicides [2, 3].

In this presentation, we will compare the microstructural properties of the NiSi films formed on a Si substrate and a strained Si:P film. The strained Si:P film (P concentration of ~1.9%) was epitaxially grown on Si using a low-pressure chemical vapor deposition system. After HF cleaning and Ni deposition, silicidation was performed by rapid thermal annealing at 400~800 °C for 1 min in N₂ ambient. According to microstructural and electrical comparison with the NiSi film formed on Si, a number of large-sized grains with a flat interface existed and a delay of thermal agglomeration was observed in the NiSi film on Si:P. The possible difference in the grain-growth mechanism of the NiSi films on Si and Si:P will be discussed.

9:40am TF-TuM6 Low Temperature Chemical Vapor Deposition of Manganese and Iron Nitride from Bis(2,2,6,6-Tetramethylpiperidido)metal (ii) and Ammonia, Elham Mohimi, B.B. Trinh, S. Babar, G.S. Girolami, J.R. Abelson, University of Illinois at Urbana-Champaign, USA

Manganese and iron nitride phases are an interesting class of materials for applications such as optoelectronics, microelectronics, magnetic recording, and spintronics. Since chemical vapor deposition (CVD) can conformally coat high aspect ratio (deep) features used in design of nanoscale devices, it is highly desirable to develop CVD routes for manganese and iron nitride films. However, the lack of suitable precursors has hindered this development.

Here, we report CVD growth of manganese and iron nitride films from a novel and practical precursor, bis(2,2,6,6-tetramethylpiperidido)metal (II), M (tmp)₂, with ammonia as co-reactant. The manganese and iron tmp complexes can be synthesized in high yield and are thermally stable at room temperature. Growths are done in a cold wall, high vacuum chamber at substrate temperature of 50-350 °C. Precursors are heated to 60-75 °C and delivered to the chamber using Ar carrier gas at flow rates of 5-40 sccm. Anhydrous ammonia is delivered through a separate line to afford a partial pressure of 0-13 mTorr.

XPS reveals a compositional ratio of Mn:N = 2.6:1 to 2.8:1 for manganese nitride (Mn_xN_y) and Fe:N = 4.1:1 for iron nitride (Fe_xN) films grown in the temperature range examined, with no carbon contamination within the detection limits of instrument. All films show a slightly columnar

microstructure in cross-section SEM. While there was a few min of nucleation delay for Mn_xN_y growth at 150 °C, no nucleation delay was observed for Fe_xN under the same growth conditions. There is no film growth at all in the absence of ammonia; this indicates that transamination is required to create Mn-NH₂ groups that react on the substrate surface to form the nitride film, as seen for film growth from other metal amido precursors in the presence of ammonia. Films are conformal in micro-trenches of aspect ratio 3; the thickness profiles are, however, characteristic of film growth from two reactive species, one with high and one with low sticking coefficient at the film surface. Copper diffusion barrier properties of a 12 nm manganese nitride film are investigated by annealing a test structure of 200 nm Cu / 12 nm Mn_xN_y / 300 nm SiO₂ / Si at 500 °C under Ar for 1 hour. Auger electron spectroscopy depth profiles show that manganese nitride performs well as copper diffusion barrier for microelectronic applications.

10:20am TF-TuM8 Multi-functional Thin Film Coatings formed via Nanoscale Grinding, R. Sapkota, Chris Papadopoulos, University of Victoria, Canada

Nanostructured surfaces and thin films composed of nanoscale particles can be created using a variety of nanofabrication methods for applications in electronics, photonics, energy, biotechnology, etc. Generally, such nanostructures can take many forms depending on the various top-down to bottom-up fabrication methodologies [1]. *Nanoscale grinding*, or colloidal grinding, is a unique approach to nanoparticle thin film synthesis that can directly produce large amounts of nanoscale particles in an appropriate solvent without the use of complex chemical or physical processing. Planetary ball milling is typically used to grind a starting bulk powder into a nanoscale colloidal suspension suitable for thin film coating of various functional materials from solution. Efficient energy transfer during planetary ball motion leads to a fast and inexpensive process for the creation of nanostructured films. By adjusting the grinding parameters, the size and dispersion of the particles can be controlled and optimized for applications.

Here we describe results using the nanoscale grinding approach to fabricate multi-functional nanostructured thin film coatings. Nanogrinding allows tunability of film properties that can lead to novel functions depending on the particular combination of material, solvent and nanoparticle geometries/dimensions used. These unique abilities produce a general solution-based processing approach for thin film surface coatings and devices (including non-planar geometries).

Nanostructured thin films based on grinding high-purity powders (Si and TiSi) and characterization via electron microscopy, scanning probe, electronic transport and contact angle measurements are presented. Zirconia beads in a planetary ball mill with readily available powders initially consisting of ~10-50 micron particles in solvent were used. Grinding speeds and times varied between approx. 300-1000 rpm and 10-250 minutes, respectively. The resulting colloidal dispersions are deposited on a substrate for analysis. As grinding time is increased, the particles and films display good uniformity with sizes reaching below 100 nm. Both electrical conductance and contact angle could be tuned over a wide range depending on grinding conditions thereby creating unique multi-functional nanostructured materials and films. We also discuss preliminary results on optical and photocatalytic properties of the nanostructured surfaces. Thin films created via nanogrinding possess unique and varied electrical, optical and mechanical properties, which can be used to create advanced materials and devices.

[1] C. Papadopoulos, "Nanofabrication: Principles and Applications", Springer, 2016.

10:40am TF-TuM9 Optimization of the ZnO Passivation Process on p-type In_{0.53}Ga_{0.47}As Using Atomic Layer Deposition, Changmin Lee, Y. An, S. Choi, J. Song, Sungkyunkwan University, Republic of Korea; Y.-C. Byun, J. Kim, University of Texas at Dallas, USA; H.S. Kim, Sungkyunkwan University, Republic of Korea

For the performance enhancement of the inversion-type III-V metal-oxide-semiconductor field-effect transistors (MOSFETs), it is essential to improve the interface quality between the high-*k* gate dielectric and the p-type III-V substrate. Recently, ZnO passivation using an atomic layer deposition (ALD) process was reported to be effective in removing the interface oxides and improving the electrical properties on both p-type GaAs [1] and p-type In_{0.53}Ga_{0.47}As [2].

In this study, the ALD-ZnO treatment was performed on the sulfur-passivated p-type In_{0.53}Ga_{0.47}As substrates with different numbers of cycles at 150 °C. According to the electrical measurement of the MOS capacitors

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with HfO₂ gate dielectrics (ALD at 200 °C), a minimum capacitance increased with a flat band voltage shift when the number of treatment cycles was increased after an optimal condition. The possible origin for the observed changes in the electrical properties will be discussed based on various characterization results, such as the low temperature C-V measurement and chemical analysis using X-ray photoelectron spectroscopy.

[1] Y.-C. Byun et al., ACS Appl. Mater. Interfaces, 6, 10482 (2014).

[2] A. T. Lucero et al., Electron. Mater. Lett., 11, 769 (2015).

11:00am **TF-TuM10 Electrical Properties of the Atomic-Layer-Deposited Al₂O₃ on GaSb pretreated with TMA and TDMAT**, *Youngseo An, C. Lee, S. Choi, J. Song*, Sungkyunkwan University, Republic of Korea; *Y.-C. Byun, J. Kim*, University of Texas at Dallas, USA; *H.S. Kim*, Sungkyunkwan University, Republic of Korea

GaSb is one of the possible candidates for a p-channel layer in the high-speed metal-oxide-semiconductor field-effect transistors (MOSFETs). However, its poor thermal stability and high reactivity with ambient air produce a poor interface with the high-*k* gate dielectrics, and there have been several attempts to resolve these problems [1-3].

In this presentation, the sample loading temperature was varied to find an optimal atomic layer deposition (ALD) condition of an Al₂O₃ film on p-type GaSb substrates. Then, we compared *in situ* substrate treatments of two metal precursors, trimethylaluminum (TMA) and tetrakis(dimethylamino)titanium (TDMAT), at the same loading temperature prior to the ALD-Al₂O₃ process. According to various electrical characterizations of the capacitors, lowering the loading temperature was beneficial in reducing the Fermi level pinning effect, and further suppression could be achieved by the subsequent TMA/TDMAT pretreatments. Although the TDMAT treatment showed more efficient relief of Fermi level pinning than the TMA treatment, it undermined the frequency dispersion characteristics in an accumulation region, as an adverse effect. The interface characterization results using X-ray photoelectron spectroscopy will also be discussed to understand the observed electrical properties.

[1] A. Nainani et al., J. Appl. Phys., 109, 114908 (2011).

[2] M. Yokoyama et al., Appl. Phys. Lett., 106, 122902 (2015).

[3] L. B. Ruppalt et al., Appl. Phys. Lett., 101, 231601 (2012)

11:20am **TF-TuM11 Using Surface Chemistry for Morphological Control of Metal Oxides and Chalcogenides on Organic Surfaces**, *J.K. Hedlund, Z. Shi, Amy Walker*, University of Texas at Dallas

We describe recent progress in our laboratories to build robust complex two- and three-dimensional composite metal oxide and chalcogenide - molecular constructs. This work has important applications in photovoltaics, molecular and organic electronics, sensing, photonics and other technologies. Several recent developments will be discussed including the chemical bath deposition of ZnO transition metal dichalcogenides, the atomic layer deposition of ZnO and ZnS and the formation of semiconducting nanowires and other nanostructures on micron-scale patterned surfaces. Optimization and further development of these techniques requires a detailed understanding of the reaction pathways involved in the interaction of organic thin films with organometallic compounds, ions, and other compounds in both solution and gas phases.

11:40am **TF-TuM12 Ultra-High-Density Arrays of Defect-Free AlN and GaN Nanorods: A “Space-Filling” Approach for Heteroepitaxial Thin Film Growth**, *M. Conroy*, Pacific Northwest National Laboratory; *Haoning Li, V. Zubialevich, J. Holmes, P. Parbrook*, Tyndall National Institute

Nanostructured semiconductors have a clear potential for improved optoelectronic devices, such as high-efficiency light-emitting diodes (LEDs). However, most arrays of semiconductor nanorods suffer from having relatively low densities (or “fill factors”) and a high degree of nonuniformity, especially when produced by self-organized growth. Ideally an array of nanorods for an optoelectronic emitter should have a fill factor close to 100%, with uniform rod diameter and height. In this paper we present a “space-filling” approach for forming defect-free arrays of AlN nanorods, whereby the separation between each rod can be controlled to 5 nm due to a self-limiting process. These arrays of pyramidal-topped AlN nanorods formed over wafer-scale areas by metal organic chemical vapor deposition provide a defect-free semi-polar top surface, for potential optoelectronic device applications with the highest reported fill factor at 98%. We then applied this method to GaN, in particular investigating the

desorption factor that was not an issue for the AlN growth. Here we show that the etched nanorods change morphology during the annealing step even before additional GaN is deposited, forming 6 non-polar side walls.

Tuesday Afternoon Poster Sessions, December 13, 2016

Thin Films

Room Mauka - Session TF-TuP

Thin Films Poster Session

TF-TuP1 P-Type Nitrogen Doped Zinc Oxide Films Prepared By Magnetron Sputtering, *J.Y. Chen*, Ming Chi University of Technology, Taiwan; *H.T. Zhang, G. Zhao, Q. Chen*, Beijing Institute of Graphic Communication, China; *Jyh-Shiarn Cherng*, Ming Chi University of Technology, Taiwan, Republic of China

P-type nitrogen doped zinc oxide (NZO) was prepared on a glass substrate by RF magnetron sputtering using N_2 as the nitrogen source. The structural, electrical and optical properties of the NZO films were investigated by X-ray diffractometry, X-ray photoelectron spectroscopy, Raman spectroscopy, Hall effect and Seebeck effect measurements, and UV-Vis spectroscopy. The electrical properties of the p-type NZO showed a conductivity of $7.6 \times 10^{-2} (\Omega\text{-cm})^{-1}$ and remained stable for over 259 days at the optimized process conditions. With the increase of N_2 flow rate during sputtering, the conductivity of the NZO films exhibited an n-p-n transition. The corresponding mechanism of this transition and the origin of the p-type conductivity were discussed accordingly.

TF-TuP2 Low Temperature Deposition of nc-Silicon Thin Films using SiH_4/H_2 Mixture, *Moniruzzaman Syed*, Lemoyne Owen College, USA; *B. Goh, N. Nazarudin*, University of Malaya, Malaysia; *J. Alam*, University of Memphis; *Y. Hamada*, Lemoyne Owen College, USA; *A. Ali*, King Khalid University, Saudi Arabia

Nanocrystalline-silicon (nc-Si) films were simultaneously deposited on glass and single-crystal Si substrates that were exposed to H_2 plasma excited using RF power = 80 W prior to the film deposition, under 250°C by plasma enhanced chemical vapor deposition using a SiH_4/H_2 mixture. Structural changes of the nc-Si films were investigated by X-ray diffraction, Raman spectroscopy, infrared absorption, UV-VIS and AFM measurements. All nc-Si films were deposited as a function of RF power conditions. $\langle 110 \rangle$ preferentially oriented nc-Si films were observed to grow suddenly with RF power of 80 W resulted in improved crystalline qualities. These results were examined on the basis of the effect of various mechanisms on the crystalline properties, although these mechanisms may jointly determine the properties.

TF-TuP3 Effect of Laser Assisted Local Heating on Mechanical Properties during Indirect Hot Stamping of Tubes, *M.N. Chowdhury, T.T. Nguyen, GiDong Park, T.K.A. Dinh, S.-T. Hong*, University of Ulsan, Republic of Korea; *J.W. Jung, H.N. Han*, Seoul National University, Republic of Korea

Mechanical behaviors of a hot stamping steel tube are experimentally investigated using laser assisted local heating. A partial surface with spiral shape along the length of tube is heated to austenitic temperature by combining the linear movement of the laser and the rotation of the tube. The result of axial crush tests suggests that the laser assisted local heating is capable to enhance mechanical strength and hardness of the tube. A microstructural analysis shows that the laser locally induces a martensitic phase transformation in the heated region along the length of the tube.

TF-TuP4 High Quality ALD of Silicon Nitride Films Via Microwave Plasma, *Kihyun Kim*, Samsung Electronics, Republic of Korea; *J. Provine, P. Schindler, Stephen. Walch, Y. Kim, HyoJin. Kim, F.B. Prinz*, Stanford University, USA

Modern integrated circuit processing for DRAM, flash, and logic devices require silicon nitride (SiN) spacer layers with exacting requirements for chemical, physical, and electrical performance. High quality SiN thin films can be achieved by low pressure chemical vapor deposition (LPCVD) at elevated deposition temperatures (>800°C). However, modern device design rules require low thermal budget (<400°C) for these and other applications.

In this abstract, we demonstrate with a custom built PEALD system utilizing a high power (~1kW) microwave plasma source. Utilizing this system, we can achieve composition with low oxygen, carbon, and hydrogen content similar to what is achieved in higher temperature LPCVD reactions.

The dependence of the SiN film properties on process parameters including plasma power and plasma treatment cycle, are investigated. Specifically, the wet etch rates in dilute hydrofluoric acid ($H_2O:HF$ 200:1) with respect to plasma power and treatment cycle times can be varied because of the effects of radicals and ions generated by the plasma source during deposition. Wet etch rates comparable to LPCVD SiN films can be

demonstrated at significantly reduced temperature by PEALD. X-ray reflectometry (XRR) and X-ray photoemission spectroscopy (XPS) studies show the higher plasma power and extended plasma treatment cycles can vary the density and the composition of SiN films.

TF-TuP5 Homeotropic Liquid Crystal Alignment on Aluminum Oxide Films and its Application for Liquid Crystal Display, *Hong-Gyu Park*, Changwon National University, Republic of Korea; *H.Y. Mun, H.-C. Jeong, J.H. Lee*, Yonsei University, Korea, Republic of Korea; *B.-Y. Oh*, ZeSHTech Co. Ltd., Republic of Korea; *D.-S. Seo*, Yonsei University, Korea, Republic of Korea

Liquid crystal display (LCD) technology is still occupying a strong position in the display industry. The orientational control of liquid crystal (LC) molecules is essential for high-quality LCDs and interactions between LC molecules and solid-substrate surfaces are still significant in both fundamental research and industrial applications. Achieving sophisticated control and uniform alignment of LCs with a regular pretilt angle on the alignment layer is an important step in the manufacture of LC displays (LCDs). Intensive research on the use of organic or inorganic films as LC alignment layers has been conducted to obtain uniform LC alignment using various alignment techniques such as rubbing, ultraviolet (UV) photoalignment technique, nanoimprint lithography, oblique deposition, and ion-beam (IB) irradiation. Among these, the rubbing process has still attracted much attention in terms of simplicity, high cost-effectivity, and reliability. Recently, transparent inorganic materials have been investigated by many research groups as alignment layers, because of their low power consumption achieved via the reduction of LC threshold voltage. In addition, oxide-based inorganic materials are more durable than organic materials and are insensitive to oxygen and water, which slows the degradation of the device performance compared to organic materials.

We previously reported on LC alignments on aluminum oxide (Al_2O_3) films deposited using various techniques including atomic layer deposition (ALD), RF magnetron sputter, and e-beam evaporation via IB irradiation. In this paper, we demonstrate the effects of LC alignment on Al_2O_3 films using a rubbing process. Through a simple technique, uniform and vertical LC alignment was achieved on the Al_2O_3 films. Optical retardations and contact angles were observed on the Al_2O_3 films to measure the effect of the rubbing treatment on Al_2O_3 films. Finally, the electro-optical (EO) characteristics of vertically aligned (VA) cells on Al_2O_3 films were measured.

TF-TuP6 A Pulsed Supersonic Valve System for Researches on Collision-Induced Reactive Thin Film Etching Phenomena, *Masahito Tagawa, K. Yokota, T. Yasukochi*, Kobe University, Japan; *S.K. Chee*, Mechano Transformer Corporation, Japan

A pulsed supersonic valve (PSV) with fast operation capability is essential for many molecular/atomic beam experiments. A reliable PSV is a key device for not only scientific molecular beam experiments, but also engineering applications such as future digital molecular beam epitaxy (MBE) and molecular beam-induced etching. Among these applications, laser-detonation hyperthermal beam source, which has been applied for space environmental effect studies on thin film erosion, requires highly reliable and fast response PSV system. We have developed a fast and reliable piezoelectric-driven PSV system. It consists of conventional low-voltage piezoelectric actuator (max 150V) with a displacement enlargement mechanism (displacement is greater than 0.1mm). These mechanisms are covered by a stainless steel body. Size of PSV is approximately 15 x 10 x 4 cm. Gas is ejected by a 1 mm hole. The poppet clearance is adjustable by the micrometer. The poppet system with a Viton O-ring and Au reflector was specially designed for laser-detonation applications, which requires the focusing 7 J laser pulse near the O-ring. A pressure profile of ejected gas from the nozzle was measured. It is clearly indicated that the PSV is able to operate less than 100 microseconds. It should be mentioned that even faster operation is possible with a high-current PSV driver. It was also confirmed the specification below;

Max. Pressure of supply gas: > 0.8 MPa, Max. Repetition rate: > 50 Hz, Poppet life: > 0.6 million shot (with CO_2 laser irradiation)

One of the unique features of this system is that two PSVs independently eject gas pulses into one hole, such that time-variation of the composition of a gas pulse could be controlled. This capability provides controllability of the dissociation of molecules in a pulsed laser plasma.

Time-of-flight spectra of "thermal" molecular beam generated with this PSV system were measured. It was obvious that the velocity distribution was consistent with the Maxwell-Boltzmann distribution. Also the capability of forming "hyperthermal" atomic beam with laser-detonation for space environmental simulation of thin film erosion problems as well as

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a wide variety of applications on applied surface sciences of this fast and reliable PSV system will also be discussed.

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TF-TuP7 Synthesis of High-quality MoS₂ Atomic Layers with Inorganic Seeding Promoters by Chemical Vapor Deposition, Woonchul Yang, S.H. Choi, Y.J. Kim, Dongguk university, Republic of Korea; K.K. Kim, Dongguk University, Republic of Korea

Molybdenum disulfide (MoS₂) is highlighted due to their unique physical and electrical properties such as ultrathin layered structure, high on/off ratio, and high mobility. The Band gap of layered-semiconductor MoS₂ is changed from 1.2 eV to 1.9 eV depending on the layered thickness. Monolayer MoS₂ with direct band gap is an optimal material to develop novel optoelectronic devices. There are many methods to prepare monolayer MoS₂ such as mechanically, chemically exfoliation, and chemical vapor deposition (CVD) method. Among them, the CVD method is inexpensive and easy to synthesize MoS₂ films with large scale and uniform thickness. In the CVD process, the absorption of vapor phase molybdenum and sulfur on the substrate is a problem for laterally layered growth of MoS₂. Recently, organic aromatic molecules help the nucleation of MoS₂ in the CVD process. However, the organic materials are easily decomposed due to their thermal instability at the growth temperature. Herein, we first report the inorganic seeding promoter including alkali metal ions to grow high quality MoS₂ flakes. The size of the grown flakes was up to 200 nm. The crystalline quality and the thickness of the MoS₂ were confirmed by AFM, Raman, and PL. The difference of typical Raman peaks of E_{2g} and A_{1g} is lower than ~19 cm⁻¹ with full width half maximum values of 3.8 cm⁻¹ and 4.5 cm⁻¹, respectively. This high quality is similar with mechanically exfoliated MoS₂. In addition, the size of the grown MoS₂ flakes can be tuned by concentration of the seeding promoters. The growth process with seeding promoters will be suggested in terms of surface reaction and nucleation of participating atoms and promoters on the surface. Our suggested inorganic seeding promoter will open the way to grow high quality monolayer MoS₂ flakes with scalable size.

TF-TuP8 Effect of Al₂O₃ Passivation Layer on the Stability of Al-IZO Thin-film Transistors, Ji-in Park, Y.S. Lim, M.H. Jang, S.I. Choi, N.G. Hwang, M.S. Yi, Pusan National University, Republic of Korea

We investigated the effect of aluminum oxide (Al₂O₃) passivation layer on the stability of aluminum-indium-zinc oxide (Al-IZO) thin-film transistors (TFTs) under positive bias stress (PBS) and negative bias illumination stress (NBIS). 20-nm thick Al-IZO channel layers were deposited by radio-frequency (RF) magnetron co-sputtering, and then annealed in air for 1h at 250°C. Processing parameters such as the IZO, Al₂O₃ target power (50, 10W) and oxygen partial pressure (13%) were fixed. After depositing the channel layers, 20-nm thick Al₂O₃ passivation layers were deposited by RF magnetron sputtering at room temperature, and annealed again at 250°C.

The TFTs without any passivation were taken as reference devices for comparison (device A). Fig. 1 shows the cross-sectional schematic diagram of Al₂O₃ passivated Al-IZO TFTs (device B). The measured electrical parameters of each device were summarized in Table 1, and it indicates that Al-IZO channel layer is not degraded during the passivation layer deposition by sputtering.

Fig. 2 (a) and (b) show the transfer characteristic curves of the device A and B depending on the stress durations (7200 s) under the positive bias stress (V_{GS}= +20V, V_{DS}= 0V, PBS) in dark, respectively. It can be easily seen that threshold voltage shift (ΔV_{th}) of the device B is much smaller than that of the device A, and indicates that more charge trapping sites (O₂+e⁻→O₂⁻) is created in device A during PBS condition. In other words, Al₂O₃ passivation layer could effectively prevent the oxygen absorption on surface of the Al-IZO film under the influence of gate voltage stress.

To investigate the stability of the TFTs under bias illumination stress, a negative bias stress (V_{GS}= -20V, V_{DS}= 0V, NBS) were repeatedly applied to the device A and B under green light illumination in air for 7200s. The brightness of the green light source was 2047cd/m². Fig. 3 (a) and (b) show the evolution of the transfer characteristic curves of each device for various stress durations under NBIS condition, and it can be concluded that the stability of device B is better than that of device A under NBIS condition. In general, the degradation mechanism of the NBS under illumination of Al-IZO TFTs is dominated by the photo-generated hole trapping states (V_o→V_o²⁺+2e⁻) at gate insulator and/or interface between insulator and channel. In this result, the Al₂O₃ passivation layer could effectively

passivate the defect in the Al-IZO films. We demonstrated that the Al₂O₃ could be an effective passivation layer to suppress O₂ absorption on Al-IZO back channel and decrease photo-excitation on Al-IZO films.

TF-TuP9 Extreme Ultraviolet Emission from Laser-induced O₂+Ar Plasmas Relevance to Ground-based Simulation of Thin Film Etching Reactions in Low Earth Orbit, Kumiko Yokota, T. Ohyabu, J. Ohira, K. Morimoto, M. Tagawa, Kobe University, Japan

The environmental factors in space, for example, ultraviolet (including EUV and VUV wavelength), x-rays, ion and electron radiations, thermal cycling, and neutral species such as atomic oxygen (AO), give serious effects on many thin film materials used in space systems. The incompleteness of the ground-based simulation technology arises problems on the accuracy of assessment of the material survivability in real space environment. It has been reported that FEP Teflon eroded much faster in ground-based facilities than in space. This discrepancy is believed due to the ultraviolet which is a byproduct from the oxygen plasma. A laser detonation AO source, which has widely been used as a ground-based AO environmental simulator, uses high-power CO₂ laser to create laser-induced oxygen plasma. The basic configuration of laser detonation AO beam source is similar to that of EUV light source using xenon gas. However, EUV from laser-detonation AO beam source has not been evaluated.

In this presentation, EUV spectra from laser-induced oxygen (and mixed gas) plasmas were reported. The flat-field EUV spectrometer especially designed for this purpose was equipped to laser-detonation AO beam source, and confirmed the capability to measure EUV spectra from oxygen plasma. Also, the cross relationship between EUV spectra, time-of-flight (TOF) spectra of AO beam and effect of addition of Ar were investigated related to the low altitude orbital applications.

It was clearly observed that EUV emission intensity from 100%Ar plasma was greater than that from 100%O₂ plasma. However, Ar emission was not observed from the laser-sustained plasma consisting of 50%Ar+50%O₂ gas mixture, i.e., EUV lines only originated from oxygen were observed. Emission intensities originated from O increased with Ar content and disappeared in the pure Ar plasma. The EUV emission property was considered to be related to the collisional processes in the mixed plasma. This hypothesis was proved by the TOF spectra, i.e., dissociation reaction of O₂ into AO was promoted by adding Ar in the gas. It was also observed that the EUV emission intensity decreased with increasing the supply gas pressure of the PSV. This could be a practical way to reduce the side effect of EUV on the ground-based AO simulations.

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TF-TuP11 Device Performance of Tungsten doped InZnO Thin Film Transistor depending on Active Layer Thickness, Hyun-Woo Park, D.-Y. Kim, Dongguk university, Republic of Korea; W.-C. Yang, Dongguk University, Republic of Korea; M.-D. Kim, Chungnam National University, Republic of Korea; K.-B. Chung, Dongguk university, Republic of Korea

Tungsten doped InZnO thin film transistors (WIZO-TFTs) were fabricated using by radio frequency (RF) sputtering system as a function of active layer thickness. In order to explain the degradation of the device performance depending on the active layer thickness, we investigated the correlations between the device performance and physical properties including the film density, surface/interface roughness, band edge state below the conduction band, refractive index and composition along the depth direction. The 10 nm-thick WIZO film is showed the highest film density and the flat interface roughness. In addition, increase of the band edge state and thickness of interface layers could be related to the device performance, which resulted in changes of interfacial trap density.

TF-TuP12 Influence of Macro-Confinement on the Thermochromic Transition Temperature of VO₂ Thin Films, Adetayo Adedeji, T. Patel, A.D. Agyapong, Elizabeth City State University, USA

Vanadium dioxide (VO₂) in bulk and thin film forms are well known thermochromic materials. VO₂ switches optically from IR transparent to IR reflecting at a transition temperature of about 68°C (about 150°F). Because of the easily accessible transition temperature, researchers are interested in driving the transition temperature to lower or higher values depending on the intended application. The goal of this research is to investigate the effect of thin film macro-size confinement on the transition temperature of

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VO₂. To achieve this goal, pure vanadium metal was deposited on clean quartz substrate using magnetron sputtering system. Different sizes of copper mesh were used as template for the depositions. The samples were oxidized in 800 mtorr N₂/O₂ gas mixture at 500°C for 4 hours. Surface morphology of the sample and chemical composition were obtained using SEM with EDS. Various grain sizes and orientations were observed at different depth from the quartz-VO₂ interface with aberration corrected Scanning Tunneling Electron Microscope (STEM). Optical transmittance in air ambient was measured as the samples were taken through thermal cycle. It was observed that the transition temperatures of samples deposited through Cu meshes are different from those obtained from plain 2D VO₂ films and films shielded with transparent Ta-Si-N barrier layer.

TF-TuP13 Nitrogen Plasma Treatment of Polytetrafluoroethylene, P. Garcia, C. Rangel, Steven Durrant, UNESP - Sorocaba, Brazil

Cold plasma treatment is well established for the modification of metal, glass and polymers. Treatments of polymers in plasmas of inert gases can alter the degree of cross-linking, release hydrogen, and produce dangling bonds, thus affecting the surface morphology and reactivity. In addition to such effects, treatments in plasmas of gases such as oxygen, carbon tetrafluoride or nitrogen, can cause etching and introduce new elements, such as O, F or N, to the polymer surface. It is known that cold nitrogen plasma treatment of polytetrafluoroethylene (PTFE) can strongly modify its properties; for example, reducing its surface contact angle to zero. There is still much to be learnt, however, about the effect of the system parameters on the modifications produced. In this study, PTFE is treated in cold nitrogen plasmas as a function of the gas pressure, P, RF plasma power, W, and exposure time, t. The variables P, W and t range from zero to 100 mTorr, 200 W, and 30 min. respectively. The induced chemical structural and compositional changes are examined using Infrared spectroscopy with attenuated total reflection (ATR) and Energy dispersive X-ray spectroscopy (EDS). Surface roughness and morphology are examined using Scanning electron microscopy (SEM). Surface contact angles are measured using goniometry.

TF-TuP14 Effects of Photogenerated Carrier Scattering on the Decay Process of Coherent Longitudinal Optical Phonons in an *i*-GaAs/*n*-GaAs Epitaxial Structure Investigated by Terahertz Time-domain Spectroscopy, Hideo Takeuchi, T. Sumioka, M. Nakayama, Osaka City University, Japan

Terahertz (THz) electromagnetic waves are generated by illumination of femtosecond (fs) laser pulses on semiconductor surfaces. The THz wave, therefore, supplies time-domain information on the dynamical phenomena around the surface. In the THz-wave emission from the coherent longitudinal optical (LO) phonons, initial polarization, which corresponds to the LO-phonon amplitude, is launched by a surge current of carriers generated by laser-pulse illumination. Subsequently, the coherent LO phonon, the dynamical polarization, starts oscillating and the THz wave is emitted. Here, we point out the possibility that the surge current scatters the coherent LO phonon in the launch stage. For clarifying the above possibility, we investigated the coherent LO phonon in an *i*-GaAs/*n*-GaAs epitaxial structure, focusing our attention on the decay time.

The sample used was grown by MOVPE. The *i*-GaAs (*n*-GaAs) layer thickness was 100 nm (300 μm). The doping density of the *n*-GaAs layer was 3x10¹⁸ cm⁻³. In the *i*-GaAs/*n*-GaAs structure, a uniform built-in electric field is produced in the *i*-GaAs layer, which induces the initial polarization. The THz wave was measured at room temperature and at the humidity below 10%. We used an optical gating method. The fs laser pulse had a photon energy of 1.55 eV and a pulse duration of 60 fs. The laser beam had a Gaussian shape. The pump powers were varied from 30 to 110 mW.

The THz waveforms show a monocycle signal from the surge current, which is followed by long-lived oscillations due to the coherent LO phonon. The Fourier power spectra of the waveforms show the surge current and coherent LO phonon bands. In addition, two bands, the frequencies of which depend on the pump power corresponding to the photogenerated carrier density, were observed. The frequencies of the latter two bands were evaluated using the Gaussian decomposition, and compared with the dispersion curve of the LO-phonon-plasmon coupled (LOPC) mode. We consider that the THz wave from the coherent LOPC mode is emitted from almost the center position of the Gaussian beam spot on the sample surface because of the presence of sufficient photogenerated carriers forming the plasmon. In contrast, the coherent LO phonon is generated around the beam-spot tail. The waveform shows only the coherent LO phonons in the time-delay range larger than 1.0 ps. The decay time of the coherent LO phonon, which is 3.0 ps at the pump power of 30 mW, is monotonically decreased with increasing the pump power: The decay time

is 1.3 ps at 110 mW. Since the increase in the pump power enhances the surge current, we conclude that the surge current disturbs the coherent LO phonon through the scattering.

TF-TuP16 Effects of Borate Polyester Electrolyte on the Anodizing Behaviors and Electrical Properties of ZrO₂-Coated Al Foil, Kaiqiang Zhang, S.S. Park, Kyungpook National University, Korea, Republic of Korea

ZrO₂-Al₂O₃ composite oxide films are promising dielectric material for future use in aluminum electrolytic capacitors. The films were prepared on etched Al foils by ZrO₂ coating and anodizing. The anodizing of Al foils has been carried out generally in aqueous boric acid solution. But when Al foils are anodized above about 700V, boric acid solution is not suitable as electrolyte due to severe O₂ evolution. In this study, we used borate polyester solution as electrolyte to inhibit the O₂ evolution, and discussed the effects of the borate polyester concentration on anodizing behaviors and electrical properties of the ZrO₂ coated Al foils. The results show that borate polyester electrolyte can effectively inhibit the O₂ evolution during anodizing, and increase the withstanding voltage of the samples. The specific capacitance of the samples decreases with the increasing of borate polyester concentration. Compared to anodization in boric acid electrolyte, the use of borate polyester electrolyte led to increases in the specific capacitance of 25.9 % for 700 V, 15.6 % for 800 V and 8.9 % for 900 V.

TF-TuP17 Selectivity of Plasma Treatment Effects on Wettability Modulation between Silicon, Glass, Polyimide and PMMA, Using Several O₂, CF₄ and CHF₃ Gas Ratios, Shogo Uehara, P. Wood, SAMCO Inc., USA

Surface wettability of materials is influenced by surface energy as well as surface roughness, and the surface energy can be modulated by changing surface chemistries. Plasma treatment is one of the techniques to control the surface chemistries, and is used for the surface wettability modulation of materials in device fabrication. However, few papers have investigated the selectivity of plasma treatment effects on the wettability modulation between two or more materials in a batch process [1], [2]. In this research, the roles of reactive species of oxygen- and fluorine-based plasma chemistries were investigated for selective surface wettability modulation of materials. Using a reactive ion etching system (RIE-10NR, SAMCO Inc.), various plasma chemistries with several gas flow ratios of O₂, CF₄ and CHF₃ were formed over inorganic (silicon and glass) and organic (polyimide and PMMA) materials. Static contact angle and XPS were utilized to study the surface wettability and surface chemical bonding structure before and after plasma treatment. The contact angle was also investigated over the course of 20+ days storage in a N₂-purged desiccator in order to examine the stability of the wettability modulation effects.

With a gas flow ratio adjustment, a large contact angle contrast was observed between the materials. In pure CF₄ plasma treatment, the inorganic materials showed contact angle reduction after the plasma treatment, while the organic materials showed significant contact angle increase. XPS analysis revealed that the silicon surface retained 9.5 at.% fluorine, while 35.4 at.% fluorine was observed on PMMA surface after the pure CF₄ plasma treatment. This indicates that the PMMA wettability modulation was caused by the fluorine-containing chemical functional groups at the outermost surface layers.

After ageing the samples in storage, the contact angle contrast was gradually decreased due to a contact angle increase of the inorganic materials after pure O₂ or CF₄ plasma treatment. On the other hand, samples processed in a plasma using a gas mixture of CF₄ and CHF₃ showed stable contact angles. This difference is attributed to the existence of a thin fluorocarbon layer deposited during the CHF₃ based plasma treatment.

These results indicate that the reaction of oxygen and fluorine-containing active species on substrate surfaces influences wettability modulation effects of materials and also the stability of these effects.

[1] P. Svarnas, L. Yang, M. Munz, A.J. Edward, A.G. Shard, and J. W. Bradley., *J. Appl. Phys.* **107**, 103313 (2010)

[2] H. Inui, K. Takeda, K. Ishikawa, T. Yara, T. Uehara, M. Sekine, and M. Hori., *J. Appl. Phys.* **109**, 013310 (2011)

TF-TuP18 Annealing Behaviors for High-k ZrO₂ Grown on Ge, Deuk-Young Kim, W.-C. Yang, K.-B. Chung, S. Lee, Dongguk University, Republic of Korea; M.-D. Kim, Chungnam National University, Republic of Korea; H. Lee, N. An, Y. Lee, Dongguk University, Republic of Korea

The thermal annealing behaviors of electrostatic properties for high-k ZrO₂ layers were investigated. ZrO₂ layers were grown on p-type Ge substrates at 500°C by RF magnetron sputtering. To reduce the native defect density in ZrO₂, we adopted the higher oxygen-partial pressure (*i.e.*, O₂/Ar > 1). The RF power was 150 W, and the growth time was 20 min. After the growth of

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ZrO₂, the samples were annealed at 600-700°C in Ar ambient by using a rapid thermal annealing method. For the capacitance-voltage characteristics, the as-grown sample exhibited its maximum electrostatic capacitance (*i.e.*, C_{max} at the accumulation mode) to drastically decrease with increasing the frequency of ac signals. However, the dielectric characteristics of ZrO₂ were much improved after thermal annealing at temperatures above 600°C. Particularly, the magnitude of C_{max} was increased by more than 3-times after annealing at 600°C. In addition, C_{max} was much stabilized at wide frequency ranges. For higher annealing temperatures, the above feature became more significant. This indicates that the defects in ZrO₂ could be effectively eliminated by thermal annealing; particularly, at temperatures above 600°C. Through x-ray photoelectron spectroscopy measurements, we confirmed the above thermal-annealing behaviors to arise from the stabilization of Zr-O bonds due to the interdiffusion of Ge at the interface between ZrO₂ and Ge. The best electrostatic permittivity was more than 20, and the equivalent-oxide-thickness was less than 4 nm. Owing to the improvement of interface bonding structures at ZrO₂/Ge, the dielectric breakdown field was increased up to ~1 MV/cm. The results suggest that sputter-grown high-k dielectric ZrO₂ can be utilized for Ge-based MOS devices, and that thermal annealing is effective to improve the dielectric characteristics of ZrO₂.

TF-TuP19 Surface Energy Controlled Patterning of Carbon Nanomaterials for Electronic Devices, *SungMin Lee*, S.G. Yoon, Chung Ang university, Republic of Korea

Comparing with traditional coating technique, solution-based patterning method has its strength in process cost as it can be proceeded in room temperature and pressure condition. Because of its merits, solution-based patterning method has been actively exploited in various application such as field effect transistor, flexible transparent electrode, solar cell. However there are some drawbacks in these techniques: controllability of pattern thickness, high material consumption, extended process time. In our study, we design high speed, low cost, thickness controllable, solution-based patterning technique by controlling surface energy of substrate and demonstrate its application to electronic device. Furthermore we also study application for deposition of nano particles. Solution based metal deposition process is very competitive to currently used method vacuum based deposition in point of cost and processing time.

TF-TuP20 Physicochemistry of Chemical Bath Deposited ZnS Films at Near Ambient Temperatures, *Irving Gonzalez*, *I. Oliva Arias*, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, Unidad Mérida, Mexico

Zinc sulfide (ZnS) is a semiconductor material that has increased its importance in recent years due to its wide range of applications. For solar applications, ZnS has shown great potential as optical window for developing high efficiency CIGS solar cells. Chemical bath deposition (CBD) technique has been used for several years to obtain ZnS thin films. Deposition time, bath temperature and chemical reagents concentration are some parameters that have been investigated through time. However, there are scarce reports conducted to understand the physicochemistry of the CBD technique. In recent years, the development of physicochemical tools such as the species distribution diagrams (SDDs) and the solubility curves (SCs) gives light to understand the growth mechanisms to obtain the growth parameters for depositing high quality ZnS films. Nevertheless, most of these contributions have been carried out at temperatures between 60 and 90 °C leaving aside near ambient temperatures. Research on these conditions could bring benefits for industrial applications. This work aims to provide the physicochemical conditions in which high quality ZnS films at near ambient temperature can be obtained. A chemical bath containing ZnCl₂, KOH, NH₄NO₃, and SC(NH₂)₂ as chemical reagents was used for depositing the ZnS films. Temperatures of 25, 40, and 55 °C were selected for films deposition. The SDDs and SCs were obtained for each temperature at three conditions (by varying [SC(NH₂)₂]) in order to study the influence of the chemical species onto the ZnS formation. The $R=[HS^-]/[Zn(OH)_2^{2-}]$ ratio as a main parameter for CDB-ZnS films deposition was investigated. The SCs show that higher values of R assure enough amount of HS⁻ ions and better conditions for depositing ZnS, avoiding the formation of Zn(OH)₂. The SDDs show that at near ambient temperatures the ZnS formation is attributed to the Zn(OH)₃⁻ and Zn(OH)₄²⁻ complexes and the HS⁻ ions.

ZnS films deposited onto glass substrates were characterized by x-ray photoelectron spectroscopy, atomic force microscopy, x-ray diffraction, and spectrophotometry techniques. Results indicate that when the R ratio and temperature are increased, better stoichiometry is obtained. The Zn is

bonded mainly to hydroxide ions for lower R ratios, but when R increases bonding changes to S ions. The band gap energy of films was measured between 3.4 and 3.7 eV. The lower values are due to that samples contained ZnS and Zn(OH)₂ because of the low value of R. ZnS films deposited at 55 °C presents a (111) cubic orientation (sphalerita); meanwhile, films deposited at 25 °C present an orthorhombic orientation due to the Zn(OH)₂ formation.

TF-TuP22 Improvement of Detection Limit for Hydrogen by High-resolution ERDA, *Daiichiro Sekiba*, *I. Harayama*, *T. Tamura*, *Y. Watahiki*, *K. Tsujita*, University of Tsukuba, Japan

Recently high-resolution ERDA (Elastic Recoil Detection Analysis) is installed in UTTAC (University of Tsukuba, Tandem Accelerator Complex) in Japan, which consists of a 90 degree magnetic sector lens and a position sensitive detector (PSD). High-resolution ERDA is one of the powerful tools to obtain the depth profile of hydrogen with the depth resolution of sub-nanometer, while its detection limit for hydrogen has not been good enough to discuss the hydrogen concentration at interfaces made on semiconductor substrates. The main origins of noise, which makes the detection limit worse, are dark current in the micro-channel plate (MCP) used as PSD and stray particles in the vacuum chambers. We found out that the dark current can be distinguished from the desirable signal by a coincidence measurement using two MCPs. The two MCPs detect the recoil of hydrogen ion and secondary electrons from stopper foil, respectively. The dark current noise can be suppressed under the 1% to take the coincidence not only of the detection time but also the positions on the two MCP. The second coincidence can remove the chance coincidence of two dark current signals. We have also tried to develop a new PSD based on solid state detector (SSD) usually made by silicon. In this case the PSD has the energy resolution of detected particle, so that, we can distinguish also the stray particles. We report the recent achievement using these new detectors.

TF-TuP23 Investigation of the Low Temperature Formation of DLC Thin Film by Ion Assistance, *Tsuyoshi Inoue*, *I. Takano*, Kogakuin University, Japan

DLC is amorphous carbon that contains a significant fraction of sp² and sp³ bonds. It is known that their films show a low friction coefficient and its high hardness is applied in a mechanical field such as cutting tools or frictional parts. DLC films were formed by the ion beam assisted evaporation method in the early 1970's, and after that have been manufactured by various methods. The film formation of DLC is performed in a high temperature basically. On the contrary the film formation in the negative temperature is hardly performed. In our experiment, an N₂⁺ ion beam to the substrate was irradiated with introduction of a hydrocarbon gas in a vacuum chamber. This deposition method has some independent parameters from the film formation condition in comparison with other dry process methods. Therefore this method is anticipated in appearance of superior characteristics such as a high adhesion. In our previous research, iced water was used to urge adsorption of a hydrocarbon gas on the substrate temperature control. It was suggested that adsorption of a hydrocarbon gas depended on the substrate temperature.

In this study, the control of a substrate temperature was performed by using the LN₂ and heater controlled by PID. Stainless steels (304SS), Si plates and slide glasses were prepared for sample substrates. The formation conditions of DLC films were changed from -150 degrees to 25 degrees and were an N₂ gas pressure of 4x10⁻³ Pa under an ultimate pressure of 6x10⁻⁴ Pa. C₇H₈ as an ambient gas was introduced by to determine the gas ratio using QMS. The ion beam irradiation was performed with 1 kV in an accelerating voltage and 30 μA/cm² in a current density, through an exposure time of 3600 s. The film structure was determined by Raman spectroscopy and the thickness was measured using a spectrometer of a fiber injection type. Vickers hardness and the friction coefficient were measured by a micro hardness tester and a tribotester of a ball-on-disk type, respectively. The tribotester was set with an Si₃N₄ ball as a counter material and the examination was carried out with a constant load of 0.98 N until a sliding distance of 100 m.

I_b/I_g ratios of DLC thin films measured by Raman spectroscopy showed the higher sp³ contents at -100°C of a cooling substrate temperature. The suitable mechanical property of the DLC films was obtained by a temperature of -100 degrees and the friction coefficient was 0.20 at a distance of 100 m.

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TF-TuP24 Understanding the Effect of Nitrogen Plasma PulseTime on Plasma Assisted Atomic Layer Epitaxy of InN Monitored by Real Time GISAXS, *N. Nepal, V.R. Anderson, S.D. Johnson, D.J. Meyer, B.P. Downey*, U.S. Naval Research Laboratory, USA; *Z.R. Robinson*, The College at Brockport SUNY, USA; *K.F. Ludwig*, Boston University, USA; **Charles Eddy, Jr.**, U.S. Naval Research Laboratory, USA

A challenge to the development of III-N semiconductors (AlN, GaN and InN and their ternaries and quaternaries) is the requisite heteroepitaxy on foreign substrates, compounded by increasing device structure complexity. To address ternary layer miscibility gaps, substrate versatility and low strain heterojunctions the growth temperature must be reduced. Recently, plasma assisted atomic layer epitaxy (PA-ALE) has been used to grow InN and In containing ternaries at temperatures ≤ 260 °C [1-2]. At these growth temperatures, ad-atom mobility is low and understanding the mechanism of nucleation and growth is critical for improved material quality. Traditional ultra-high vacuum *in situ* monitoring methods are impractical as the growth pressure for PA-ALE is too high (1-500 mTorr). High intensity coherent x-rays, such as from a synchrotron light source, offer an effective alternative to study PA-ALE nucleation and growth process.

Here we present *in situ* studies of the effect of nitrogen plasma pulse time on temporal evolution of the growth surface for InN growth on a-plane sapphire at 250 °C as revealed by real-time grazing incidence small angle x-ray scattering (GISAXS) measurements. *Ex situ* atomic force microscopy, x-ray photoelectron spectroscopy and reflectivity, and Hall measurements were employed to characterize the resulting films.

GISAXS measurements show that H₂ plasma cleaning roughens the substrate surface, but this same surface is recovered during subsequent N₂ plasma treatment. During the initial cycles of growth the diffuse specular reflection broadens and correlated peaks (CPs) evolve along the native wing with different correlated length scales (CLSs). For a nitrogen plasma pulse time (t_p) of 15 seconds, CPs have two different CLSs of 33.36 and 8.38 nm. With increasing t_p to ≥ 20 s, a single CP evolves and the longest CLS of 11.22 nm is for $t_p = 25$ s. Additionally at $t_p = 25$ s, the growth rate is largest (0.035nm/cycle – consistent with self-limited growth [1]) with root mean square surface roughness and carbon impurity at or below instrument sensitivity limits. Thus the nature of GISAXS CP CLS directly correlate with the material quality. For the $t_p = 25$ s film, measurements show electron sheet carrier density and resistance of 3.5×10^{13} cm⁻² and 3.59 kW/sq, respectively. An electron mobility of 50 cm²/V-s is measured for a 5.6 nm thick InN film, which is higher than the reported value of 30 cm²/V-s for a 1300 nm thick InN grown by molecular beam epitaxy directly on sapphire [3].

[1] Nepal et al., Cryst. Growth and Des. **13**, 1485 (2013).

[2] Nepal et al., Thin Solid Films **589**, 47 (2015).

[3] Kuo et al., Diamond & Related Materials **20**, 1188 (2011).

TF-TuP25 Adsorption Isotherms and the Mean Residence Time of Hydrogen Physisorbed on a Copper Surface, *Yuki Kato*, Gakushuin University, Japan; *K. Kawahara, H. Yamazaki, K. Yamakawa, I. Arakawa*, Gakushuin University

In order to achieve ultimate pressure in extreme high vacuum (XHV) region, it is necessary to exhaust hydrogen which is the dominant residual gas in XHV. Cryopumping has been regarded as an effective mean to exhaust hydrogen and widely used in a variety of vacuum systems. Several studies have reported unexpected outcomes in either the static or the dynamic characteristics of H₂ cryopumping, which is likely due to incident thermal radiation, the diffusion of H₂ in porous adsorbents, or the lack of equilibrium of the H₂ distribution on a surface [1,2,3], but its origin has not been clarified yet. The adsorption isotherms measured in the pressure range below 10⁻⁸ Pa were far from being sufficient for quantitative analysis. This is mainly due to the difficulty in determining the density of H₂ physisorbed on a cold surface. In the present study, we utilized electron stimulated desorption (ESD) and time-of-flight (TOF) techniques to determine the density of H₂ physisorbed on a copper surface [4]. The ejection of H⁺ is mainly caused by the dissociative ionization of the H₂ molecule physisorbed. We assume that, in submonolayer range, the ESD yield of H⁺ ions is proportional to the surface density of physisorbed H₂. Using the above methods, we measured the adsorption isotherms of submonolayer H₂ at equilibrium pressures between 10⁻¹⁰ and 10⁻⁶ Pa in the temperature range of 3.8 - 6.5 K. By monitoring the time development of the H⁺ ESD yield in the transition state approaching adsorption equilibrium, we also determined the mean residence time of physisorbed H₂ at various temperatures. One example of the transition measurements, where the initial H₂ coverage is less than 0.001 (the equilibrium pressure as low as

6×10⁻¹¹ Pa) and the final coverage is 0.3 which is in equilibrium with the pressure of 3×10⁻⁸ Pa, gives the mean residence time of 4400 s.

[1] C. Benvenuti, R. S. Calder, and G. Passardi, J. Vac. Sci. Technol. **13**, 1172 (1976).

[2] I. Arakawa and Y. Tuzi, J. Vac. Sci. Technol. **A4**, 293 (1986).

[3] I. Arakawa, J. Vac. Sci. Technol. **A4**, 1459 (1986).

[4] I. Arakawa, H. Shimizu, T. Kawarabuki, K. Yamakawa and T. Miura, J. Vac. Sci. Technol. **A33**, 021602 (2015).

TF-TuP26 Far- and Mid-infrared Spectroscopy of Amorphous H₂O Ice Films formed by Matrix Sublimation Method, *Natsumi Suzuki, G. Shimizu, H. Nasu, R. Tsuboi, K. Yamakawa, I. Arakawa*, Gakushuin University, Japan

To reveal the nature of the hydrogen bond is important in understanding the physical properties of gaseous, liquid and solid water. Since water clusters are the simple hydrogen bond systems, our group has investigated their structures and vibrational states in a previous study using infrared absorption spectroscopy combined with the matrix isolation technique.¹ We adopted CH₄ as the matrix species because its infrared active property enables us to investigate the structure of the matrix itself. In a recent study, Kouchi et al. investigated amorphous ice (ASW) formed by the matrix sublimation method showing that the ice was different in structure from vapor-deposited ASW.² Using an apparatus we have constructed for the purpose of spectroscopy in the range from 100 to 600 cm⁻¹ under ultrahigh vacuum, we measured far-infrared spectra of matrix-sublimated ice (MSI) in addition to those in the mid-infrared region.

We used two independent apparatuses for far- and mid-infrared spectroscopy. Each apparatus was equipped with a continuous-flow helium cryostat on which the gold substrate is held by a copper holder and was evacuated to ultrahigh vacuum condition. A gas mixture of CH₄ and H₂O was deposited onto the substrate at 11 K. Spectra were recorded in the reflection configuration with a liquid-helium-cooled silicon bolometer for the far-infrared region and a HgCdTe detector for the mid-infrared one.

In the mid infrared spectrum at 10 K, we observed a sharp peak at 3010 cm⁻¹ caused by the ν_3 vibrational mode of CH₄ and a broad band from 3080 to 3600 cm⁻¹ assigned to bonded-OH stretching of ASW. As the temperature was increased, the CH₄ peak decreased and the ASW band grew. At 60 K, where CH₄ was completely desorbed from the substrate, the broad band changed in structure and showed a characteristic plateau extending from 3080 to 3600cm⁻¹, which implies the formation of MSI. In the far-infrared region, a broad band ranging from 140 to 310 cm⁻¹ also appeared at 60 K. In addition, these spectral features were almost invariant until 115 K. The drastic changes of the spectra corresponding the translation from ASW to crystalline ice were observed in both the mid- and far-infrared regions at 140 K. Comparing these spectra with those of vapor-deposited ASW in detail, we will discuss the structure of MSI.

References

[1] K. Yamakawa et al., AIP Advances **6**, 075302 (2016).

[2] A. Kouchi et al., Chem. Phys. Lett. **685**, 287 (2016).

TF-TuP28 The Importance of the Empirical Modeling of the Background Signal in XPS Data for Calculating the Composition of Transition Metal Compounds, *Alberto Herrera-Gomez*, CINVESTAV-Unidad Queretaro, Mexico

The increasing scope of transition metal compounds in nanofilm and nanoparticle technology invigorates the need for an accurate characterization of these materials with X-ray photoelectron spectroscopy (XPS). It is interesting to notice that, to the knowledge of the authors, there is not a single published report about the peak fitting of, e.g., metallic iron or metallic zinc. It was not but until recently that the first calculation, through XPS, of the composition of iron¹ and cobalt² oxides was reported. The scarcity of this type of reports is related to the analytical difficulty associated to fitting transition-metal photoemission peaks: they present a steeply rising background³ and a complex multiplet and satellite structure.⁴ In this paper we will describe the analysis tools required for modeling complex background and line-shapes appropriate for composition analysis from XPS data.

¹ M.B. Sanchez, J.A. Huerta-ruelas, D. Cabrera-german, and A. Herrera-Gomez, (2016).

² D. Cabrera-German, G. Gomez-Sosa, and A. Herrera-Gomez, Surf. Interface Anal. **48**, 252 (2016).

³ G.C. Allen, M.T. Curtis, A.J. Hooper, and P.M. Tucker, J. Chem. Soc. { } Dalt. Trans. 1525 (1974).

Tuesday Afternoon Poster Sessions, December 13, 2016

⁴ R.P. Gupta and S.K. Sen, Phys. Rev. B **10**, 71 (1974).

TF-TuP29 Anlnsys On Transport-Current Characteristics According To The Material Properties Of The Outer Layer Of RebcO Thin-Film Superconducting Wire Having Composite Structure, Ho-Ik Du, S.C. Yang, H.G. 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-TuP30 Electric Field Strength in Vapor Deposited CO Films determined from Induced Infrared Absorption of H₂, Koichiro Yamakawa, A. Ishibashi, I. Arakawa, Gakushuin University, Japan

Field and co-workers recently reported that the strong electric field, whose strength may exceed 10^8 V/m, exists in a vacuum-deposited film of dipolar molecules and attributed it to the spontaneous alignment of the molecular axes [1-4]. They have utilized two experimental techniques: the direct measurement of the electrostatic potential at the film surface for N₂O [1] and reflection-absorption infrared spectroscopy for N₂O and CO [2-4]. In the latter method, the infrared absorption band due to the intramolecular stretching vibration split into two peaks owing to the coupling with phonons in the film, so that the temperature dependence of the split was attributed to the intense electric field. In order to judge the validity of their argument, one needs experimental data obtained by other techniques as well as theoretical models to explain the mechanism where such thermodynamically unstable film structure is realized simply after vapor deposition onto a cold substrate. In the present study, we directly determine the strength of the electric field in CO films using induced infrared absorption due to H₂.

A sample chamber equipped with a liquid-helium continuous-flow cryostat was in the ultra-high vacuum condition after baking at 373 K for 24 hours. The substrate was a gold plate mechanically fixed on a copper block placed at the end of the cryostat. Temperatures of the substrate were measured with a silicon diode. We prepared two kinds of samples on the substrate maintained at 5 K; I) CO and H₂ were premixed in a gas handling with the molar ratio of CO/ H₂ = 10 and were deposited; II) We condensed two gasses alternatively through different variable leak valves to form their periodic films, where the thickness of each CO (H₂) film was ~40 (1) monolayer. Fourier transform infrared spectroscopy was performed with a HgCdTe detector in the reflection configuration.

For both the kinds of samples, infrared spectra showed a strong absorption peak at 2142 cm⁻¹ due to the CO stretch along with satellite features at 2047 and 2092 cm⁻¹. In addition, weak absorption peaks were found in the H₂ stretch region. We will give detailed assignment of these peaks and will determine the strength of the electric field in each film from the infrared absorption intensity of the H₂ stretch. Temperature dependence of the field strength will be also discussed.

[1] R. Balog et al., Phys. Rev. Lett. **102**, 073003 (2009).

[2] J. Lasne et al., Phys. Chem. Chem. Phys. **17**, 20971 (2015).

[3] J. Lasne et al., Phys. Chem. Chem. Phys. **17**, 30177 (2015).

[4] A. Rosu-Finsen et al., Phys. Chem. Chem. Phys. **18**, 5159 (2016).

Thin Films

Room Makai - Session TF-TuE

Growth & Characterization of 2D Materials

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

5:40pm **TF-TuE1 Characterizing 2D-materials and Hetero-structure of MoS₂ and WSe₂ by Spectroscopic Imaging Ellipsometry**, **Sebastian Funke**, Accurion GmbH, Germany; **U. Wurstbauer**, **E. Parzinger**, **B. Miller**, Walter Schottky Institute and Physics Department, TU München; **P. Thiesen**, Accurion GmbH, Germany

Characterizing 2D-materials and Hetero-structure of MoS₂ and WSe₂ by Spectroscopic Imaging Ellipsometry

Sebastian Funke¹, **Ursula Wurstbauer^{2,3}**, **Eric Parzinger^{2,3}**, **Bastian Miller^{2,3}**, **Peter H. Thiesen¹**

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3. Nanosystems Initiative Munic 80799, Germany

By stacking different 2D-materials into hetero-structures new optoelectronic devices are formed[1,2]. The advantage of these new hetero-structures compared to conventional devices may be superior material properties and its significant lower height. For the design of efficient hetero-structures the knowledge of the materials properties is essential. We show that spectroscopic imaging ellipsometry (SIE) is capable of measuring the optical properties of different types of 2D-materials. With the lateral resolution down to 1 μm SIE is able to localize and characterize small flakes of e.g. 2D-materials. It also enables the characterization of stacked materials.

In the talk we present spectral investigations on Molybdenum-disulphide from the UV- to NIR. To describe the dispersion for MoS₂ an anisotropic approach is shown[3]. It reveals an anisotropic behaviour in the out-of-plane direction. Further, investigations on a hetero-structure of MoS₂ and WSe₂ are done as seen in Figure 1. All regions can be measured simultaneously, so a comparison of the spectral response of the single 2D-materials can be compared to the stacked response. Spectral investigations around the bandgap of MoS₂ at around 650 nm will be shown and discussed for the overlapping and non-overlapping regions.

Figure 1: Heterostructure of MoS₂ and WSe₂. Green area denotes the overlapping hetero-structure.

References

[1] L. Britnell, R. M. Ribeiro, A. Eckmann, R. Jalil, B. D. Belle, A. Mishchenko, Y.-J. Kim, R. V. Gorbachev, T. Georgiou, S. V. Morozov, and others, *Strong light-matter interactions in heterostructures of atomically thin films*, *Science*, **340**, 1311–1314, (2013).

[2] G.-H. Lee, Y.-J. Yu, X. Cui, N. Petrone, C.-H. Lee, M. S. Choi, D.-Y. Lee, C. Lee, W. J. Yoo, K. Watanabe, T. Taniguchi, C. Nuckolls, P. Kim, and J. Hone, *Flexible and Transparent MoS₂ Field-Effect Transistors on Hexagonal Boron Nitride-Graphene Heterostructures*, *ACS Nano*, **7**, 7931–7936, (2013).

[3] S. Funke, B. Miller, E. Parzinger, A. Holleitner, P. H. Thiesen, U. Wurstbauer, *Spectroscopic Imaging Ellipsometry of MoS₂*, *Journal of Physics: Condensed Matter*, accepted July 2016

6:20pm **TF-TuE3 2D vs. 1D Structures at Stepped Si Surfaces and in Organic Molecules**, **Franz Himpel**, University of Wisconsin Madison, USA; **J.M. Garcia Lastra**, Technical University of Denmark, Denmark; **A. Rubio**, Universidad del Pais Vasco; **I. Boukahil**, University of Wisconsin Madison, USA; **R. Qiao**, Advanced Light Source, LBNL, USA; **S.C. Erwin**, Naval Research Laboratory, USA; **I. Barke**, University of Rostock, Germany

INVITED

The dimensionality of a structure plays an important role in its electronic properties, as demonstrated recently by a variety of layered compounds who behave very differently as single layer. This raises the question what happens when reducing the dimensionality further to one-dimensional atomic chains - the finest conceivable nanowires. Theory predicts exotic behavior, such as the elusive Luttinger liquid. Strong correlations are established between electrons propagating along an atomic chain, since they are not able to avoid each other. One might also expect reduced dielectric screening and higher chemical activity in 1D structures due to the reduced number of neighbors.

This talk focuses on two types of atomically-precise structures that bridge the gap between 2D and 1D. Both their preparation and their electronic structure are considered. Stepped surfaces can be prepared on vicinal Si with great precision (less than one kink in 10⁴ edge atoms), since the high energy cost of a broken Si-Si bond leads to stable surface reconstructions. These can be decorated with a wide variety of metal atoms, frequently leading to metallic wires on a semiconducting substrate. The transition from 2D to 1D is explored by varying the step spacing. A variety of interesting phases have been found in these wires, such as charge density waves [1], spin-polarized energy bands, and an ordered array of spin-polarized Si edge atoms [2].

The other approach uses organic molecules to compare π -bonded carbon sheets and chains [3]. First-principles calculations show that 1D wires exhibit very simple molecular orbitals which mimic the overtones of a vibrating string, while 2D structures form more complex orbital patterns related to the modes of a drum. The dielectric screening is found to scale with the number of atoms in a molecule rather than the number of neighbor atoms, suggesting delocalized screening.

Looking into the future, we discuss molecular complexes combining 2D and 1D structures with atomic precision, such as the donor- π -acceptor complexes used in dye-sensitized solar cells [4]. Computational screening of the energy levels for thousands of dye molecules provides the blueprint for tandem solar cells where two π -absorbers are connected by molecular wires [5].

[1] Paul C. Snijders and Hanno H. Weitering, *Rev. Mod. Phys.* **82**, 307 (2010)

[2] Steven C. Erwin and F. J. Himpel, *Nature Communications* **1**:58 (2010).

[3] J. M. Garcia-Lastra et al., *J. Phys. Chem. C* **120**, 12362 (2016).

[4] A. Yella et al., *Science* **334**, 629 (2011); Ioannis Zegkinoglou et al., *J. Phys. Chem. C* **117**, 13357 (2013).

[5] Kristian B. Ørnsø et al., *Chemical Science* **6**, 3018 (2015).

7:00pm **TF-TuE5 Probing Atomic Structure of 2D TMDs by High Resolution STEM**, **Moon Kim**, **Q. Wang**, **J. Wang**, The University of Texas at Dallas, USA

As the scaling of various functional devices continues, the future of these devices will rely on new class of materials. Research in graphene and the methodology of preparing ultrathin layers has led to the exploration of other 2D materials. In particular, single layers of transition metal dichalcogenides (TMDs) with lamellar structures similar to those of graphite have drawn significant attention because of their tunable bandgaps. TMDs exhibit diverse properties that depend on their composition: semiconductors, semimetals, metals, or superconductors. TMD properties also strongly depend on the crystalline structure, including the number and stacking sequence of layers. In exploring and developing these emerging materials, nanoscale characterization becomes ever more important. In particular, high resolution electron microscopy-based techniques now are capable of analyzing these 2D nano-materials and devices with better than 0.1 nm resolution. Here, we present our recent studies on the characterization of 2D layered materials by means of Scanning Transmission Electron Microscopy (STEM), specifically High Angle Annular Dark Field (HAADF) imaging and *in-situ* Transmission Electron Microscopy (TEM). We have identified the atomic arrangements and defects in single layer MoS₂, 2H stacked TMDs, 1T stacked TMDs, and distorted 1T stacked TMDs by HAADF STEM imaging. The location and nature of individual atoms, defects, phase transformation, and layer by layer shearing of 2D crystals will be presented and discussed in detail.

7:40pm **TF-TuE7 Synthesis of Transitional Dichalcogenide Films by Chemical Transformations of Thin Films**, **Shaul Aloni**, Lawrence Berkeley National Laboratory, USA; **C.T. Chen**, **T.R. Kuykendall**, Lawrence Berkeley National Laboratory, USA; **C. Kastl**, Lawrence Berkeley National Laboratory, USA; **T.P. Darlington**, **P.J. Schuck**, **N.J. Borys**, Lawrence Berkeley National Laboratory, USA; **A.M. Schwartzberg**, Lawrence Berkeley Lab, USA

The promising properties of transition metal chalcogenides (TMD's) continue to inspire great deal of research on optical and electronic devices. However, the progress in this field is limited by challenges in materials synthesis and device fabrication. In this work we present a new approach for the synthesis of TMD's with digital control of layer thickness. This method utilizes chemical transformation of solid thin films of oxides deposited with submonolayer precision by ALD. Following their deposition the films are exposed to a chalcogen containing gas resulting in smooth and continuous TMD films whose thickness is defined by the thickness of the ALD deposited oxide film.

Tuesday Evening, December 13, 2016

Typical experiments involve deposition of metal oxide, WO₃ or MoO₃, followed by a short conversion procedure involving annealing of the oxide film in presence of a chalcogenation agent, *e.g.* hydrogen disulfide gas or organochalcogen vapor. Typical composition of the gas phase is equivalent to 1% of H₂S in argon. However, precise control of water content in the gas phase composition provides means for controlling the reaction mechanism. At low water vapor content (2-10 ppm) metal oxide films are chalcogenized in place with the thickness of the continuous TMD film defined by the thickness of the oxide layer. The resulting WS₂ thin films are nanocrystalline, and moderately luminescent. At higher water concentrations (> 200 ppm) the process is dominated by vapor transport. Under these conditions, the volatility of the oxide species is significantly enhanced, resulting in minimal residual metal disulfide after growth. Under optimized conditions, highly luminescent, triangular monolayer WS₂ and MoS₂ islands with good island-to-island uniformity can be grown directly on the previously metal-oxide-coated substrate or onto a bare substrate placed downstream of a source. Carefully controlled humidity (~ 100 ppm) consistently produces high quality highly luminescent triangular WS₂ and MoS₂ islands.

The chemical transformation of solid films by a gas phase precursors offers additional benefits. In addition to precise control of thickness and compatibility with many transition metals, it is also compatible with any substrate that is not adversely affected by the chalcogenation agent. We present deposition of WS₂ on variety of substrates including amorphous SiO₂ and Si₃N₄ as well as SiC, TiO₂ and GaN. Moreover, we suggest that the use of controlled amounts of water vapor is a new knob by which to tune growth of these materials, and these results demonstrate a route to improved material quality and unprecedented reproducibility of chemical vapor transport of many transition metal dichalcogenides.

8:00pm **TF-TuE8 Growth and Characterization of hBN/Graphene Heterostructures on Metal Substrates**, *Boris Feigelson*, U.S. Naval Research Laboratory, USA; *K. Sridhara*, Texas A & M, USA; *J.K. Hite*, U.S. Naval Research Laboratory, USA; *A. Nath*, George Mason University; *J.A. Wollmershauser*, U.S. Naval Research Laboratory, USA

The development of 2D hBN/graphene heterostructures is still in the early stages and largely depends on possibility to grow these heterostructures as well as on rapid and accurate characterization of the grown hBN/graphene layers. Along with graphene, atomically thin two dimensional hexagonal boron nitride (2D hBN) 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.

In this work, hBN/graphene films were grown by atmospheric-pressure CVD on metal substrates (mainly Cu, but also Cu-Ni alloys). A vertical custom-made CVD reactor was used to grow 2D hBN/graphene films. The design of the vertical reactor allows the simultaneous growth of a few samples of hBN/graphene layers on different substrates in the same run.

As it was shown in our previous work [1], 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) 2D h-BN.

The IR-active out-of-plane vibrational mode was exploited to identify and characterize 2D hBN in grown heterostructures directly on metal substrates, while graphene was characterized by micro Raman spectroscopy. Combining FTIR and Raman spectroscopy allows express and in-depth characterization of hBN/graphene heterostructures directly on metal substrates used for growth.

The approach also provides an opportunity to determine which growth conditions lead to the absorption of foreign species on the substrate prior to the heterostructure deposition. Such interfacial layers were shown to result in easily-recognizable shifts in the A_{2u}(LO) peak. The degree to which the interaction of the hBN layer with the substrate is uniform and homogenous can also be assessed easily by examining the width and fine structure of the A_{2u}(LO) band.

B. N. Feigelson, V. M. Bermudez, J. K. Hite, Z. R. Robinson, V. D. Wheeler, K. Sridhara, and S. C. Hernandez, *Nanoscale* **7**, 3694 (2015)

Thin Films

Room Makai - Session TF-WeM

Plasma-based Film Growth, Etching, & Processing

Moderator: Davide Sangiovanni, Linköping University, Sweden

8:00am TF-WeM1 Flexible Electrochromic Electrodes on the Substrate of Crystalline Indium Tin Oxide with Graphene, Yekyung Kim, S.J. Lee, J.W. Seo, S.H. Han, H. Kim, Korea Electronics Technology Institute (KETI), Republic of Korea

Electrochromic technology is recently getting attention due to the requirement of the energy saving technology and the advancement of paired technology which shows synergistic effect together, such as light-responding mirrors, smart window, light shutter, etc. Nickel oxide are the most well-known anodic coloration material which is generally used as a counter electrode with enhancing coloration efficiency together with tungsten oxide, the main determinant of the coloration efficiency of whole device. The enhancement of electrochromic and cyclic stability of the electrochromic device is performed, in this study, by conditioning of nickel oxide with various methods of tungsten alloying, optimization of sputtering condition, lithiation, and so on. Also, to concrete a flexible electrochromic device, transparent conducting oxide should be deposited on a plastic substrate under the electrochromic layer. In this study, nickel and tungsten oxide were deposited on the crystalline indium tin oxide (c-ITO)/graphene/polyethylene terephthalate (PET) film. The thermally and mechanically stable graphene helps to prepare c-ITO on PET film which is hardly fabricated due to the high temperature requirement for ITO crystallization. The prepared flexible electrochromic electrodes on c-ITO/graphene/PET showed reasonable coloration performance. Also, the electrochemical and cyclic properties of electrochromic full-cell were determined.

8:20am TF-WeM2 Maximizing Retention of Complex Chemical Functionality in Plasma Polymers Via the Alpha-Gamma Transition, Andrew Michelmore, S. Saboohi, B.R. Coad, University of South Australia, Australia; *R.D. Short,* University of Lancaster, UK; *H.J. Griesser,* University of South Australia, Australia

There is increasing need for fabrication of thin polymeric films with complex chemical functionality for a variety of applications including cell therapies, biosensing, microelectronics and as platforms for surface initiated atom-transfer radical polymerization (ATRP). Conventional polymerisation techniques are not suitable in many instances as control of film thickness and topography is difficult. Plasma polymerisation is a technique which can overcome these issues, but has typically suffered from difficulty in retaining chemical structure due to fragmentation in the plasma phase and/or ion bombardment on the surface.

We have shown that pressure plays a critical role in plasma processes. By tuning the plasma from collisionless to collisional sheaths (the alpha to gamma transition) the chemistry of the plasma and the plasma polymer are drastically changed [1]; in gamma mode, the plasma chemistry is biased towards protonated precursor ions and the contribution of ions to the deposit increases. For example, we have studied deposition of ethyl α -bromoisobutyrate (EBIB) for fabricating surfaces for initiating ATRP [2]. This requires that the intact α -bromoisobutryl structure be retained on the surface of the plasma polymer. Using plasma phase mass spectrometry we show that at the transition from alpha to gamma mode protonated EBIB are formed which arrive at the surface intact and dominate the deposition process. This results in high retention of groups capable of initiating ATRP. High pressure also limits the ion energy, such that ions can be 'soft landed' and do not scramble chemical structures on the surface by ion bombardment.

More recent results on a family of ester compounds will be presented which highlight the critical roles of pressure, power and ion energy. Methods for predicting optimum conditions will also be discussed. These results open possibilities to fabricate functionalized surfaces with higher retention of chemical structure than has been possible previously.

1. Saboohi, S.; Jasieniak, M.; Coad, B.R.; Griesser, H.J.; Short, R.D.; Michelmore, A.; Comparison of Plasma Polymerization under Collisional and Collision-Less Pressure Regimes, *J. Phys. Chem. B*, 2015, 119, 15359–15369

2. Saboohi, S.; Coad, B.R.; Michelmore, A.; Short, R.D.; Griesser, H.J. Hyperthermal Intact Molecular Ions Play Key Role in Retention of ATRP

Surface Initiation Capability of Plasma Polymer Films from Ethyl α -Bromoisobutyrate, *ACS Appl. Mater. Interfaces*, 2016, 8, 16493–16502

8:40am TF-WeM3 Layer-by-layer Etching of LaAlSiO_x, Mitsuhiro Omura, K. Furumoto, K. Matsuda, T. Sasaki, I. Sakai, H. Hayashi, Toshiba Corporation, Japan

INVITED

With downscaling of metal-oxide-semiconductor (MOS) devices, high dielectric constant (high-k) oxide materials have been proposed as gate oxide, to reduce the gate leakage current. LaAlSiO_x is one of the attractive candidates. In gate transistor fabrication, removal of high-k oxide films after gate electrode etching is a critical step for the formation of ohmic contacts on source and drain regions. Dry etching is a potential process to minimize the recess of the Si substrate which leads to the degradation of device performances. The conventional approach is to use an etching process with high selectivity to the Si substrate. Sasaki et al. have achieved a high LaAlSiO_x-to-Si selectivity of 6.7 using C₄F₈/Ar/H₂ plasma [1]. Another approach to reduce the Si substrate recess is precise control of etching depth using atomic layer etching (ALE) or layer by layer etching. ALE is defined to be an etching technique that uses sequential self-limiting reactions consisting of two steps, surface modification to form a reactive layer, followed by a removal step which takes off only this modified layer keeping the underlying film intact [2]. It is reported that by ALE using an energetic Ar beam and BCl₃ gas in HFO₂ etching, drain current and leakage current characteristics of MOSFET device improved, compared with conventional reactive ion etching (RIE) [3]. To control the etching depth of LaAlSiO_x, layer by layer etching using a sequential process has been studied, focusing on the selective removal of surface modification layer and repeatability of the sequential process.

[1] T. Sasaki, K. Matsuda, M. Omura, I. Sakai, and H. Hayashi: *Jpn. J. Appl. Phys.* 54 (2015) 06GB03.

[2] K. J. Kanarik, T. Lill, E. A. Hudson, S. Sriraman, S. Tan, J. Marks, V. Vahedi, and R. A. Gottscho: *J. Vac. Sci. Technol. A* 33(2) (2015) 020802.

[3] J. B. Park, W. S. Lim, B. J. Park, I. H. Park, Y. W. Kim, and G. Y. Yeom: *J. Phys. D: Appl. Phys.* 42 (2009) 055202.

9:20am TF-WeM5 Effect of Ar⁺ Ion Assist on the Properties of a-C:H Films Deposited on a Trench, Yuki Hirata, Tokyo University of Science, The University of Tokyo, Japan; *K. Onishi,* The University of Tokyo, Japan; *S. Sasaki,* Tokyo University of Science, Japan

Hydrogenated amorphous carbon (a-C:H) film have attracted considerable interest because of their high hardness, extremely low friction, high wear resistance, chemical inertness, and excellent gas barrier properties. These aforementioned characteristics make a-C:H films suitable for use in a wide range of applications such as tribological, anti-corrosional and gas barrier applications.

In our previous study, a-C:H film was prepared using the bipolar PBII&D technique on a trench-shaped target (20 mm pitch and 10 mm depth), and the coating uniformity was evaluated. In the bipolar PBII&D process, glow discharge plasma is generated by a positive pulse voltage applied to the target, and subsequently, a high-voltage negative pulse is applied for omnidirectional ion implantation and/or deposition to the target. However, this study revealed that the mechanical or structural properties of the a-C:H film differed greatly depending on whether the coating area was the top, sidewall, or bottom surface of the trench-shaped target. To reveal them, behavior of the ions or radicals around the trench-shaped target was analyzed through plasma simulation. Then it became apparent that these results were attribute to the nonuniformities of the incident flux or energy of the ions. Thus, in this study, non-reactive Ar gas was added to a toluene gas for deposition of a-C:H films to enhance the incident energy of the ions, and such ion-assisted effect was investigated simultaneously. The mechanical properties of the a-C:H film, including the internal stress in the thickness direction, were measured using a surface profilometer, the hardness and adhesiveness were measured using a nanoindentation hardness test and micro-scratch test, respectively. Furthermore, to evaluate the a-C:H film structure, Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR) were also conducted.

As a results, the uniformity of the film thickness was improved as the amount of introduced argon gas increased. Moreover, the hardness, internal stress, and adhesiveness were also improved in the case of an a-C:H film coated on a Si plate or at the top or bottom surface of a trench-shaped target. Such superior tendencies were considered to be caused by ion-assisted effects. On the other hand, in the case of the a-C:H film coated on the side wall, no improvement in film properties was seen. According to the Raman spectroscopy and FTIR, structure of a-C:H films were destroyed

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by Ar⁺ ion sputtering. That's why, it could be considered that Ar gas addition did not lead to the improvements for its properties but lead to the destruction of its structure.

9:40am **TF-WeM6 Characterization of PECVD a-C:H:Si:O:Cl Films**, *D. Rossi*, UNESP - Sorocaba, Brazil; *R. Landers*, Ifgw - Unicamp, Brazil; *J.R. Bortoleto*, *Steven Durrant*, UNESP - Sorocaba, Brazil

Thin films were produced by plasma enhanced chemical vapor deposition (PECVD) of tetramethylsilane, chloroform, argon mixtures. The partial pressure of chloroform in the chamber feed, C_{Cl} , was varied from 0 to 40%. Amorphous hydrogenated carbon films also containing silicon, oxygen and small amounts of chlorine, a-C:H:Si:O:Cl, were produced at deposition rates of up to about 220 nm min⁻¹ (for a C_{Cl} of 40%). Transmission infrared-analyses revealed the presence of OH groups in the chlorinated films, along with, amongst others, CH, C=C, Si-CH, Si-CH₂ and Si-O-Si groups. As revealed by X-ray photoelectron analysis, the films could be doped with chlorine to a maximum of about 2 at%. Surface morphology and roughness were examined using Scanning electron microscopy (SEM) and Atomic force microscopy (AFM). Tauc band gaps, calculated from transmission ultraviolet-visible near infrared spectra, tend to decrease from ~3.4 eV for the unchlorinated film to around 2.5 eV for those doped with chlorine.

10:20am **TF-WeM8 Plasma-assisted Atomic Layer Deposition of SiN_x Films**, *R.A. Ovanesyan*, *N. Leick*, *R.J. Gasvoda*, *J.M. Klein*, Colorado School of Mines, USA; *D.M. Hausmann*, Lam Research Corporation, USA; **Sumit Agarwal**, Colorado School of Mines, USA **INVITED**

The introduction of 3-D device architectures in integrated circuits has created a need for atomic layer deposition (ALD) of highly conformal ultra-thin films. In particular, ALD of low-dielectric-constant, carbon-containing silicon nitride (SiC_xN_y) films at temperatures ≤400 °C is required. However, controlled incorporation of C atoms into SiN_x during ALD remains challenging. In this work, we report the C incorporation mechanism during two plasma-enhanced SiC_xN_yALD processes. The first ALD process consisted of three steps, Si₂Cl₆/thermal CH₃NH₂/N₂ plasma, while the second process consists of two steps, Si₂Cl₆/CH₃NH₂ plasma. In both ALD processes, we have determined the film composition, reactive sites, and adsorbed surface species using *in situ* attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy. In addition, the growth per cycle (GPC) and refractive index were determined using *in situ* four-wavelength ellipsometry.

Our IR spectra show that in the first ALD process, the CH₃NH₂ thermally reacts with -SiCl_x surface species created after the Si₂Cl₆ half-cycle to form -CH_x terminated surface amides. During the subsequent N₂ plasma half-cycle, in addition to nitridation of Si, a fraction of the surface CH_x groups were incorporated into the SiC_xN_y film as -N=C-N- species, which appear as a strong vibrational mode at ~2170 cm⁻¹. The composition of the SiN_x films in the two-step ALD process was very similar, with C incorporated primarily as -N=C-N- groups created during the CH₃NH₂ plasma half-cycle. We find that during the exposure of the film to Si₂Cl₆ following a CH₃NH₂ plasma half-cycle, surface carbodiimides (-N=C=NH) react to nitriles (-NH-C≡N), while most of the surface is terminated with -SiCl_x species. The subsequent CH₃NH₂ plasma half-cycle, shows that the -NH-C≡N species formed during the Si₂Cl₆ half-cycle are removed, and the N=C=NH surface species are restored along with -NH_x groups. For the Si₂Cl₆/CH₃NH₂ plasma ALD process, SiN_x films grown at 400 °C show a carbon content of ~4 at.% as measured through Rutherford backscattering spectroscopy combined with hydrogen forward scattering. Transmission electron microscopy shows a conformality of >95% for the SiC_xN_y films. The GPC for both processes was ~0.9 Å, with a refractive index of 1.95 and 1.86 for the N₂ plasma and CH₃NH₂ plasma ALD processes, respectively.

11:00am **TF-WeM10 Atomic Scale Analyses of Plasma Surface Reactions using Molecular Dynamics Simulations and Ion/radical Beam Experiments**, *Satoshi Hamaguchi*, *H. Li*, *T. Ito*, *M. Isobe*, *K. Karahashi*, Osaka University, Japan

As the sizes of semiconductor devices continue to diminish and are now approaching atomic scales, the downsizing of transistors following Moore's law is bound to end in the near future. However, the continuing market demand for higher performance and lower energy consumption of large-scale integrated (LSI) circuits has driven a series of innovations in device technologies, such as three-dimensional (3D) device structures and devices based on non-silicon materials. Manufacturing of these non-conventional devices also poses new challenges for processing technologies. For example, magnetic materials used in magnetoresistive random-access memories (MRAMs) cannot be etched efficiently by the existing reactive ion etching (RIE) technologies, which has so far limited the level of

integration of MRAM devices. The modern near-atomic-scale devices also require atomic level precision in their manufacturing processes, which has also driven new technologies such as atomic layer deposition (ALD) and atomic layer etching (ALE). In this work, we have developed analytical techniques to examine plasma-surface interactions at the atomic scale using molecular dynamics (MD) simulation and multi-beam (i.e., ion and radical beam) injection experiments [1], in order to understand atomic layer reaction mechanisms that largely determine efficiencies of such atomic-level processing technologies. Some of our recent analyses include surface chemical reactions for magnetic materials [2,3] metal oxides [4], Si-based materials [5] as well as damage formation mechanisms [6,7] due to ion bombardment during RIE processes.

References

- [1] K. Karahashi and S. Hamaguchi, *J. Phys. D: Appl. Phys.* 47 (2014) 224008.
- [2] M. Satake, M. Yamada, H. Li, K. Karahashi, and S. Hamaguchi, *J. Vac. Sci. Tech. B* 33 (2015) 051810.
- [3] H. Li, Y. Muraki, K. Karahashi, and S. Hamaguchi, *J. Vac. Sci. Tech. A* 33 (2015) 040602.
- [4] H. Li, K. Karahashi, M. Fukasawa, K. Nagahata, T. Tatsumi, and S. Hamaguchi, *J. Vac. Sci. Tech. A* 33 (2015) 060606.
- [5] K. Miyake, T. Ito, M. Isobe, K. Karahashi, M. Fukasawa, K. Nagahata, T. Tatsumi, and S. Hamaguchi, *Jpn. J. App. Phys.* 53 (2014) 03DD02.
- [6] K. Mizotani, M. Isobe, and S. Hamaguchi, *J. Vac. Sci. Tech. A* 33 (2015) 021313.
- [7] K. Mizotani, M. Isobe, M. Fukasawa, K. Nagahata, T. Tatsumi and S. Hamaguchi, *J. Phys. D: Appl. Phys.* 48 (2015) 152002.

11:20am **TF-WeM11 Low-temperature Fabrication of Amorphous Zinc Tin Oxide Thin Film Transistors without Annealing Process**, *Sungmin Kim*, *J.M. Kim*, *H.J. Kim*, Seoul National University, Korea, Republic of Korea

Amorphous oxide semiconductor (AOS) such as InGaZnO_x (IGZO) and ZnSnO_x (ZTO) attracts an attention as a new channel material for thin film transistors (TFT). It has outstanding properties such as high field effect mobility (>10cm²/V-s) as well as transparency and uniformity. Therefore, display industry has named it as a prime candidate of channel material for large-sized and flexible display devices. However, considering that substrates in use for flexible display devices are polymer materials like PEN or PI, AOS has a critical drawback that it requires annealing process over 350°C. This is a quite low temperature compared to conventional silicon-based process (over 800°C), but the process temperature must be under 200°C to prevent deformation of polymer substrates.

In this study, the fabricated ZTO TFTs have a ZTO bottom gate and ITO top contacts, and all of them were made by RF magnetron sputtering system. And we replaced post annealing step with heating up the sputter stage up to 200°C during sputtering and forming 10% oxygen atmosphere. Electrical properties such as threshold voltage (V_{th}), mobility and subthreshold swing (SS) of ZTO TFTs were compared to convince that our new process could replace post annealing over 350°C. Analyses for morphology and chemical compositions are also conducted.

Saturation mobility of ZTO TFTs with 350°C annealing process and with our novel process were measured to be 17.4 and 11.7cm²/V-s, respectively. Post annealing at 200°C cannot activate ZTO TFTs at all, but by heating up the sputter stage, heating of 200°C was sufficient to activate TFTs. There was a little reduction of mobility, but 11.7cm²/V-s is still good enough giving that mobility of 10cm²/V-s is enough for large sized display (>70 inches). And SS values of 350°C annealed sample and one sputtered at 200°C was 0.31V/decade and 0.50 V/decade, respectively. Also, chemical composition and surface roughness was analyzed by XPS and AFM. These results also show that our new low temperature process is suitable for manufacturing AOS TFTs.

The main reason of this phenomenon can be served by combination of plasma and thermal energy in sputter chamber. Generally, it is obvious that as-deposited AOS channel needs oxygen curing to connect broken bonds between metal and oxygen atoms. While Ar/O₂ plasma in sputter chamber redeems relatively low thermal energy (200°C), curing reaction immediately occurs on as-deposited ZTO. Consequently, we made ZTO TFTs below 200°C process, rather than post annealing over 350°C. Performances of them were still applicable for next generation display. But it shows a little bit poor performance, so there must be further study to advance properties

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Thin Films

Room Mauka - Session TF-WeP

Thin Films Posters Session II

TF-WeP1 High Hardness and Oxidation Resistance of Ti–Al–Si–N Nanocomposite Coatings for Machining of Aircraft Mechanical Parts, *Wang-Ryeol Kim*, Korea Institute of Industrial Technology, Korea; *T.H. Nam*, University of Ulsan, Republic of Korea; *I.-O. Baek, E.Y. Choi, J.B. Jeon*, Korea Institute of Industrial Technology, Korea

Superhardness Ti–Al–Si–N nanocomposite coatings were deposited on SKD 61 and inconel substrates by hybrid coating system (AIP+Sputtering) in various Si target powers for machining of aircraft mechanical parts. The relationship among microstructures, mechanical properties, and tribological properties was investigated. The synthesized Ti–Al–Si–N coatings were characterized using x–ray diffraction (XRD) and x–ray photoelectron spectroscopy (XPS). These analyses revealed that the Ti–B–N–Si coatings are nanocomposites consisting of solid-solution (Ti,Al)N crystallites distributed in an amorphous Si_xN_y matrix. The addition of Si into the Ti–Al–N coating led to percolation of amorphous Si_xN_y and BN phases. The Ti–Al–Si–N coatings exhibited high hardness and H/E values, indicating high fracture toughness, of approximately 42 GPa and 0.097, respectively. Furthermore, the minimum friction coefficient of the Ti–Al–Si–N coatings was approximately 0.25 at low Si target powers. A systematic investigation on the microstructures, mechanical properties, and tribological properties of Ti–Al–Si–N coatings prepared from three Ti–Al composite targets and pure Si target is reported in this study.

TF-WeP2 Microstructure, Mechanical Properties and Tribological Properties of ZrN Based Nanocomposite Hard Coatings Deposited by a Hybrid Coating System, *Yeongha Song*, Korea Institute of Industrial Technology (KITECH), Pusan National University, Republic of Korea; *H.D. Kim*, University of Ulsan, South Korea; *K.-S. Kim, S.M. Shin*, Korea Institute of Industrial Technology (KITECH); *J.-H. Kim*, Korea Institute of Industrial Technology (KITECH), Republic of Korea

Zr–Si–N coatings with various Si contents were synthesized by a hybrid coating 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 Si₃N₄ matrix and further increases of Si content lead to amorphous-like coatings. The maximum hardness (H) of 33 GPa, Young's modulus (E) 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 SiO₂ or Si(OH)₄ self-lubricating layer due to the interface tribo-chemical reaction.

TF-WeP3 Advanced High Toughness Hard Coatings for Tribological Applications, *Sung-bo Heo*, U.C. Jung, Korea Institute of Industrial Technology (KITECH), Republic of Korea; *H.J. Son*, University of Ulsan, Republic of Korea; *I.W. Park*, Korea Institute of Industrial Technology (KITECH), Republic of Korea

A number of multi-component, nanostructured coatings have been produced for a range of tribological applications. The paper will discuss four such nanocomposite coating systems: (i) Ti–B–C–N; (ii) Ti–Al–Si–N; (iii) Cr–Al–Si–N; and (iv) Zr–Al–Si–N produced by hybrid coating deposition system in which the deposition parameters have been varied to control the structure and properties of the films. In each case, the coating system needs to exhibit a range of tribological properties to meet the required application, such as high wear resistance, low coefficient of friction, self-lubrication, high oxidation and/or corrosion resistance. In particular, the effect of the film chemistry, pulsing the magnetron and utilizing a closed field configuration will be discussed as suitable control parameters in tailoring the structure and properties of the coatings to meet specific tribological applications.

TF-WeP5 Migration-enhanced Epitaxy using Ga Droplets of GaAsNSe Thin Films on Si(110) Substrates, *Katsuhiro Uesugi, T. Ozawa, Y. Igarashi, Y. Shimomura, S. Kimura, K. Obara*, Muroran Institute of Technology, Japan

The development of strain relaxation buffer layers between GaAs and Si(110) that controlled large lattice mismatch and surface orientation influences are expected to integrate GaAs-based optical-fiber communication devices to Si(110) wafers. The growth of Ge and GeSi layers is mainly studied on Si(001) substrates, but absorb light signal of 1.55 μm wavelength due to the narrow bandgap energy of ~0.67 eV. A two-dimensional growth technique of GaAs(110) films on Si(110) surfaces is also necessary. In this paper, we report the migration-enhanced epitaxy of n-type GaAsNSe thin films with Ga droplets prepared on Si substrate surfaces, as the strain relaxation layers between GaAs and Si(110).

GaAsNSe films were grown by using metal-organic molecular beam epitaxy (MOMBE) equipped with the nitrogen radio-frequency discharge plasma system. MO precursors used were triethylgallium, trisdimethylaminoarsenic (TDMAs), trisdimethylaminoantimony (TDMASb), and ditertiarybutylselenide. The Si(110) substrate surfaces were thermally cleaned at 550 °C with the simultaneous supply of TDMAs. Ga droplets were formed on Sb-terminated Si surfaces which prepared by the supply of TDMASb at the substrate temperature of 470 °C. Then GaAsNSe films were grown at the temperature of 370–510 °C. The growth process of the films was characterized by using RHEED, AFM, and x-ray diffraction methods.

The Si- and As-terminated Si(110) surfaces were not covered with Ga layers, and Ga droplets of 40–75 nm height were formed at a density of 1×10⁸ cm⁻². On the other hand, small Ga droplets of 2 nm height were formed on the Sb-terminated Si surfaces at a high density of 2×10¹⁰ cm⁻², which suggest the anti-surfactant effect of Sb surface atom. The growth of a GaAsNSe ring structure occurred by the isotropic Ga diffusion from the droplet at low temperature. The step-flow growth mode of GaAsNSe was promoted as the increase of growth temperature. The activation energy of the Ga diffusion from the droplet during the growth was estimated to be 0.46 eV. At a high growth temperature of 510 °C, the two-dimensional growth of GaAsSe(110) with a large lattice mismatch of 3.5% was promoted considerably by using the effect of the surface Ga diffusion from the droplets. The formation of the pits and three-dimensional islands was suppressed in comparison with the films prepared by normal MOMBE growth. The migration enhanced MOMBE using surface Ga nano-droplets is a very useful technique for the fabrication of the flat GaAsNSe lattice relaxation layers on Si(110) substrates.

TF-WeP6 Formation of Low Friction Interface Utilizing Diamond-like Carbon Coating Containing Molybdenum Disulfide in Vacuum, Oxygen and Nitrogen, *Junko Masuda, K. Adachi, T. Takeno*, Tohoku University, Japan

Molybdenum disulfide (MoS₂) is widely used as a solid lubricant in vacuum. It produces very low friction due to its lamellar structure. However, one of the drawback of MoS₂ is weak for oxidation. Recently, the coating that MoS₂ nanoparticles are dispersed into diamond-like carbon (DLC) host matrix is proposed to overcome this problem utilizing gas barrier effect of DLC in addition, its hardness increases. Such coating is called MoS₂-containing DLC (MD). The coating shows lower friction, $\mu \sim 0.01$, than MoS₂ in vacuum when the coating is prepared under specific condition. When it shows low friction, unique transfer layer onto counter surface is formed. The structure of the transfer layer is consisted of 5 nm carbon layer on counter surface and mixed layer composed of MoS₂ and C on it. These facts clearly indicate that such specific structure is organized thanks to the coating. We have also demonstrated that low friction can be achieved depending not only on MoS₂ concentration but also bias voltage during deposition. Carbon matrix is important for achieving low friction. It is indicated that in order to form unique transfer layer, carbon has something potential to support MoS₂ to arrange lamellar structure. The purpose of this study is to clarify mechanisms of low friction.

Friction tests were conducted with ball-on-disk type apparatus in well-controlled environmental conditions. Dry nitrogen, dry oxygen and humid nitrogen gases are used to change atmospheric condition during friction tests. Various observation techniques including scanning electron microscope (SEM) and transmission electron microscope (TEM) equipped with energy dispersive X-ray spectrometer (EDS) are employed in this study.

Under nitrogen gases, both MoS₂ and MD coatings show low friction with vacuum. Actually, it is natural that MD coating shows low friction in nitrogen because MoS₂ and DLC give low friction in this condition. In case

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of oxygen condition, MoS₂ shows higher friction coefficient, ~ 0.2, in oxygen condition than in vacuum. On the other hand, friction coefficient of 0.02 is achieved utilizing MD coating, and very thin transfer layer was formed on the counter surface, which clearly shows the potential for low friction utilizing MD coating. A cross-sectional TEM image of the layer shows that structure of the transfer is also same as the one obtained in vacuum. In addition, EDS mapping on the TEM image revealed that oxygen from atmosphere is included in the whole transfer. It suggests that composite structure of MD coating can contribute the formation of a thin transfer layer.

TF-WeP7 Stability on O₂ Plasma Treatment of DLC Coating as Biocompatibility, Kyoichi Terai, Tokyo Denki University, Japan

Diamond-like carbon (DLC) films have been investigated in domestic fields because of their many attractive properties. In especially, mechanical high hardness, low wear resistance and gas barrier property of DLC films can be mentioned as the dominant advantages. DLC coating has already applied to surface finishing technology of metallic molds, cutting tools and polyethylene terephthalate (PET) bottles. In recent, many researchers have reported the characteristics of chemical stabilities, blood compatibilities and cell affinities on the DLC films. Modification of the surface condition of DLC films has been rapidly expected to demand of the advanced medical care.

In order to improve the biocompatibility of DLC films, plasma treatment of oxygen (O₂) and nitrogen (N₂) gases are proposed on the DLC surfaces¹. Surface conditions of the DLC films are delicate because bonds between carbon and oxygen are not so strong. The stability of effect of plasma treatment for DLC films has to investigate by systematic approach. In this study, we investigate that stability of the surface characteristics for time of O₂ plasma treatment. DLC films were prepared on Si substrate by using r. f. plasma chemical vapor deposition (r. f. plasma CVD) in methane (CH₄) gas. After DLC films deposition, surface modification was carried out by O₂ plasma. To evaluate stabilities of the plasma treatment on surface characteristics, surface conditions were analyzed by contact angle measurement and X-ray photoelectron spectroscopy (XPS). The cell affinity is estimated by *in-vitro* examination with a cell proliferation test using mouse-derived fibroblasts.

In case of contact angle measurement, DLC films without plasma treatments have water repellency and are almost constant. Hydrophilicity of surfaces immediately O₂ plasma treatments is stables for several days, after that their change to the saturation value.

From the result of XPS, intensity ratio of oxygen and carbon peak on the surfaces of the DLC films without plasma treatment is increased as function of time. In contrast, the intensity ratio between oxygen and carbon is decreased with time in case of sample with O₂ plasma treatments. The results revealed that adsorption and desorption of oxygen play important role to shift of the wettability in the plasma treatment on DLC films.

Reference

1. S. Murata, S. Ito, J. Mizuno, K. Hirakuri, K. Sato et., Phys. Status Solidi C9, No. 6 (2012) pp1439-1442.

TF-WeP8 Characterization of Compound Thin Films of CeO₂ and SiO₂ deposited by MOCVD, Tomonari Furuya, Hosei University, Japan; T. Matsumura, TOSHIBA Corporation, Japan; K. Kikuchi, Hosei University, Japan; K. Ishibashi, S. Suzuki, COMET Inc., Japan; Y. Yamamoto, Hosei University, Japan

Chemical states and electrical properties of the CeO₂ based compound oxide doped with SiO₂ as the promising gate stack material for MOS devices were investigated, based on the consideration that the crystallization could be suppressed by mixing materials having different crystalline structures. The X-ray photoelectron spectroscopy (XPS) analysis revealed that the compound oxide was successfully prepared on p-type Si (100) substrates by pyrolytic MOCVD using Ce(OC(Et)₂Me)₄ at the substrate temperature of 350 °C for 30 min with the intermittent introduction of TEOS (TetraethoxyOrthoSilicate) for 10 sec every 3, 5, or 10 min. The decomposition temperature of TEOS was lowered by the hydrolysis utilizing H₂O generated from Ce source decomposition. In the X-ray diffraction (XRD) patterns, the pure CeO₂ films represented the distinct cubic CeO₂ peaks, while CeO₂ peaks decreased to the trace level for the samples with TEOS introduction; the CeO₂ films with TEOS introduction were essentially amorphous.

From the X-ray photoelectron spectroscopy (XPS) spectra of Ce3d, Si2s and O1s, the average molar concentrations of SiO₂ in the films with the introduction of TEOS for 10 sec every 3, 5, or 10 min were determined to

be 15%, 6% and 6%, respectively. Although TEOS was intermittently introduced during CeO₂ deposition, the distribution of Si in CeO₂ films was uniform and the amount of incorporated Si was not directly related to the TEOS supply rate. Cerium silicate formation in the film prepared with TEOS introduction was confirmed from Si2s peaks at 153.5 eV and O1s spectra appearing with the shoulder at the higher binding energy.

The electrical properties after annealing at 500°C for 30 min in the ambient of O₂ were analyzed by I-V and C-V measurements using the Pt dot electrodes. The sample with TEOS introduction for 10 sec every 3 min represented the lowest leakage current around 1.0×10⁻⁵ A/cm² at 1.5 MV/cm, which was one order of magnitude lower than that of the pure CeO₂ films. The relative dielectric constant ranged between 16.6 and 21.6 depending on the TEOS introduction interval. These values were rather higher than that of pure CeO₂ films without Si doping which was usually lower than that of bulk relative dielectric constant of 26. These results suggest that Si doping brought about the change in the interface structure between Si substrates and deposited films such as the disappearance of the interfacial layer with lower dielectric constant. The flat band voltage shifted toward lower gate voltages for the samples prepared with TEOS introduction probably due to the introduction of fixed positive charge by silicate formation.

TF-WeP9 Development of Visualization System of Permeated Hydrogen Map on Stainless Steel Membrane, Naoya Miyauchi, Toho University, Japan; Y. Murase, National Institute for Materials Science, Japan; H.A. Sakaue, National institute for fusion Science, Japan; A.N. Itakura, National Institute for Materials Science, Japan; S. Takagi, Toho University, Japan

Hydrogen outgassing from an inside wall is the most important issue for vacuum chambers in ultrahigh vacuum (UHV) and extremely high vacuum (XHV). In addition, the behavior of hydrogen in metals should be made clear to understand the mechanisms of hydrogen embrittlement and storage. We have observed the behavior of hydrogen in metals by visualizing sequentially spatial distributions of permeated hydrogen on the surface of stainless steel membrane. The distributions of surface hydrogen were obtained using ions emitted by the method of desorption induced by electronic transition (DIET) process with the scanning electron microscope (SEM). The diffusion pass of hydrogen can be revealed from comparison of hydrogen maps obtained by this technique with the surface grain structure. In addition, physical information on permeation, which contains the processes of solution, diffusion, adsorption, is obtained by conjunction with a measurement on time dependence of permeated hydrogen pressure in the vacuum. The experimental setup is shown in Figure 1. We equipped the SEM (JEOL JAMP10) to the sample holder with hydrogen supply system and collecting electrode of DIET ions, the detection system of DIET ions and the quadrupole mass analyzer (Pfeiffer Vacuum QMG220). The collecting electrode is attached due to focusing DIET ions on the detector system. The DIET signals are measured in two-dimensional pulse counting system constructed by LabVIEW. This two-dimensional pulse counting system is synchronized with the scanning electron beam. The sample is SUS304 stainless steel, which has austenite structure with martensite dislocations caused by cold working of 20 %. The sizes of austenite grains are about 100 μm. The thickness of membrane is 200 μm. After outgassing of hydrogen in the sample (573K: 48 hours) the following experiments were performed under the outgassing temperature. The back side of SUS membrane was exposed to hydrogen (2.7×10⁵ Pa) and the permeated hydrogen on the opposite observation side was observed by DIET method. The vacuum chamber was evacuated by the sputter ion pump (100 l/s) under the experiments. The pressure was 1×10⁻⁷ Pa under the experiment. Both H₂ and D₂ gases were used to investigate an isotope effect for permeation.

Figures 2 and 3 are the secondary electron image and the permeated hydrogen map, which is obtained by accumulating DIET ions for 50 hours at 473 K, respectively. A comparison of two kinds of image suggested that the hydrogen permeation from the inside of grain and more permeation in austenite grains than martensite grains.

TF-WeP10 Hydrogen Diffusion in Stainless Steel and the Surface Stress Due to the Hydrogen, Akiko N. Itakura, Y. Murase, T. Yakabe, M. Tosa, National Institute for Materials Science, Japan; N. Miyauchi, S. Takagi, Toho University, Japan

Hydrogen in metals causes hydrogen embrittlement, which is the process of various metals to become brittle and fracture. Surface stress measurement is an effective technique for gas detection. In this study we focused on the stress of hydrogen contained in metals. We have detected a surface stress of stainless steel coated micro-cantilever under hydrogen

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irradiation. Meanwhile, it is not known the existing position of hydrogen in an alloy attributed to the complex structure of the alloy.

Metal thin films with the thickness of 20-50nm were deposited by RF magnetron sputtering on silicon micro cantilever (MCS: thickness of 1 micron and length of 500 micron). We found both of austenite and martensite structure in the film. The stress under hydrogen plasma irradiation was measured in-situ using a bending of cantilever beam [1]. MCS bended toward compressive surface stress and saturated under the irradiation. Probably it was a stress change due to hydrogen absorption although the bending might include temperature effect. After the irradiation stop, the bending curve decreased gradually. In 2nd experiment running, the saturated value of the bending was smaller than the 1st. After 10 times of the irradiation experiments (10 h irradiation) the bending did not decrease more.

In this study we tried to investigate hydrogen behavior in metal alloys from observation of two-dimensional hydrogen distribution on metal surface using a method of DIET (Desorption Induced by Electronic Transition). For the experiment we divided a vacuum container into two rooms. A part of a vacuum wall, between the two rooms, was a sample. Surface of the sample membrane thickness of 200 nm, had ring shape lines of 40micron pitch. The lines, which is a trace of the blade, were formed when the surface was flattened by a lathe. Cutting blade made un-uniformity of dislocations, too. H₂ gas was supplied from the backside room, H atom (ion) permeated through a sample and was desorbed into the vacuum room by electron irradiation. DIET mapping shows the hydrogen concentration reflects a density of dislocations, which has 40micron pitch [2]. It should be considered more by the comparing of DIET experiments with the structure measurement, grains, grain boundaries and dislocations [3]. Schematic diagram of the new experiment is shown in fig1. In the presentation we will show higher resolution images of DIET mapping, which can be compared with grains in SEM picture.

[1] A.N. Itakura, et al, Applied Surface Science, 159-160 (2000) 62-66.

[2] A.N. Itakura, et al, Journal of Vacuum Society Japan, 57 (2014) 23-26.

[3] N. Miyauch, et al, Journal of Vacuum Society Japan, 58 (2015) 387-391.

TF-WeP11 Tight-Binding Quantum Chemical Molecular Dynamics Simulations on Tribochemical Reaction Dynamics of Carbon Nitride Thin Films, Miho Nakamura, Tohoku University, Japan; S. Sato, Tohoku University; Y. Ootani, Y. Higuchi, N. Ozawa, K. Adachi, M. Kubo, Tohoku University, Japan

Recently, carbon nitride (CN_x) has gained much attention as solid lubricant in automotive engines, aerospace instruments, etc. Experimentally, one of the authors, Adachi, discovered that CN_x gives super-low friction coefficient. However, the super-low friction mechanism of CN_x has not been clarified experimentally. It is experimentally pointed out that CN_x shows lower friction coefficient than diamond-like carbon under specific condition. It means that the role of nitrogen in CN_x is very important. However, the function of nitrogen in CN_x has not been elucidated. Therefore, the theoretical approach is desired to reveal the role of nitrogen in CN_x. In the present study, we employed our original tribochemical reaction simulator based on the tight-binding quantum chemical molecular dynamics method [1-3]. The friction dynamics of H-terminated CN_x is simulated under 1 GPa pressure. The simulation result shows low friction coefficient of 0.05. We found that hydrogen-hydrogen repulsion is source of the super-low friction. However, this reason is same with that of H-terminated diamond like carbon films. It means that the role of nitrogen has not been clarified. Then, we investigate the effect of water molecules on the friction dynamic of H-terminated CN_x. It is very interesting to see the generation and evaporation of NH₃ molecules by the tribochemical reaction of CN_x and water. The generation and evaporation of NH₃ molecules give low density diamond-like carbon thin films. Therefore, we propose that low density diamond-like carbon generated by the tribochemical reactions of CN_x and water gives super-low friction coefficient.

[1] K. Hayashi, M. Kubo et al., J. Phys. Chem. C, 115 (2011) 22981.

[2] K. Hayashi, M. Kubo et al., Faraday Discuss., 156 (2012) 137.

[3] S. Bai, M. Kubo et al., RSC Adv., 4 (2014) 33739.

TF-WeP12 Detection of 2-nitrotoluene – Comparison of Thin Film Sensors and Ion Mobility Spectrometry, Premysl Fitl, D. Tomecek, M. Pajkova, J. Vleck, L. Fiser, E. Maresova, S. Havlova, P. Hozak, M. Vrnata, University of Chemistry and Technology Prague, Czech Republic

Our work deals with comparison of detection abilities of thin film chemiresistors based on silver phthalocyanine with metallic nanoparticles and ion mobility spectrometry. In our study we focus to the detection of widely used taggant in explosives - 2-nitrotoluene.

The sensing layers of chemiresistors were deposited by vacuum evaporation (AgPc) and DC magnetron sputtering (metallic nanoparticles) on ceramic substrates with platinum interdigital electrodes. We varied type of metallic nanoparticles (Au, Pd and Ag), their amount (equivalent thickness in the range of 1 to 50 nm) and also the deposition sequence of used techniques (bottom AgPc + top nanoparticles vs top AgPc layer - bottom nanoparticles). For underlying metal nanoparticles the substrates were heated during deposition (temperature range of 20 - 600 °C) to investigate and tailor nanoparticle shape and conductivity properties.

Growth of metallic nanoparticles was continuously monitored by in-situ resistance measurements during sputtering and annealing operations. These measurements enable also detection of percolation threshold. The morphology of prepared layers was investigated by electron microscopy.

For as-deposited layers of metal on AgPc it was found that when the amount of metal is relatively low (i.e. less than layer with equivalent thickness of 4 nm for Pd, 5 nm for Au and 8 nm for Ag) metal clusters on organic surface are created. Continuous but incompact layers are formed for slightly greater amounts of sputtered metals. Finally, continuous and compact layers were observed when equivalent thicknesses achieved ≈ 15 nm. When the layers are annealed the percolation threshold is in general shifted to greater amounts of sputtered metal.

Optimized sub-threshold layers containing metallic cluster arrays on chemiresistor substrates were used for detection of 2-nitrotoluene. The taggant vapors were detected in two modes: without or with photoactivation (λ = 266 nm). While the dc-response of AgPc/Au(10 nm) sensor to 189 ppm of non-activated 2-nitrotoluene vapors was negligible, after photoactivation the dc-response rose to 373.

The sensing properties of thin films were compared with sensitivity of commercially available GC-IMS system. The detection limit of our thin film sensors is in range of hundreds of ppb. The ion mobility spectrometer is cable to reach lower detection limits (ppt). Although the ion mobility spectrometry shown the higher sensitivity, the possibility of overexposure and contamination of sampling valve and drift tube may cause fatal ion mobility spectrometer failure. Our phthalocyanine thin film sensors can be used as low cost alternative for detection of 2-nitrotoluene.

TF-WeP13 Development of SiC-DLC cOatings for Super Low Friction Mechanical Systems in Water, Takanori Takeno, T. Hayase, K. Adachi, Tohoku University, Japan

Water is environmentally friendly liquid. When we used it as a lubricant, it gives very low friction. Silicon carbide and silicon nitride can produce very low friction, < 0.01, under water lubricating condition. However, one of the drawback is low load carrying capacity due to low viscosity of water. With increase of load, direct contact between the materials occurs, which leads to seizure. Some researchers have shown increase of load-carrying capacity thanks to DLC that can reduce friction under direct contact condition. Although it works as protective coating to avoid seizure, friction under such severe condition is still high, ~0.1-0.2. So, the target of this study is to produce the coating to show low friction and high load carrying capacity under water lubricating condition. To achieve the goal, we are developing SiC-containing DLC coatings.

Investigated coatings are prepared by RF generated methane plasma and DC magnetron co-sputtering of silicon carbide target (Purity: 99.99%). Silicon carbide disk is used as a substrate material. Various coatings are deposited by changing methane and argon flow rate (CH₄/Ar). Composition, structural analyses and hardness are measured by Rutherford backscattering spectroscopy (RBS), X-ray photoelectron spectroscopy (XPS) and nanoindentation technique. Friction tests are performed using ball-on-disk tribometer. Silicon carbide ball is used as a counter material. Ball and disk are immersed in water and friction tests are carried out.

By changing flow rate of methane and argon, various coatings with different composition are achieved. Hardness of the coatings decreases with increase flow rate. Friction properties also vary with composition of the coatings. With CH₄/Ar = 0.1, coating is removed at very beginning of the friction test. When the coating is deposited with CH₄/Ar = 0.2, very low

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friction of 0.05 can be achieved. Almost similar friction curve is obtained with further increase of the ratio but fluctuation of the friction coefficient is also observed with $\text{CH}_4/\text{Ar} = 0.3$. It suggests that these is optimum structure or composition of the coating. We also changed speed and load for friction tests. Surprisingly, friction coefficient of the coating with $\text{CH}_4/\text{Ar} = 0.2$ decreases with increase of load and decrease of speed condition, meaning lower friction is obtained with more severe contact condition. According to the literature, lowering friction coefficient is due to the termination of OH bonds by reacting SiC surface with water. Thanks to the hydrogen bonding between O from OH and H from H_2O , water is captured on the frictional surface and friction force can be derived from shearing the low viscos water.

TF-WeP14 Atomic Layer Deposition of 2D MoS_2 on Si/SiO₂ and Quartz Substrates, A. Valdivia, John Conley, Jr., Oregon State University, USA

The synthesis of high quality single layer 2D MoS_2 on large area substrates remains challenging. Mechanical exfoliation is capable of producing high quality material, but it is limited to small areas, requires transfer to the device substrate, is not scalable, and is impractical for manufacturing. Chemical vapor deposition (CVD) has been shown to yield MoS_2 on a variety of substrates, but is limited by non-uniform electrical properties, poor process stability, and high deposition temperature ($>600^\circ\text{C}$). A natural method for the synthesis of 2D materials is atomic layer deposition (ALD) in which alternating, purge separated, self-limiting surface reactions allow for precise thickness control, high conformality, and scalability to large surface areas. Although reports of ALD MoS_2 are beginning to emerge, ALD of single layer MoS_2 has typically required specialty sapphire substrates and high temperature (800°C) post deposition anneals and/or has been limited to small diameter wafers.

In this work, we demonstrate low temperature ALD of single to few monolayer MoS_2 uniformly across 150 mm diameter patterned SiO_2/Si and quartz substrates.¹ Purge separated cycles of MoCl_5 and H_2S precursors were used at ALD reactor temperatures ranging from 375°C to 475°C . Raman scattering measurements show clearly the in-plane (E_{2g}^1) and out-of-plane (A_{1g}) modes for ALD films deposited at 375°C or 475°C , indicating the presence of mono- to few layer MoS_2 . The separation of the E_{2g}^1 and A_{1g} peaks is a function of the number of ALD cycles, shifting closer together with fewer layers. Films deposited at 475°C are of much higher quality than films deposited at 375°C . While the E_{2g}^1 - A_{1g} peak separation of the 375°C film corresponds to bulk-like MoS_2 , the smaller peak separation of the 475°C film suggests a thickness of approximately two monolayers. Raman polarization tests confirm the MoS_2 crystals have the desired orientation parallel to the surface. High temperature H_2S and sulfur annealed films produce a sharpening of the E_{2g}^1 and A_{1g} peaks as well as the appearance of the band edge PL and spin orbit splitting peaks, a further indication of the presence of monolayer MoS_2 . High resolution transmission electron microscopy images confirms the presence of monolayer to bilayer MoS_2 films. X-ray photoelectron spectroscopy indicates that a sub-stoichiometric sulfur ratio in the as-deposited films is increased to the stoichiometric S/Mo ratio after annealing in H_2S at 600°C and above. Results suggest that ALD may be a promising method for production of 2D MoS_2 .

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1. A. Valdivia, D.J. Tweet, and J.F. Conley, Jr., J. Vac. Sci Tech A **34**, 021515 (2016).

TF-WeP16 Optical and Structural Study of GaN Films Grown by Pulsed Laser Deposition in Nitrogen Atmosphere, LuisArturo Martínez-Ara, P. Maldonado-Altamirano, R.Y. Ponce-Cano, J.R. Aguilar-Hernandez, ESFM-IPN, Mexico; M.A. Hernandez-Perez, ESQIE-IPN, Mexico; G.S. Contreras-Puente, ESFM-IPN, Mexico

Results about processing and characterization of gallium nitride (GaN) films grown by pulsed laser deposition technique are presented. The films were grown on sapphire (0001) and silicon (111) substrates, under the following conditions: substrate temperature of 850°C , time deposition of 60 minutes and pressure of 4.2×10^{-6} torr. A Nd: YAG laser was used with wavelength of 1064 nm, repetition frequency of 50 Hz and power of 2.8 W. To study the GaN films structural properties, X-ray diffraction was used obtaining peaks around 34.5° corresponding to GaN. To study the optical properties, UV-Vis absorption spectroscopy, photoluminescence (PL) and Raman spectroscopy were used. From the UV-Vis spectroscopy a band-gap value of 3.2 eV was obtained. Photoluminescence at room temperature was observed, the PL spectra shows two bands, one of these associated to yellow band of GaN at 2.2 eV, and the other one around 3.0 eV associated with recombination

centers, such as interstitials Gallium or Nitrogen atoms. Raman shift in 722 cm^{-1} was obtained corresponding to GaN in its wurtzite structure.

TF-WeP17 Electrical and Chemical Properties of $\text{HfO}_2/\text{Al}_2\text{O}_3$ on $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ Annealed at Different H_2 Pressures, Sungho Choi, Y. An, C. Lee, J. Song, Sungkyunkwan University, Republic of Korea; M.-C. Nguyen, Inha University, Republic of Korea; Y.-C. Byun, J. Kim, University of Texas at Dallas, USA; R.C. Choi, Inha University, Republic of Korea; H.S. Kim, Sungkyunkwan University, Republic of Korea

Passivation of a high- k /III-V interface is the most important process to be developed for future III-V-based transistors. Recently, there have been several attempts to passivate the interface defects by performing H_2 annealing after the high- k deposition on $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$: forming gas annealing [1] or H_2 high pressure annealing [2].

In this study, we deposited a $\text{HfO}_2/\text{Al}_2\text{O}_3$ gate stack using atomic layer deposition on the $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ substrates with different doping types and carried out H_2 high pressure annealing (400°C) at different pressures (10 bar and 30 bar). According to the time-of-flight secondary ion mass spectrometry and X-ray photoelectron spectroscopy measurements, out-diffusion of In and Ga atoms toward the high- k film was escalated as the H_2 pressure increased. The relationship between the observed H_2 -induced out-diffusion and the resulting electrical properties will be discussed.

- [1] K. Tang, R. Droopad, and P. C. McIntyre, ECS Transactions, **69**, 53 (2015).

- [2] T.-W. Kim, H.-M. Kwon, S. H. Shin, C.-S. Shin, W.-K. Park, E. Chiu, M. Rivera, J. I. Lew, D. Veksler, T. Orzali, and D.-H. Kim, IEEE Elec. Dev. Lett. **36**, 672 (2015).

TF-WeP18 In-situ Visualization of Graphene Grain Boundary by Optical Microscopy, K.-P. Hong, S.-H. Park, D.-J. Oh, Yekyung Kim, Korea Electronics Technology Institute (KETI), Republic of Korea; K.-S. Kim, Sejong University, Republic of Korea; K.-H. Kim, J.-B. Choi, Sungkyunkwan University, Republic of Korea; H. Kim, Korea Electronics Technology Institute (KETI), Republic of Korea

The graphene consisting with carbon atoms to honeycomb structure has the excellent properties about mechanical, chemical and thermal and it has been research in a variety of fields. In order to commercialize graphene with these outstanding properties, as well as a large area, mass production is essential for precise and fast measurement. In this study, for measuring the shape and size of the oxidation graphene fast and precisely, we configured the measuring system with an optical microscope, a heating stage and 3 W level laser. Through the configured system we can keep the graphene in a vacuum and wet condition to 200°C and measure the grain boundary of the oxidation graphene by irradiating the laser to locally. Later by proceeding the additional experiment and analyzing the correlation between the degree of graphene oxide and the laser irradiation time, through this process we develop the optimized visualization method of the graphene defects.

TF-WeP21 Thin Films of Sustainable Materials by UV Photo-transformation, Lopamudra Das, M.J. Kelley, College of William & Mary, USA

The expanding availability of narrow-wavelength deep UV lamps and powerful tools for numerical modelling afford growing opportunity to create precisely tailored organic thin films by transformation of an original substrate. Having begun with synthetic polymers (polyesters), application to natural materials (cellulose) is now proving successful, as revealed by surface spectroscopies (XPS and ToF-SIMS), AFM and wetting.

TF-WeP22 Nanostructured Oxide Thin Films as an Active Layers of Chemiresistive Sensors for Detection of Chemical Warfare Agents and Their Simulants, Jan Vlcek, P. Hozak, D. Tomecek, E. Maresova, P. Fítl, L. Fiser, University of Chemistry and Technology Prague, Czech Republic; T. Rozsypal, M. Haskovcova, Z. Koblíha, Z. Skalican, University of Defense, Czech Republic; J. Lancok, L. Fekete, Institute of Physics, Academy of Science of the Czech Republic; M. Vrnata, University of Chemistry and Technology Prague, Czech Republic

The aim of this work is to investigate the response of nanostructured chemiresistive gas sensors with an active layers based on nanostructured metal oxides (nanoporous structures) to a significant group of chemical warfare agents (CWAs) - (G-series: sarin, cyclosarin, soman, choking agent: diphsogene) and their simulants - (diethyl-malonate, ethyl-chloroacetate and difenyl-phosphochloridate). The active layers of sensors (based on SnO_2 , ZnO , PdO) with thicknesses of 100 - 400 nm were prepared on sensor substrates by (i) sputtering of source metal and subsequent anodic oxidation, (ii) sputtering of source metal and subsequent thermal oxidation

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in oxygen atmosphere, (iii) thermal evaporation of source material metal and subsequent oxidation in oxygen atmosphere. Sensor platform consists of a planar sensor aluminium oxide substrate with interdigital platinum electrodes.

We present results of morphology investigation of nanostructured oxide films by AFM and SEM microscopy and structural analysis by XRD. Conventional dc-sensitivity of sensors S_{dc} was evaluated as a ratio of their resistance in air containing given concentration of analyte and that in "pure" air respectively. Detection was tested for concentrations of CWAs up to 50 ppm in air. SnO₂-based sensors feature a high sensitivity towards CWAs, where S_{dc} reaches a values of 3 - 10. On the other hand ZnO-based sensors exhibit significant selectivity to CWAs, whereas the responses to a common interferents are negligible. We show the connection between material morphology properties (porosity, crystalline size) and detection ability of CWAs.

TF-WeP23 Effect of Substrate Temperature on the Mechanical Properties and Structure of Sputtered Titanium Nitride Film by a Pure Nitrogen Plasma, C.-H. Park, B.-S. Jang, Chang-Hyun Lee, Catholic University of Daegu, Republic of Korea; S.-Y. Son, Pohang University of Science and Technology, Republic of Korea; B. Kim, H.-M. Kim, Catholic University of Daegu, Republic of Korea

Titanium nitride (TiN) films were prepared by rf magnetron sputtering technique. The depositions were carried out by a pure N₂ plasma sputtering. Their mechanical properties, such as nano-indentation hardness, friction coefficient, and water contact angle have been investigated. XRD studies revealed that TiNx films grown at temperatures more than 360°C exhibits an intense compressive stress as compared with the films grown at temperatures less than 360°C. The orientation of TiNx films changes toward (111) orientation at 360°C due to increased ion bombardment which favors low surface energy at (111) orientation. The increase of Ts, which means the distance between target and substrate, increases the mobility of adatoms promoting closed packing structures in near thermodynamic equilibrium conditions. Thus, for high adatom mobility the TiNx films expected to grow along the (111) orientation corresponding to that with the lowest surface free energy. On the other hand, for low adatom mobility the preferred orientation is the (002) in which the highest number of atoms per unit area can be incorporated at low energy sites. The mechanical properties of TiNx films grown at a pure N₂ atmosphere strongly dependent on the Ts. The highest hardness and the smallest friction coefficient of 26 GPa and $\mu=0.13$, respectively were in a TiNx film deposited at 400°C. This film was found to be accompanied by a water repellent surface.

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TF-WeP24 Study of a Temperature and Humidity Sensor Constructed by the Multi-layer Film including a TiO₂ Layer, Takahisa Kawaguchi, I. Takano, Kogakuin University, Japan

Currently, commercial temperature and humidity sensors have a low sensitivity for both sides of a high humidity and a low humidity. Moreover, because the main parts of these sensors are manufactured using polymer materials, there is the problem of a short life in environments such as high temperature or high humidity. Therefore, the next-type sensors are required in a longer life and a higher sensitivity.

As a material satisfying some of the above-mentioned function, TiO₂ was adopted. TiO₂ is an n-type oxide semiconductor, and has the stable photo-excited state and causes no autolysis. In addition, TiO₂ shows the hydrophilicity under ultraviolet irradiation. The next-type sensor with a high sensitivity is promised by the suitable junction of between a TiO₂ layer and a Cu₂O (p-type oxide semiconductor) layer.

In this study, the investigation of TiO₂ thin films on sensor characteristics and the improvement of the sensor sensitivity by using the TiO₂/NiO/Cu₂O multi-layer thin film were carried out. The rutile-type TiO₂ thin film (TiO₂-R) with a thickness of 200 nm, the anatase-type TiO₂ thin film (TiO₂-A) with a thickness of 200 nm and the TiO₂/NiO/Cu₂O (200/10/200 nm) thin film

were prepared by reactive magnetron sputtering. The electric resistance of each sample was measured by changing a voltage from 0 V to 10 V. The resistance changes for a temperature and a humidity were measured by changing a temperature from 25 °C to 60 °C by changing a humidity from 30 % to 60 %. As the characteristic relating to the humidity, a water contact angle was measured by the $\theta/2$ method. In these experiments, the photoreaction on a semiconductor characteristic was examined by irradiating the white-LED light or UV-LED light to the sample surface.

The resistances of the TiO₂-R thin film and the TiO₂-A thin film decreased by the photo-excitation under the UV-LED light irradiation. The resistance of the TiO₂/NiO/Cu₂O thin film under the white-LED light irradiation showed the value as well as that of UV-LED. The temperature coefficient of resistance of the TiO₂-R thin film, the TiO₂-A thin film and the TiO₂/NiO/Cu₂O thin film were -8354×10^{-6} [1/K], -5264×10^{-6} [1/K] and -16390×10^{-6} [1/K], respectively. In the case of a humidity characteristic, there was no large change in the electric resistance against the humidity change for any sample. In addition, the improvement of hydrophilicity by light irradiation was not confirmed from the water contact angle examination.

The TiO₂/NiO/Cu₂O thin film showed a superior temperature characteristic in comparison with the TiO₂-R thin film or the TiO₂-A thin film.

TF-WeP25 Improvement of the Photocatalyst Effect by the Intermediate Layer Insertion to TiO₂/Cu₂O Films, Toshiya Souma, I. Takano, Kogakuin University, Japan

In recent years, various characteristics of TiO₂ have attracted considerable attention. One of their characteristics is a photocatalytic effect. The photocatalytic effect of TiO₂ shows antifouling or antimicrobial activity, and has the ability to decompose environmental pollutants. The most important characteristic as a photocatalysis of TiO₂ is well known that the photo-excited state is very stable and does not cause self-decomposition. Therefore, TiO₂ can perform the electrolysis of water by light, however a light reaction of TiO₂ is limited at ultraviolet region corresponded with only about 3 % of sunlight.

In this study, to improve the photocatalytic property of TiO₂ the double layer films were fabricated by the constitution of the TiO₂ layer with 3.0 - 3.2 eV and the Cu₂O layer with 2.2 eV in a band gap energy. In order to prevent the diffusion of Cu, an NiO or TaON layer was inserted between the TiO₂ layer and the Cu₂O layer. NiO has a high melting point, high hardness and has been used as a barrier layer in various fields. TaON is used as electrode materials for a semiconductor and light electronics devices. Each oxide layer was prepared by reactive magnetron sputtering.

The film composition and microstructure were investigated by the X-ray photoelectron spectroscopy and X-ray diffraction, respectively. The chromatic change of a methylene blue solution was applied to the measurement of the photocatalytic property. The light irradiation to the TiO₂/NiO/Cu₂O film or the TiO₂/TaON/Cu₂O film in a methylene blue solution was carried out using a commercial sterilizing lamp as ultraviolet light and an artificial sun lamp as visible light. The transmittance of a methylene blue solution was measured by a spectrophotometer.

It was confirmed that Cu on the TiO₂ surface was not observed by inserting the NiO or the TaON layer. The crystal structure of the TiO₂/Cu₂O film showed a rutile type while the ratio of rutile (110) / anatase (101) changed with the NiO film thickness. In the case of the intermediate layer of NiO, the suitable photocatalytic effect was obtained by the film with the NiO layer of 20 nm thickness, when the transmittance showed about 57 % under an artificial sun lamp and about 77 % under a sterilization lamp. In the case of the TaON layer, the suitable photocatalytic effect was obtained by the TaON layer of 10 nm thickness, when the transmittance showed about 75 % under an artificial sun lamp and about 82 % under a sterilization lamp.

It is considered that the role of the intermediate layer is not only the protection of Cu diffusion from the Cu₂O layer but also the activation of the mobility of carriers.

TF-WeP26 Combining XPS and UPS Measurements in Thin Film Depth Profiles, Joseph Robinson, Thermo Scientific, USA; T. Nunney, Thermo Scientific, USA, UK; A. Bushell, J. Treacy, Thermo Scientific; C. Deeks, P. Mack, Thermo Scientific, USA

X-ray Photoelectron Spectroscopy (XPS) depth profiling has been widely utilized to provide detailed elemental and chemical state information of thin films, such as those used in microelectronic devices and protective coatings. These measurements have often been combined with valence electronic information obtained using the related technique of Ultraviolet Photoelectron Spectroscopy (UPS). Such detailed and complementary

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information is essential when attempting to fine-tune specific thin film parameters for best device or coating performance.

While useful information is acquired from XPS and UPS in isolation, a more powerful insight into the structure of a material comes from using these two techniques in conjunction, allowing a more complete material characterisation to be performed. Previously, switching between techniques throughout the course of an experiment has been an involved and often laborious process, discouraging more widespread use. Recently the automation of UPS has allowed acquisition of XPS and UPS data at each level of a depth profile, providing a much sought after insight into the correlation between chemical and electronic structure at within a substrate at various depths.

Of particular interest is the ability to access the valence electronic structure at mixed oxide interfaces using small argon ion gas clusters, which was not previously possible due to the loss of electronic structure in semiconductors or organic materials on exposure to monatomic argon ion beams. This presentation demonstrates the wealth of information that can be acquired by performing combined XPS-UPS depth profiles and the ease with which this information can be acquired and processed, due to recent instrumentation and software developments.

TF-WeP27 Enhancement of Oxidation Resistance of Metal Surface by a Polymer Monomolecular Layer and Its Influence on Electrical Conductivity, T. Ikeda, H.T. Nguyen, J. Takagi, K. Yamakawa, K. Adachi, Yasuhisa Tsukahara, Kyoto Institute of Technology, Japan

Metals like copper are easily oxidized in air to form metal oxides on the surface. This is often problematic for their applications because of reduction of the electrical conductivity. We studied influence of molecular coating of organic thiol compounds on copper plates and fine particles on their oxidation resistance and electrical conductivity.

Copper and nickel surfaces were coated with thiol terminated polystyrenes (PSt-SH)s and alkanethiols by dipping copper into solutions of the thiol compounds. XPS measurements revealed that the molecular thin layer of PSt-SH lead to a resistance against oxidation. Coating with alkanethiols like 1-dodecanethiol (Dod-SH) was also effective. However, only the PSt-SH layer kept the oxidation resistance against heating at high temperature, which was also confirmed by the color change of the metal surface by heating.

We also used cyclic voltammetry (CV) to evaluate the oxidation resistance. The oxidation resistance was determined from the integral value at the anode and cathode regions in the oxidation-reduction curve. We found that the oxidation resistance of copper covered with PSt-SH was excellent at high temperatures under atmosphere and was not decreased even by heating up to 150°C.

The temperature dependences of the contact electrical resistance measured by the four-point method indicated that the electrical conductivity was not reduced for the metal surface coated with PSt-SH even at high temperatures which is consistent with the results of XPS and CV measurements.

[1] Takuya IKEDA, Kaoru ADACHI and Yasuhisa TSUKAHARA, *Journal of MMIJ*, Vol.132, No.2, pp.39 - 46 (2016).

[2] Takuya IKEDA, Tomoki TAKATA, Juri TAKAGI, Kaoru ADACHI, and Yasuhisa TSUKAHARA, *Kobunshi Ronbunshu*, Vol.73, No.2, pp.198 - 206 (2016).

[3] Juri TAKAGI, Takuya IKEDA, Kaoru ADACHI, and Yasuhisa TSUKAHARA, *Kobunshi Ronbunshu*, Vol.73, No.3, pp.294 - 301 (2016).

TF-WeP28 Study of the Influence of the Abrasive Slurry Concentration on the Coefficient of Friction of Thin Films submitted to Micro-abrasive Wear, Ronaldo Cozza, G.H.B. Donato, University Center of FEI, Brazil

The purpose of this work is to study the influence of the abrasive slurry concentration on the coefficient of friction of thin films submitted to micro-abrasive wear. Initially, a micro-abrasive wear testing by free rotative ball equipment was designed and constructed, able to measure the coefficient of friction on the tribo-system "thin-film - abrasive slurry - ball". After, experiments were conducted with thin films of TiN, TiC, CrN, TiAlN, HfN, ZrN, TiZrN, TiN/TiAl (multi-layer), TiHfC and TiHfCN, balls of AISI 52100 steel and abrasive slurries prepared with black silicon carbide (SiC) particles + glycerin. All tests were conducted without interruption, and the abrasive slurry was continuously agitated and fed between the ball and specimen. The tangential (T) and normal (N) forces were monitored throughout the tests and the coefficient of friction (μ) was calculated by the equation $\mu = T/N$. The results obtained have shown that the concentration of abrasive

slurry affected the actions of the abrasive wear modes (grooving abrasion or rolling abrasion) and, consequently, the magnitude of the coefficient of friction: high abrasive slurry concentration was related with low coefficient of friction.

TF-WeP29 A Study on Coefficient of Wear and Coefficient of Friction of Thin Films submitted to Micro-scale Abrasion, Fabiano Silva, S.O. Santos, CEETEPS - Centro Estadual de Educação Tecnológica "Paula Souza" - FATEC-Mauá; R.C. Cozza, CEETEPS - Centro Estadual de Educação Tecnológica "Paula Souza" - FATEC-Mauá, Brazil; C.F. Silva, M.O. Gentil, A.J. Moura Jr., CEETEPS - Centro Estadual de Educação Tecnológica "Paula Souza" - FATEC-Mauá

Several works on the coefficient of friction during abrasive wear tests are available in the literature, but only a few were dedicated to the coefficient of friction in micro-abrasive wear tests conducted with rotating ball. This work aims to study the influence of titanium nitride (TiN) and titanium carbide (TiC) coatings hardness on the coefficient of friction and coefficient of wear in ball-cratering micro-abrasive wear tests. A ball of AISI 52100 steel and two specimens of AISI D2 tool steel, one coated with TiN and another coated with TiC, were used in the experiments. The abrasive slurry was prepared with black silicon carbide (SiC) particles and distilled water. Two normal forces and six sliding distances were defined, and both normal and tangential forces were monitored constantly during all tests. The movement of the specimen in the direction parallel to the applied force was also constantly monitored with the help of an electronic linear ruler. This procedure allowed the calculation of crater geometry, and thus the coefficient of wear for the different sliding distances without the need to stop the test. The coefficient of friction was determined by the ratio between the tangential and the normal forces, and for both TiN and TiC coatings, the values remained, approximately, in the same range (from $\mu = 0.4$ to $\mu = 0.9$). On the other hand, the coefficient of wear decreased with the increase in coating hardness.

Thin Films

Room Makai - Session TF-WeE

Microstructure & Surface Morphological Evolution in Organic & Inorganic Films

Moderator: Satoshi Hamaguchi, Osaka University, Japan

6:20pm TF-WeE3 Understanding Organic-Organic Quasiepitaxy, *Richard Lunt*, Michigan State University, USA **INVITED**

The presence of excitons in organic materials offer new opportunities for low-cost photovoltaics and electronic systems and provide prospects for unique energy science and applications. In this talk I will review our understanding of organic quasiepitaxy. I will then discuss our demonstration of the growth of ordered organic-organic hetero-quasiepitaxial superlattices, composed of incommensurate organic semiconductors with sustained registry grown from the bottom up via a new step-edge nucleation driven growth mechanism. By probing a range of molecular pairings with in-situ and real-time diffraction, we further uncover driving forces that can broadly enable this type of growth, which are completely distinct from the requirements of inorganic epitaxy. It is well known that crystalline order, orientation, and quantum confinement of highly anisotropic organic semiconductors can significantly alter the properties and performance of organic electronics. Thus, these demonstrations can enable entirely new photophysical phenomena and provide opportunities for manipulating energy in a variety of excitonic structures.

7:00pm TF-WeE5 Characterization of Aluminum Nitride Grown by Atomic Layer Epitaxy with real time Grazing Incidence Small Angle X-ray Scattering, *Virginia Anderson, N. Nepal, S.D. Johnson*, US Naval Research Laboratory, USA; *Z.R. Robinson*, The College at Brockport SUNY, USA; *A. Nath, A. Kozen*, US Naval Research Laboratory, USA; *A. DeMasi*, Boston University, USA; *J.K. Hite*, US Naval Research Laboratory, USA; *K.F. Ludwig*, Boston University, USA; *C.R. Eddy, Jr.*, US Naval Research Laboratory, USA

A focus area of research on III-nitrides attempts to lower the growth temperature of films, because molecular beam epitaxy and metalorganic chemical vapor deposition (MOCVD) must be done at relatively high temperatures to produce a high quality material. As an example, aluminum nitride MOCVD takes place at over 1000°C. Tunable band gaps, high breakdown voltages, and piezoelectric properties are attractive qualities of aluminum nitride films, and thus motivate the search for alternate fabrication methods. Atomic layer epitaxy (ALE) of GaN, AlN, and InN films have been shown at temperatures far below that required for MOCVD. [1] Further exploration of the growth parameters of these films is underway. Research during the actual growth process allows much more information on early stages of film deposition, and eliminates many of the *ex-situ* issues with surface oxidation upon sample removal from the reactor. The X-ray photons available at some synchrotrons allow insight into the growth process from grazing incidence small angle X-ray scattering (GISAXS), a technique that can be carried out at ALE pressures and is extremely sensitive to surface morphological evolution.

The work presented will describe film growth of aluminum nitride using trimethylaluminum and a nitrogen/argon or hydrogen/nitrogen/argon plasma. Based on *ex-situ* examinations, aluminum nitride ALE on MOCVD GaN at 500°C was previously seen to exhibit single crystal character, with a full-width at half maximum of 670 arc-seconds. [2] Work presented here describes results on changing the temperature and the plasma conditions for ALE AlN. The substrates were sapphire and the growth took place at Brookhaven National Laboratory and at the Cornell High Energy Synchrotron Source in a custom reactor designed to facilitate GISAXS monitoring during growth.

These results suggest that surface feature distances are related to the final quality of the aluminum nitride films. Samples grown at 350-400°C have higher impurities than samples grown at 450-500°C, and GISAXS shows closer features at the lower temperatures. In addition, holding the flow constant and changing the nitrogen to argon ratio resulted in changes in the atomic species present in the plasma source, and changes in nucleation and growth behavior.

References:

- 1 N. Nepal et al., *Thin Solid Films* **589** 47 (2015)
- 2 N. Nepal et al., *Appl. Phys. Lett.* **103** 0 82110 (2013)

7:40pm TF-WeE7 Study of Structural Phase Transitions during Growth of Tetracene and Pentacene Films on H/Si(001) via NEXAFS and AFM, *Xiaorong Qin, J. Shi*, University of Guelph, Canada; *T. Regier*, Canadian Light Source, Canada; *D.T. Jiang*, University of Guelph, Canada

To understand the formation of organic thin films and substrate influences to the molecular structures, we investigated the orientation of polyacene molecules (i.e., tetracene, pentacene) on hydrogen-passivated Si(001) as a function of coverage, using polarization-dependent C1s near-edge x-ray absorption fine structure spectroscopy (NEXAFS). Molecular films were prepared via vacuum molecular beam deposition, and in situ NEXAFS measurements were performed on the films of different coverage (from 0.2 ML to 12 ML). We report that under the film growth condition, at the early stages of the film growth the average orientation of the molecules is largely disordered. Clear upwards tilting of the molecules start when coverage exceeds a significant portion of a monolayer. With further increasing the film coverage to around 3-4 ML, a structural phase transition occurs, leading to the average molecule tilting angle around the bulk value. We conclude that, in both tetracene and pentacene growth, after the coverage of 3-4 ML, the molecules adopt the organization similar to that in the bulk-phase structure due to strong the self-assembly effect and less influence from the molecule-substrate interface. Atomic force microscopy (AFM) imaging of the films was carried out *ex situ* to show the morphology of the surfaces at different coverage. The film formation mechanisms and their impact to the charge transport properties of the film will be discussed.

8:00pm TF-WeE8 RF-Sputtering Reactive used for Depositing Thin Films CdS:O, *Juan Luis Pena Chapa, M. Loeza-Poot, I. Rimmaudo*, CINVESTAV-IPN Unidad Merida, Mexico; *I. Riech Mendez*, Universidad Autónoma de Yucatán, Mexico; *R. Mis Fernandez, V. Rejon Moo*, CINVESTAV-IPN Unidad Merida, Mexico

We present the effects of the variation oxygen concentration in the thin films of CdS:O deposited by RF-Sputtering. This kind of thin film was studied with the purpose to be used as a window layer in a solar cell. The films were deposited on Corning glass substrate (area 1 in²) from a ceramic target of CdS with 99.99% purity, in an atmosphere of mixture of gases Ar + O₂. Deposition was performance at room temperature with a working pressure of 25 mTorr and a sputtered power of 40 Watts. Films with different oxygen content were prepared with a variation of the oxygen concentration in a range from 1% to 1.5% with respect to the total pressure. The structural and morphological properties were characterized by using X-ray Diffraction (XRD) and field emission scanning electron microscopy (FE-SEM), respectively. The diffraction patterns showed that samples prepared with oxygen concentration less to 1.1% are crystalline and present the hexagonal CdS (h-CdS) structure, while samples with oxygen concentrations greater than 1.1% are amorphous, all crystalline films were oriented preferentially (002). Also we observed a decrease in the crystallite size in a range from 5.9 nm to 4.3 nm, which can be correlated in the micrographs. SEM images show that is possible to obtain nanostructure thin films of CdS varying the grain size in a range from 20nm to 70nm, the grain size decrease as the oxygen percentage raises, all samples present high uniformity.

ACKNOWLEDGEMENTS: This work has been supported by CONACYT-SENER (México) under projects CeMiESol 207450/P25 and CeMiE-Sol 207450/P26. M. Loeza-Poot acknowledges CONACYT-Mexico for scholarship (number 556332) in the Applied Physics Department of CINVESTAV-Merida. Measurements were performed at LANNBIO CINVESTAV-Mérida, supported from projects FOMIX-Yucatán 2008-108160, CONACYT LAB-2009-01 No. 123913 and CB2012/ 178947. The authors gratefully acknowledge to D. Huerta and Wiliam Cauch for technical support, and to L. Pinelo as secretarial assistant.

8:20pm TF-WeE9 Spatio-Time-Resolved Cathodoluminescence Study of Thick III-polar and N-polar InGaN, *Zakaria Al Balushi, J. Redwing*, The Pennsylvania State University, USA

InGaN quantum wells (QWs) have been well established as active layers in LEDs and laser diodes. Recently, there has been interest in the growth of thick InGaN to serve as strain-reducing layers for deep-green and red emitters. The growth of thick layers is, however, challenging. The miscibility gap between InN and GaN leads to InGaN phase separation and indium clustering. In addition to low indium incorporation at high growth temperatures, a high density of V-pits are observed in InGaN films grown in the III-polar direction. Alternatively, the growth of films in the N-polar direction offers advantages that are attractive for the growth of thick InGaN. N-polar growth enables higher indium incorporation and V-pits are

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less favorable to form. Despite these advantages, limited studies on thick N-polar InGaN films have been reported. This is because N-polar InGaN grown by MOCVD typically suffer from high densities of hexagonal hillocks that originate from low quality N-polar GaN templates. Therefore, in order to assess the quality of thick N-polar InGaN films, it is necessary to probe the local structure and optical properties of high quality grown films.

In this study, we compare the structural and optical properties of thick III-polar and N-polar InGaN. Both III-polar and N-polar InGaN growth was carried out by MOCVD under identical conditions (130 nm, 780°C, 300 Torr, V/III=2450) on high quality GaN base layers. The N-polar InGaN films were free of hexagonal hillocks and exhibited a reduced RMS roughness of 0.66 nm in comparison to the RMS roughness of 2.30 nm for III-polar InGaN. High resolution XRD, SIMS and EDX measurements revealed higher indium incorporation in the N-polar films (13%) when compared to III-polar InGaN (7.5%). From PL measurements, two distinct peak emissions located at different depths of the film were observed for both film polarities, one peak originating from a pseudomorphically strained region and the other from a partially relaxed region. To further investigate the optical properties of InGaN films, we performed both steady state and time-resolved cathodoluminescence mapping of the III-polar and N-polar films at room and liquid helium temperatures. From CL measurements, distinct emission from indium clusters and threading dislocation around V-pits were observed in III-polar InGaN films. In the case of N-polar InGaN, CL emission was homogenous across the film surface. With the combination of spectroscopic techniques, this study elucidates the differences in the luminescence in thick InGaN as a function of film polarity and gives new insights into possible mechanisms of luminescence quenching commonly observed N-polar InGaN.

8:40pm **TF-WeE10 3D Image of Coating and Diffusion Species, Lei Zhang**, Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Science, China

Morphology, composition and crystallography are three common objects for microanalysis in material science. The developments of 3D techniques in material microanalysis facilitate researchers to explore in 3D space. 3D chemical analysis is of important in 3D microanalysis family but need to be improved and promoted. Combining 2D imaging in lateral with sputtering in depth, layered SIMS imaging can be reconstructed in 3D. Detailed 3D-SIMS analysis of interfaces between phases, such as concentration change and inhomogeneity of diffused species near interface, provide diffusion information between coating and substrate with new view. Such 3D-SIMS technique become a useful and popular tool to generate full-view images in 3D space for various specimens with layered or complex structure from inorganic, organic and biological research. It provides a wealth of composition information and gives deep insights that cannot easily be attained in other interfacial analysis.

Normal approach in 3D-SIMS can display the species in layered or complex structure. However, detailed analysis of interfaces between phases, such as concentration change and inhomogeneity of diffused species near interface, attract more attention that need to be explored. For example, diffused interface is expected to be a sign of solid bonding for the safety of coating service life. New 3D imaging approach is developed to separate the diffused species through the interface. In terms of the ion imaging of CsAl⁺ in diffusion region, diffused Al at the interface between the ceramic coating and Zircaloy substrate were investigated in both as-deposited and annealed states.

The new analytics toolkit to resolve diffused species is a key evaluation to develop coating layer on alloys. The new method based on 3D-SIMS analytics is expected to provide diffusion information between coating and substrate with new view. It will continue to advance and gives more information about the formation of diffusion interface which facilitate the interface analysis from variety of research interest.

References

- [1] Erin H. Seeley et al. *Anal. Chem.*, 2012, 84 (5), 2105–2110
- [2] James Bailey et al. *ACS Appl. Mater. Interfaces* 2015, 7, 2654–2659
- [3] Alam et al. *Nucl. Eng. Des.* 241(2011)3658-3677
- [4] Pint et al. *J. Nucl. Mater.* 440(2013)420-427
- [5] Houssiau et al. *Appl. Surf. Sci.* 231-232(2004)585-589

Thin Films

Room Makai - Session TF-ThM

Advanced Protective Coatings/Stress Evolution, Nanostructure, and Physical Properties of Thin Films

Moderator: Grzegorz Greczynski, Linköping University, Sweden

8:00am **TF-ThM1 XPS Analysis of a Super-hard Material – Application of Ar Cluster Ions to Probe New Depths in Surface Analysis**, *David Surman*, Kratos Analytical Inc.; *J. Counsell, S.J. Coultas*, Kratos Analytical Ltd., UK; *C. Moffitt*, Kratos Analytical Inc.; *C.J. Blomfield, A.J. Roberts*, Kratos Analytical Ltd., UK

Super-hard inorganic multilayers have emerged in recent times as a distinct class of material, currently used in coatings of cutting tools for machining and in the aerospace industry. There has been significant effort to develop new coatings due to increased need for wear protection and friction reduction.

One such material we will discuss in this work is a TiN/CrN superlattice consisting of alternating TiN and CrN layers of nanometer-scale, deposited by the means of the reactive magnetron sputtering technique. This superlattice has been studied previously, examining performance properties under stress and temperature and the mechanisms of wear [1,2]. This material has been shown to have high oxidation resistance as well as superior mechanical properties. The hardness, high wear resistance and inertness of transition metal nitrides has been attributed to the unique bond structure. Typically 12-52 layers are deposited in a lattice with the extent of alloying, contamination, and roughening all critical to the performance of the lattice. Also, as the layers thin there are distinct changes in crystallinity and alloying affecting the tribological properties. As expected, deposition is difficult due to differences in the heat of formation of CrN and TiN – they each require different partial pressures of N₂ to form stoichiometric coatings.

To explore the stoichiometry and the extent of alloying in a TiN/CrN superlattice, we have employed the traditional surface analysis techniques of ion etch depth profiling with XPS. It has been historically accepted that monatomic Argon will typically suffice for this process however in this presentation a comparison will be made between conventional monatomic Ar⁺ ions and the more recent cluster Ar_n⁺ ions. The choice of impinging ion will be discussed with respect to stoichiometry and blending as will the practicalities of the depth profiling experiment and analysis. A novel method is proposed for the analysis of these materials, free of erroneous results.

S. Gallegos-Cantú *et al.*, *Wear*, **330–331**, 2015, pp 439–447.

H. C. Barshilia *et al.*, *J. Mater. Research*, **19**, 2004, pp 3196–3205

8:20am **TF-ThM2 Hydrogen Permeability of Hydrogenated Amorphous Carbons**, *Motonori Tamura*, The University of Electro-Communications (UEC-Tokyo), Tokyo, Japan

Diamond-like carbon (DLC) is an amorphous carbon with a significant fraction of CC sp³ bonds. Tetrahedral amorphous carbon (ta-C) is the DLC with the maximum sp³ content. These hydrogenated amorphous carbons have been classified into several types, such as a-C:H and ta-C:H.

Films of a-C:H with the highest H content (40–60 at. %) can have up to 70% sp³. However, most of the sp³ bonds are hydrogen terminated and this material is soft and has low density. Films of a-C:H with intermediate H content (20–40 at. %) have better mechanical properties. Even if these films have lower overall sp³ content, they have more C-C sp³ bonds. These films have the advantage of possessing high hardness levels – in the range of conventional tribological PVD coatings (1500 – 3200 HV), coupled with a coefficient of friction that is less than half of the conventional coatings.

In this study, hydrogen permeability of a-C:H films with intermediate H content was measured. Films were deposited by PVD + plasma-assisted CVD (PACVD) on stainless-steel substrates Type 316L. Hydrogen-permeation tests were performed on the coated stainless steel samples. These tests were based on the differential-pressure methods described in ISO15105-1:2007, the international standard for determination of gas-transmission rates.

The permeation of hydrogen through solid materials involves a series of steps including adsorption, dissociation, diffusion, and recombination coupled with desorption. In our experimental conditions, it was indicated from the relation between the permeation flux and driving pressure of hydrogen (100~800 kPa) that hydrogen passed through the samples in the diffusion-limited permeation mode.

Hydrogenated amorphous carbon films (2.0-mm-thick) were effective to reduce the rate of hydrogen permeation through stainless steel (0.1-mm-thick) less than 1/100 at 573-773 K. Effect of hydrogen content in films to hydrogen permeation behavior was studied.

8:40am **TF-ThM3 Mass Transport and Plastic Deformation in Refractory Nitrides via Density Functional Theory and Ab Initio Molecular Dynamics**, *Daive Sangiovanni*, Linköping University, Sweden **INVITED**

Surface dynamics during film growth and mobility of defects such as vacancies, dislocations, and grain boundaries in bulk determine the properties and performances of refractory nitride thin films. *Ab initio* calculations, carried out at 0 K, provide useful information regarding adatom and admolecule migration on surfaces as well as defect formation and mobility in bulk. However, phase stability and mass transport are also strongly affected by lattice vibrations at finite temperatures. This results in molecular dynamics (MD) becoming the primary computational tool for evaluating the rate of thermally activated processes and revealing the occurrence of non-intuitive reactions. Estimating the rate of rare events via accurate, but computationally expensive, *ab initio* MD is a challenging task, thus requiring the use of acceleration techniques.

I present the results for mass transport and plastic deformation in transition metal nitride compounds and alloys determined via density-functional theory and *ab initio* MD. I show that lattice vibrations significantly affect adatom, admolecule, point-defect, and dislocation mobilities, with dramatic effects on surface reaction rates and bulk properties.

9:20am **TF-ThM5 Anticorrosion yet Conductive Hf Coatings on AZ91D Magnesium Alloy by Magnetron Sputtering**, *Zhoucheng Wang, D.F. Zhang*, Xiamen University, China

Magnesium and its alloy are prone to corrosion due to the high electrochemical activity, although they are promising materials in electronics and aerospace industries. Surface coating technique has become an effective method to enhance the corrosion resistance of the Mg alloys. In addition to offering high corrosion resistance, the protective coatings should be conductive to avoid static buildup and maintain other advantageous properties when Mg alloy been used in the electronics and aerospace applications. In this study, anticorrosion yet conductive Hf coatings were fabricated on the AZ91D Mg alloys by magnetron sputtering with different bias voltages. The microstructure and corrosion behavior were investigated as a function of bias voltage range from 0 to -125 V. Both potentiodynamic polarization and neutral salt spray tests reveal that the Hf coating deposited at -100 V exhibits the best protective performance. It possesses the lowest corrosion current density of 1.032 mA/cm² and the highest protection rate of 6, respectively. This perfect anticorrosion property is due to the dense structure and low porosity induced by applying the appropriate bias voltage. The chemical inert Hf oxide formed on the coating's surface also contributes to improve the corrosion resistance. Various types of corrosion sites after corrosion tests are examined by scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS). The results indicate that the coating failure is determined by the synergy between the defects in coating and the random phase distribution in substrate.

9:40am **TF-ThM6 Effect of Oxygen on the Self-formation of Carbonaceous Tribo-layer with Carbon Nitride Coatings under a Nitrogen Atmosphere**, *Naohiro Yamada, T. Takeno, K. Adachi*, Tohoku University, Japan

Carbon nitride (CN_x) is an expected coating material which shows high hardness and relatively low friction under a nitrogen atmosphere. These properties make it a good candidate for small precision machines in order to reduce energy consumption and material losses. We have already reported that a carbonaceous tribo-layer, whose structure is altered from that of the deposited coating, has been found on the worn surface of counterpart. Thus, a structural change of carbon is necessary condition for super-low friction. However, the outstanding properties cannot be achieved in the presence of oxygen or humidity, which has meant these coatings has not been used in practical applications under ambient air. In contrast, CN_x coatings can give super-low friction under ambient air when they are heated to 100 °C. Besides, we have reported that hydrogen atoms

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derived from water molecules in a nitrogen atmosphere chemisorb the worn surfaces, which provides super-low friction. These results indicate that CN_x coating has possibility to reduce friction and wear regardless of whether the nitrogen gas is mixed with oxygen and humidity. In this study, the effect of oxygen and humidity on friction and wear of CN_x coatings are clarified in detail. The possibility of super-low friction under an oxygen-containing humid nitrogen atmosphere is discussed from the viewpoint of formatting carbonaceous tribo-layer.

The CN_x coating is produced on the surfaces of SiC ball and disk using an ion beam assisted deposition system. We conduct a ball-on-disk friction and wear test in a glove box, which allows for control of the relative humidity (RH) and oxygen concentration within the range of 0.01-40 %RH and 0.01-25 vol.%, respectively.

When friction and wear tests of CN_x coatings are conducted, friction coefficients and wear volumes increase with increasing RH (3-40 %RH) and oxygen concentration (0.01-25 vol.%). However, friction coefficients and wear volumes remain low values regardless of RH and oxygen concentration when CN_x slides against hydrogenated-CN_x (CN_x:H) coating. Besides, we found that CN_x coatings gave specific wear rate below 3×10^{-8} mm³/Nm when they achieved low friction coefficients below 0.05. These results indicate that there is a critical value of specific wear rate for formatting carbonaceous tribo-layer on the worn surfaces. TOF-SIMS depth analysis provides evidences that carbon derived from CN_x:H transfer to the surface of CN_x. This means that the carbonaceous tribo-layer is self-formed during friction. CN_x slid against CN_x:H achieved low friction coefficient below 0.05 regardless of RH and oxygen on the condition that the carbonaceous tribo-layer is self-formed.

10:20am TF-ThM8 Complex Stress Evolutions during Sputter-deposition of Metal Films: Interface Reactivity, Alloying and Phase Transformation, G. Abadias, Jonathan Colin, C. Furgeaud, A. Michel, Institut Pprime, CNRS-Université de Poitiers, France

INVITED

The understanding of morphological and microstructural development during thin film growth is of particular relevance to control islands shape, nucleation and growth of nanoparticles, phase transformation, texture or surface roughness. Due to oversaturated vapour fluxes employed in physical vapor deposition (PVD) techniques, dynamics usually prevails over thermodynamics in dictating growth and microstructural evolution in PVD films. Depending on the material type and process conditions, the film can develop different stress levels, evolving usually with film thickness. Recently, real-time wafer curvature measurements have contributed to increase our knowledge on the underlying mechanisms of stress development during growth, and to propose comprehensive physical models [1].

In this presentation, we will provide some examples of *in situ* and real-time diagnostics based on optical techniques (wafer curvature, surface differential reflectance spectroscopy) and electrical resistance measurements to probe with high sensitivity the early growth stages of a variety of metal films on Si during sputter-deposition. We will first review some typical compressive-tensile-compressive stress evolutions observed for high-mobility metals (e.g. Ag, Cu, Au) [2]. The influence of interface reactivity (using different buffer layers- SiO_x, a-Si or a-Ge) will be highlighted, and for the specific case of Cu, alloying with Ge (using co-sputtering) will be addressed.

In the second part of the talk, special focus will be placed on low-mobility metal systems (e.g., Mo, Ta, W) deposited on amorphous Silicon (a-Si), which exhibit a complex stress development with film thickness. In the case of Mo and Fe films, our *in situ* measurements reveal a structural transition at a film thickness of ~ 2-3 nm manifested by a concomitant tensile stress variation [3] and decrease in electrical resistance. Insights on the kinetics of the amorphous-to-crystalline phase transformation were gained from *in situ* synchrotron studies, coupling simultaneously X-ray diffraction, X-ray reflectivity and wafer curvature during sputter-deposition of a series of Mo_{1-x}Si_x alloys.

[1] E. Chason, P.R. Guduru, J. Appl. Phys. 119 (2016) 191101.

[2] G. Abadias, L. Simonot, J.J. Colin, A. Michel, S. Camelio, D. Babonneau, Appl. Phys. Lett. 107 (2015).

[3] A. Fillon, G. Abadias, A. Michel, C. Jaouen, P. Villechaise, Phys. Rev. Lett. 104 (2010) 096101.

11:00am TF-ThM10 First Steps Towards Accessing Aluminum's Far UV Reflectance for Space-based Telescopes, David Allred, R.S. Turley, S.B. Perry, S.M. Thomas, S.G. Willett, Brigham Young University, USA

We report on our progress on vacuum removal of protective layers on aluminum mirror surfaces using hydrogen plasmas and/or heating. One of NASA's flagship astrophysical missions of the 2020's or 30's will likely be a LUVOIR (large, UV-optical-IR) telescope. This space-based observatory will employ the largest mirrors ever flown. The reflective coating will almost certainly be aluminum since such telescopes would profit from truly broadband mirrors. The top surface of such aluminum mirrors, however, need to be bare without the oxide layers that naturally form in air. (The local space environment for the observatory should be sufficiently oxygen-free that a pristine surface should remain bare for decades.) We will discuss our research into protecting as-deposited aluminum mirrors before atmosphere exposure with a robust, protective layer, or layers, that could be deposited to coat the aluminum immediately after its deposition, before it comes in contact with air, and cleanly and relatively easily removed once the mirror is in space. This removal must be gentle enough to not roughen the mirror surface nor redepositing material removed from the protective layer on the mirror or other spacecraft components. Thus our choice of hydrogen plasmas. We will specifically discuss the deposition and removal of organic and inorganic (Cd-containing and Zn) films that were evaporated onto the aluminum immediately after its deposition. This could open up the 11-15eV band for space-based astrophysics without sacrificing IR, visible and UV reflectance.

11:20am TF-ThM11 Microscale Measurement of Coating/Substrate Interfacial Shear Failures, X. Zhang, Y. Mu, Wenjin Meng, Louisiana State University, USA

Quantitative evaluation of critical stresses governing interfacial failures in coating/substrate systems is crucial for surface engineering via the application of coatings to substrates. While a number of measurement techniques have been developed and studied over the past two decades, quantitative measurement of critical stresses leading to interfacial failures in coating/substrate systems has remained a challenge.

We report a new micro pillar compression testing protocol for quantitative measurement of interfacial shear failure stress in ceramic coating/metal adhesion layer/substrate systems. Three specimen series were investigated: CrN/Cu/Si, CrN/Ti/Si, and CrN/Cr/Si. All film/coating depositions occurred in a UHV plasma assisted magnetron sputtering system. Specimen characterization was accomplished through X-ray diffraction (XRD), focused ion beam and scanning electron microscope (FIB/SEM), and transmitted electron microscope (TEM). Scripted FIB cutting was used to fabricate cylindrical micro-pillars of the three specimen series, with interfaces inclined at 45deg with respect to the pillar axes. Compression loading of micro-pillars was carried out on an instrumented nano-indentation device. Depending on the interfacial adhesion layer used, the testing results show clear differences in the critical shear failure stress. The present results show the efficacy of this new microscale testing protocol, and motivate further study of the mechanical integrity of coating/substrate interfaces.

11:40am TF-ThM12 Selectivity Control in the Electroreduction of CO₂ over Nanostructured Catalysts, Beatriz Roldan Cuenya, Ruhr University Bochum, Germany

The electrocatalytic reduction of CO₂ to industrial chemicals and fuels is a promising pathway to sustainable electrical energy storage and to an artificial carbon cycle, but is currently hindered by the low energy efficiency and low activity displayed by traditional electrode materials.

Using colloidal synthesis, nanoparticles (NPs) with well-defined size and interparticle distance were prepared and tested as catalysts for CO₂ electroreduction. Cu NP catalysts displayed a drastic increase in activity and selectivity for H₂ and CO with decreasing NP size below 5 nm. Hydrocarbon (methane and ethylene) selectivity was increasingly suppressed with decreasing NP size. For Au NPs, a drastic increase in current density was observed with decreasing NP size, along with a decrease in faradaic selectivity towards CO. The H₂/CO product ratio could be specifically tailored for different industrial processes by tuning the size of the Au NPs. In addition, we demonstrated that interparticle distance (IP) is also a critical parameter for controlling reactivity. For largely spaced NPs, selectivity to CO is enhanced, since this reaction intermediate is less likely to readsorb on neighboring NPs after formation. On the contrary, for closely spaced NPs we find that hydrocarbon selectivity is enhanced, since the re-adsorption of reaction intermediates on neighboring NPs can facilitate the multi-step pathway required for hydrocarbon production. This

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study addresses previously unexplored aspects of how product selectivity can be controlled using mesoscale transport processes during CO₂ electroreduction.

Another critical parameter for selectivity control in nanostructured electrocatalysts is the chemical state. We will discuss new oxide-derived metal catalysts that can reduce CO₂ with lowered overpotential and improved ethylene selectivity. We will also present critical insights into the catalyst reaction mechanism which were unraveled using structural and chemical information on the sample obtained under *operando* conditions via X-ray absorption fine-structure spectroscopy. Finally, the role of the NP shape, in particular, the presence of (100) facets in Cu nanocubes and the evolution of the NP structure and dispersion under reaction conditions will be discussed based on *operando* electrochemical AFM data.

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