

Monday Morning, November 9, 2009

Advanced Surface Engineering

Room: B1 - Session SE1-MoM

Photocatalytic Coatings

Moderator: H. Barankova, Uppsala University, Sweden

8:20am **SE1-MoM1 Development of Highly Functional Visible Light-responsive TiO₂ Thin Film Photocatalyst Materials by a RF Magnetron Sputtering Method and their Applications for our better Environment and Production of Clean Energies using Sunlight**, M. Anpo, M. Matsuoka, M. Takeuchi, Osaka Prefecture University, Japan **INVITED**

Titanium oxide-based catalysts have attracted a great deal of attention for their application in photocatalytic materials with high reactivity, thermal stability and nontoxic properties¹. However, unlike natural photosynthesis in green plants, they can make use of only 3-4% of solar light, necessitating the use of a UV light source. Recently, we have successfully applied a RF magnetron sputtering deposition method to design unique and efficient titanium oxide photocatalysts which enable the absorption of visible light of longer than 550 nm. These newly developed titanium oxide catalysts were found to work as environmentally-friendly photocatalyst, leading to the efficient use of solar energy for the production of clean H₂ and O₂ from water with a separate evolution and other significant reactions²⁻⁴.

In the present lecture, the results obtained for the photocatalytic decomposition of H₂O with the separate evolution of H₂ and O₂ under sunlight irradiation of the visible light-responsive titanium oxide thin film photocatalysts will be presented.

References

- 1) M. Anpo, et al., in "Annu Rev. Mater. Res.", Eds. J. M. Thomas and P. L. Gai, **35**, 1 (2005).
- 2) M. Kitano, M. Takeuchi, M. Matsuoka, M. Anpo, et al., *Catal. Today*, **120**, 133 (2007).
- 3) M. Kitano, M. Matsuoka, J. M. Thomas, M. Anpo, et al., *Top. Catal.*, **49**, 24 (2008).
- 4) S. Fukumoto, M. Kitano, M. Takeuchi, M. Matsuoka, M. Anpo, *Catal. Lett.*, **127**, 39 (2009).

9:00am **SE1-MoM3 The Effect of Nb Additions on the Synthesis, Photo-Response, and Photo-Activity of TiO₂ Thin Films**, P.A. DeSario, M.E. Graham, K.A. Gray, Northwestern University

A deeper understanding of the relationships between synthesis, structure and function is needed to improve the design of materials tailored to solar energy conversion and storage. The objective of this research is to synthesize TiO₂ composites with properties tailored to the harvesting and conversion of solar energy. Unbalanced reactive dc magnetron sputtering with partial pressure control of oxygen was utilized to synthesize a series of pure and mixed phase TiO₂ films. Films were doped with Nb (Ti_{1-x}Nb_xO₂) in the range of 0 < x < 0.45 to evaluate the effect of cation doping on optical, chemical and physical properties. The films were interrogated structurally and functionally using SEM, EDX, XPS, AFM, UV-Vis absorption spectroscopy, and XRD. Selected films were evaluated with respect to gas phase CO₂ reduction and gas phase oxidation of acetaldehyde and the action spectra were determined.

Improvements in catalytic efficiency can be made by shifting the photo-response of tiania-based materials to utilize a larger portion of the solar spectrum. Many attempts have been made to red-shift the photoresponse of TiO₂ through cation doping or anion doping. It is not yet proven, however, if the shift in photoresponse correlates to enhanced photoactivity under visible light or simply the creation of color centers. Preliminary findings show that Nb doping enhances oxidative reactivity under visible light. Reductive chemistry does not seem to be enhanced, however, which suggests how Nb substitution is altering band gap structure.

While earlier work established the relationships between sputtering process parameters and the film structure, including phase identity and distribution in pure TiO₂, this work is focused on how the addition of Nb cations change the film growth and phase formation relative to the pure material. The work also tries to characterize the cation valence and location in the TiO₂ lattice. The parametric response of film structure still suggests that in the mixed phase system greater energy input favors the formation of rutile and lower energy favors anatase, but Nb additions shift the regions of phase stability compared to pure TiO₂ and favor the growth of rutile. The shift in optical absorption to the visible wavelength range as a function of Nb concentration and anatase-rutile phase distribution is also presented.

Our work on pure TiO₂ indicates that the films with the highest photoreactivity were nanocrystalline, mixed phase structures (~70% anatase) with substoichiometric oxygen concentration. Results are presented comparing the photoreactivity of the Nb doped films with the pure TiO₂ mixed phase films of similar structure and phase proportions.

9:20am **SE1-MoM4 Identification of Carbon Sensitization for the Visible Light Photocatalytic Titanium Oxide**, Y. Chen, G. Jhan, G. Cai, T. Lin, M.S. Wong, C. Cheng, National Dong Hwa University, Taiwan

Titania nanopowders synthesized by low-pressure flat-flame metalorganic chemical vapor condensation method are known to possess visible light photocatalytic ability even they are produced without intentional doping. While the visible-light absorption of the powder is convincing, the cause of visible light absorption is still inconclusive. There are 3 main possible causes for visible light absorption discussed earlier. First is the anatase/rutile interface that generates defect levels for visible light absorption. Second is the nitrogen doping that forms the absorption center. Third is the carbon doping that forms the absorption center. In order to confirm that carbon doping is the major cause for the visible light absorption of the powder, we modify the process using helium in place of nitrogen to eliminate the nitrogen doping possibility. Helium in place of nitrogen is used as the titanium precursor carrier gas, where the precursor is titanium isopropoxide. Using acetylene and oxygen as fuel and oxidizer for the flame, the titanium isopropoxide was decomposed and oxidized, and the nanoparticles of titania were formed. From the methylene blue decomposition study we found that the powder synthesized under low precursor feed rate possesses high photocatalytic efficiency under illumination of visible light. Since nitrogen is avoided in the process, the visible light absorption cannot be due to nitrogen doping. We also found that the nanopowder formed has a single phase of anatase. Thus the nanopowder does not have anatase/rutile interface, and we can eliminate the possibility of visible light absorption by the anatase/rutile interface. The visible light absorption should thus be resort to the carbon doping. XPS studies show the presence of several carbon related bonds except Ti-C bond. This suggests that the carbon does not incorporate into the TiO₂ crystal and should locate on the surface of the nanopowder. Thus the carbon species act as a visible light sensitizer for the titania as a photocatalyst. Among all carbon bonds the C-C bond is believed to be responsible for the light absorption, since all other carbon related bonds are not chromophores. The carbon should be in the cluster form to become colored. The visible light TiO₂ photocatalysis induced by carbon doping is confirmed and explained.

9:40am **SE1-MoM5 Effects of Oxygen Vacancies on Electro-Optic Properties of Reactively Co-Sputtered Nb-doped Titania Films**, H.C. Hsing, H.T. Chang, T.Y. Lu, C.C. Mo, M.S. Wong, National Dong Hwa University, Taiwan

Transparent conducting niobium-doped titania was prepared by reactive co-sputtering of Ti and Nb metal targets in oxygen and argon plasma. The as-deposit films were annealed at 650°C under air atmosphere for 8 hr and then hydrogen annealed. Two different H₂-annealing procedures were executed to generate different concentration of oxygen vacancies: the H₂-annealing time ranges from 10 min to 4 hr under constant temperature and H₂-annealing temperature ranges from 200°C to 800°C under constant time. From the XPS spectra, the concentration of oxygen vacancies was observed, and directly affects the carrier concentrations in the thin film. The thin film's structure and optical properties was also measured and discussed.

10:00am **SE1-MoM6 Micro-Structure of Photo-Catalytic TiO₂ Films Deposited by Oxygen Ion Assist Reactive Evaporation Method and Reactive Sputtering**, Y. Hoshi, D. Ishihara, H. Lei, T. Sakai, Tokyo Polytechnic University, Japan

TiO₂ films were deposited on glass slide substrates by using oxygen ion assist reactive evaporation method(IARE) and reactive sputtering method(RS), and their micro-structure was investigated by using FE-TEM.

The films of above 1um thick deposited by IARE at the substrate temperature of 300 °C and ion accelerating voltage of 200 V has excellent photo-catalytic properties. However, the films with thickness lower than 1um shows poor photo-catalytic properties. In these films, the crystallization in the initial layer on the substrate was suppressed so that the film near the substrate contains large amount of amorphous phase. As the film grew, crystallization was enhanced and clear columnar structure was developed in the films. As a result, most of the amorphous phase was disappeared at the thickness above 600 nm. In addition, the column were separated each other with clear spaces at the thickness above 800 nm. This may be the reason why the photocatalytic properties improved significantly as the film thickness increased above 1um. These results suggest that the

poor crystal structure is the main reason why the film with thickness below 800nm has poor photo-catalytic properties.

On the other hand, compared with the films deposited by IARE, crystallization was enhanced in the deposition of the films by using a reactive sputtering. As a result, crystallized film with thickness below 200 nm can be obtained at 300 °C. This may be due to the fact that the depositing atoms in the sputtering process have much larger kinetic energy than in IARE. The film, however, has much dense structure and smooth surfaces, which results in a poor photo-catalytic organic decomposition properties.

10:40am **SE1-MoM8 Enhancement of Visible-Light Activities of Photocatalytic WO₃ Films Deposited by Sputtering.** *A. Murata, M. Kikuchi, N. Oka, Y. Sato, S. Nakamura, H. Yamaguchi, Y. Shigesato*, Aoyama Gakuin University, Japan

We have been reported on photoinduced superhydrophilicity and oxidative decomposition of organic compounds under visible light irradiation on polycrystalline WO₃ films deposited by reactive magnetron sputtering at the substrate temperature at 800 °C [1,2,3]. On the other hand, Abe, et al. reported that WO₃ powder loaded with Pt nanoparticles exhibits high efficiency for the decomposition of organic compounds under visible light irradiation, certainly due to promotion of multielectron O₂ reduction [4].

In this study, we deposited the photocatalytic WO₃ films with visible-light-activity on fused silica glass substrates by dc reactive magnetron sputtering using a W metal target. The substrate temperatures and total gas pressure during the deposition were 800 °C and 5.0 Pa, respectively. In addition, Pt was deposited on WO₃ film surfaces at RT by sputtering with various sputtering power and deposition time. In the case of Pt deposited on WO₃ films, 3D growth mode (Volmer-Weber) should be expected in general, because atoms or molecules in the deposit are more strongly bound to each other than to the substrate. The surface coverage of Pt on the WO₃ films were estimated by X-ray photoelectron spectroscopy (XPS), which implied that the Pt film followed Volmer-Weber type film growth process, i.e., after an initial nucleation, an island structure grew and coalesced with each other with increasing film thickness. High resolution electron microscopy (HREM) revealed that Pt nano-particles with diameter of about 2 nm were generated at the early stages of the Pt film growth, which dispersed uniformly on the columnar polycrystalline WO₃ films possessed of large surface area.

The photocatalytic activity was evaluated by photodecomposition of acetaldehyde under the irradiation of visible light (Xe lamp with a 410-500 nm band pass filter, 1.0 mW/cm²). With increasing in the Pt deposition time upto 10 sec, the decomposition rates for the Pt loaded WO₃ films were higher than that on the pristine WO₃ film. Especially, for the WO₃ films deposited with the Pt by 7 sec, acetaldehyde was completely decomposed within 150 min, on which the surface coverage of Pt indicated about 60%.

[1] M.Ebihara, Y.Shigesato,et al., Proceedings of the 3rd ICCG (2000) 137.

[2] M. Kikuchi, Y. Shigesato, et al., Abstract of the 21st IUPAC SYMPOSIUM (2006) 496.

[3] M. Kikuchi, Y. Shigesato, et al., Proceedings of the 6th ICCG (2006) .

[4] R. Abe, B. Ohtani, et al., J. Am. Chem. Soc. 130, (2008) 7780.

11:00am **SE1-MoM9 Optimization of Photovoltaic Performance through the Integration of Electrodynamic Dust Shield Layers.** *S. Nason, K. Davis, N. Hickman*, Florida Solar Energy Center, *E. Arens, J. McFall, C. Calle*, Kennedy Space Center

The viability of photovoltaics on the Lunar and Martian surfaces may be determined by their ability to withstand significant degradation in the Lunar and Martian environments. One of the greatest threats is posed by fine dust particles which are continually blown about the surfaces. In an effort to determine the extent of the threat, and to investigate some abatement strategies, a series of experiments were conducted outdoors and in the Moon and Mars environmental chamber at the Florida Solar Energy Center .

Electrodynamic dust shield prototypes based on the electric curtain concept have been developed by our collaborators at the Kennedy Space Center [1]. These thin film layers can remove dust from surfaces and prevent dust accumulation. Several types of dust shields were designed, built and tested under high vacuum conditions and simulated lunar gravity to validate the technology for lunar exploration applications.

Gallium arsenide, single crystal and polycrystalline silicon photovoltaic integrated devices were designed, built and tested under Moon and Mars environmental conditions as well as under ambient conditions. Photovoltaic efficiency measurements were performed on each individual cell with the following configurations; without an encapsulation layer, with a glass covering, and with various thin film dust shields. It was found that the PV efficiency of the hybrid systems was unaffected by these various thin film

dust shields, proving that the optical transmission of light through the device is virtually uninhibited by these layers.

The future goal of this project is to incorporate a photovoltaic cell as the power source for the electrodynamic dust shield system, and experimentally show the effective removal of dust obstructing any light incident on the cell, thus insuring power production is maximized over time.

[1] C.I. Calle, C.R. Buhler, J.G. Mantovani, S. Clements, A. Chen, M.K. Mazumder, A.S. Biris, A.W. Nowicki, Electrodynamic dust shield for solar panels on Mars, Lunar and Planetary Science XXXV, 2004, p. 2014.

Advanced Surface Engineering

Room: C4 - Session SE2-MoM

Pulsed Plasmas in Surface Engineering

Moderator: J. Patscheider, EMPA, Switzerland

8:20am **SE2-MoM1 Industrialization of Metal Ion Sputtering.** *R. Cremer*, KCS Europe **INVITED**

Since its introduction by Kouznetsov et al. in 1999, the HIPIMS technology has seen a remarkable rise in interest from both academic and industrial viewpoint. Although the high ionization of the plasma and the resulting advantages for industrial sputter applications have been verified more than a decade ago, industrial usage of the metal ion sputtering technology has been limited due to various technical drawbacks.

Only recently, a various number of authors have reported the overcome of the hitherto existing disadvantages of the technology like low deposition rate, biasing issues, arcing and reliability of the technology.

This paper gives an overview on the industrialization of metal ion sputtering in various applications. Special focus will be given to the comparison of ionization in different coating technologies like sputtering, metal ion sputtering, arc ion plating and thermionic arc evaporation. The paper will also comment on future options and limitations of industrial metal ion sputtering.

9:00am **SE2-MoM3 Structural and Mechanical Behavior of Fullerene-Like and Amorphous Carbon Nitride Thin Films Deposited by HPPMS.** *S. Schmidt, G. Greczynski*, Linköping University, Sweden, *E. Broitman*, Carnegie Mellon University, *L. Hultman*, Linköping University, Sweden

The structural and mechanical properties of fullerene-like (FL) and amorphous carbon nitride (CN_x) films were deposited using High power pulsed magnetron sputtering (HPPMS) in an industrial CC-800/9 CemeCon chamber and compared with films deposited by DC magnetron sputtering mode of operation.

Films of 1 µm and 2 µm thickness were grown on Si and steel substrates, respectively. Carbon nitride films were deposited via HPPMS from a high purity graphite target in an Ar/N₂ discharge at 400 mPa, the N₂ fraction varied from 0 to 0.5 and different substrate temperatures ranging from ambient temperature to 300°C were chosen. Furthermore, a novel HPPMS substrate pretreatment employing two HPPMS power supplies was used to optimize the adhesion of the films: the first power supply established the discharge; the second produced a pulsed substrate bias. The created Cr-plasma cleaned the substrate surface and formed a Cr-containing gradual interface into the substrate. X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) were used to study the microstructure of both, the films and the interfaces. The hardness and the elastic recovery of the CN_x films were measured using nanoindentation. A deposition process window is demonstrated for the growth of dense fullerene-like (FL) film structures consisting of curved, frequently intersecting, and highly in-plane oriented basal planes.

9:20am **SE2-MoM4 Effects of the Working Pressure and Pulse Parameters on the Ion Energy and Mass Distributions in Modulated Pulse Power Sputtering Plasma.** *W.D. Sproul*, Reactive Sputtering, Inc., *J. Lin, J.J. Moore, B. Mishra*, Colorado School of Mines, *J.A. Rees*, Hiden Analytical Ltd, UK, *Z.L. Wu, J. Wang*, Colorado School of Mines, *R. Chistyakov, B. Abraham*, Zond/Zpulsar

The modulated pulse power (MPP) sputtering technique is a variation of high power pulsed magnetron sputtering (HPPMS) that generates a high ionization density plasma by manipulating the pulse shape, intensity, and duration. In this study, the time-averaged ion energy and ion mass distributions of the MPP plasma generated during sputtering a metal Cr target in pure Ar at different working pressures, pulse frequencies, and the strong ionization periods were investigated. The MPP plasma was studied

using an electrostatic quadrupole plasma mass spectrometer which was installed parallel to the target surface in a closed field unbalanced magnetron sputtering system. It was found that an increase in the working pressure led to an increase in the peak ion flux and a decrease in the high ion energy tail. An increase in both the gas and metal ion species was observed as the pulse frequency was increased using the same pulse shape. Additionally, the effects of different combinations of the weak and strong ionization durations on the ion energy distributions of the gas and metal ion species will be reported.

10:00am **SE2-MoM6 Effects of HiPIMS Plasma Transport on Thin Film Deposition**, *D. Lundin*, Linköping University, Sweden, *N. Brenning*, *M.A. Raadu*, Royal Institute of Technology, Sweden, *U. Helmersson*, Linköping University, Sweden

A new exciting development of magnetron sputtering was achieved when introducing high power impulse magnetron sputtering (HiPIMS). HiPIMS is one of the most promising improvements of common IPVD techniques and is already making its way to industrial applications. The HiPIMS plasma generates large quantities of ions of the sputtered material due to a high plasma density, but also acceleration of the ions increasing the bombardment of the growing film without using a substrate bias voltage. Also observed is a lower deposition rate for HiPIMS than that obtained for conventional DC sputtering, using the same average power. In order to optimize the process, controlling ion acceleration and increasing deposition rate, the mechanisms for transport of charged particles in this type of plasma need to be known. In the present work, it is shown that the electron mobility across the magnetic field is enhanced by typically an order of magnitude during the HiPIMS discharge compared to DC magnetron sputtering. This cannot be explained by classical theory of diffusion and electrical conductivity or Bohm diffusion. The transport is directly reflected by an anomalously low azimuthal-to-discharge current ratio, $J_\phi / J_D = 2$. On the microscopic scale, the anomalous transport can be shown to be mediated by observed azimuthal electric field oscillations in the lower hybrid range. Furthermore, new insights from experimental data and plasma discharge modeling will be presented, which show that a large fraction of the ionized species are attracted back towards the target, either by electric fields in the bulk of the plasma, or by the stronger local fields in the cathode sheath. In this context, it is demonstrated that the effect of the anomalously high electron mobility to reduce the bulk \mathbf{E} field is important to understand and control. The study also verifies that the resistive friction force, $\mathbf{F}_{i,\phi}$, associated with the anomalous resistivity, can accelerate the ions azimuthally, as is shown both indirectly from changes in the deposition patterns, and directly by mass spectrometry.

10:40am **SE2-MoM8 Deposition Rates of High Power Impulse Magnetron Sputtering: Physics and Economics**, *A. Anders*, Lawrence Berkeley National Laboratory **INVITED**

Deposition by high power impulse magnetron sputtering (HIPIMS) is considered by some as the new paradigm of advanced sputtering technology, yet this is met with skepticism by others for the reported lower deposition rates, if compared to direct current (DC) sputtering of equal average power. In this contribution, absolute and relative (normalized) deposition rates are compared, and the underlying physical reasons for differences are discussed, including (i) ion return for self-sputtering, (ii) the less-than-linear increase of the sputtering yield with increasing ion energy, (iii) yield changes due to the shift of species responsible for sputtering, (iv) change in plasma impedance and sheath voltage, (v) changes in film density, (vi) noticeable losses in the switch module, (vii) changes of the magnetic balance and particle confinement of the magnetron due to self-fields at high current, and (viii) superposition of sputtering and evaporation for selected materials. The situation is even more complicated in reactive systems where the target surface chemistry is a function of the discharge conditions. While generally these factors imply a reduction of the normalized deposition rate, increased rates have been reported for certain conditions. Finally, some points of economics and “value added” are considered.

This work was supported by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

11:20am **SE2-MoM10 Optical Diagnostics of HIPIMS Discharges: Dependence of Film Growth on Control Parameters**, *M. Lange*, UTC and AFRL/RXBT, *J. Jones*, AFRL/RXBT, *C. Muratore*, UTC and AFRL/RXBT, *A. Reed*, AFRL/RXBT, *A. Waite*, UTC and AFRL/RXBT, *A. Voevodin*, AFRL/RXBT

High power impulse magnetron sputtering is a physical vapor deposition process distinguished by its capability to produce a high flux of ionized target material incident upon growing film surfaces. This characteristic gives the process advantages over conventional dc sputtering in that the orientation and relative density of thin films can be controlled by

modulating the energy of ions constituting the film material. Unfortunately, the deposition rate in HIPIMS is often lower than in standard magnetron sputtering when processes conducted with the same time-averaged power are compared. The deposition rates for HIPIMS processes are dependent upon the power waveforms to the target, as well as the ionization energy, self sputtering rate, atomic mass, and other physical properties of the sputter target material. Correlation of target materials with thoughtfully selected properties to resultant plasma characteristics can reveal the nature of these relationships. For example, the ionization energies of hafnium and titanium are similar (6.8 eV), but their atomic masses of 178 amu and 48 amu respectively, affect the deposition rate in addition to the temporal-spatial plasma distributions, which were measured here using optical and electrostatic diagnostics. Studies of these materials provide insight on the effect of target mass on ion transport and film growth rates. Substrate bias and pulse duration have also been shown to effect the optical emissions from the plasma generated during HIPIMS operation. Correlation of these plasma characteristics to the structure and properties of elemental and compound thin films will be presented.

11:40am **SE2-MoM11 Time-resolved Plasma Characterization in Modulated Pulse Power (MPP) Magnetron Sputtering**, *A.N. Cloud*, *R.E. Flauta*, *M.J. Neumann*, *S.L. Rohde*, *D.N. Ruzic*, University of Illinois at Urbana-Champaign

High power impulse magnetron sputtering (HIPIMS/HPPMS) has attracted considerable attention from industry due its ability to produce thin films and features of excellent adhesion, superior density, decreased roughness, and extreme conformity. The intense pulsed plasma density – on the order of 10^{18} m^{-3} – provides a large concentration of metal ions that can be used to produce high-quality, homogeneous coatings. The high ionization fraction at the substrate allows for fine control of the sputtered species during deposition.

Modulated pulse power (MPP) can be employed to shape an arbitrary voltage waveform that is applied to the cathode. This programming freedom allows control over pulse duration, intensity, duty cycle, and average power. Voltage oscillations during the 1.0 – 3.0 ms pulse on the order of 25-65 kHz induce instabilities in the plasma discharge that may have a marked effect on the level of ionization within the discharge and distribution of the metal ions. The oscillation frequency range corresponds to the expected ion cyclotron angular frequencies. Past investigations of MPP have only revealed time-averaged plasma parameters, but knowledge of events during the pulse is required to further understanding of the physical mechanisms involved.

MPP discharges produced with a 1000 cm² circular planar magnetron were characterized. A gridded energy analyzer and quartz crystal microbalance were used to measure a higher ionization fraction than with conventional magnetron sputtering under a variety of deposition conditions. Nominal values of approximately 6% were attained for the sputtering of titanium at power densities as low as 100 W/cm². The energy spectrum and flux of these ions at the substrate location were also measured, finding the incident metal ions to be of low energy between 1 and 4 eV. Time-resolved plasma properties including saturation current, electron temperature, and density are measured and mapped over the three-dimensional space between the sputter target and substrate using a triple Langmuir probe. Plasma density is shown to decrease by greater than an order of magnitude between pulses. The effects of pulse duration, current density, pulse shape, switching frequency, and target material on the discharge are explored and discussed.

Monday Afternoon, November 9, 2009

Advanced Surface Engineering

Room: C4 - Session SE-MoA

Atmospheric Pressure Plasmas

Moderator: M.S. Wong, National Dong Hwa University, Taiwan

2:00pm SE-MoA1 Production-scale Processing of Flexible Substrates using High Power, Low Temperature, Atmospheric Pressure Plasma Technology, G.S. Selwyn, APJeT, Inc. INVITED

The application of vacuum-based plasmas in semiconductor processing has helped lead the microelectronics revolution and today is a highly-developed and mature technology. However, the high cost of operation and maintenance for vacuum-based plasma, along with the limitation for treating vacuum-compatible substrates, greatly limits future applications using this technology. In contrast to the vast expansion of vacuum-based plasma over the last 30 years, non-equilibrium, atmospheric-pressure plasma has a 125 year history dating back to Siemen's original invention of the dielectric barrier discharge. Yet, the applications for atmospheric pressure plasma industry represent only a tiny fraction of today's use of vacuum-based plasma. Part of the reason for this is the low power density that Dr. Siemen's atmospheric pressure plasma was able to achieve and the faster processing rates and improved control vacuum-based plasma was able to provide. This talk will review and compare the various kinds of atmospheric pressure plasma sources and will illustrate the use of a high-power, stable, non-equilibrium atmospheric pressure plasma that operates with a gas temperature below 30C for low-cost processing of commodity materials, such as textiles, non-wovens and plastic films. A full-scale production machine that uses 72" electrodes and which operates at 10KW will be shown, along with the unique process this technology enables.

2:40pm SE-MoA3 Effect of the Electrode Material in the Atmospheric Plasma Abatement of NO from Air Mixtures, L. Bardos, H. Barankova, Uppsala University, Sweden

Protection of the environment requires more stringent limits on engine exhausts, power plant emissions and all other sources of air pollution. Different air cleaning technologies are being developed and applied for removal of pollutant gases like NO, NO₂, SO₂ and CO₂. A very promising treatment is based on non-thermal (cold) plasmas at atmospheric pressure where dominant energy carriers are electrons and the dominant chemistry is based on formation and interactions of gaseous radicals. A widely supported method of cleaning air mixtures in the exhausts of diesels and combustion plants from NO and NO₂ utilizes the Plasma Assisted Catalytic Reduction where the cold plasma is combined with the solid-state catalyst. In this method the plasma acts as an oxidation catalyst where an atomic oxygen from air oxidizes NO to NO₂ and the solid-state catalysts are then capable to convert all NO₂ to N₂ and O₂. However, in most cases it is necessary to involve also auxiliary gases, typically hydrocarbons (propene, ammonia), to make the process efficient. The present work introduces an original cold plasma system based on atmospheric hollow cathodes working in a pulsed dc regime with variable pulse voltage and repetition frequency. The system design and parameters have been optimized for the best conversion performance. It has been found that the material of electrodes can affect the oxidation efficiency of the plasma substantially. The graphite electrodes allowed the 100% conversion of NO to NO₂ without any auxiliary gas. Effects of several materials on the conversion efficiency are compared and discussed.

3:00pm SE-MoA4 Mechanism for the Surface Activation of Polymers by Remote Atmospheric Pressure Plasma, E. Gonzalez, M. Barankin, University of California, Los Angeles, P. Guschl, SurfX Technologies, LLC, R. Hicks, University of California, Los Angeles

An atmospheric pressure oxygen and helium plasma was used to activate the surfaces of polyethylene (PE) and polymethyl methacrylate (PMMA). The plasma physics and chemistry was investigated by numerical modeling. It was shown that as the electron density of the plasma increased from 3×10^{10} to 1×10^{12} cm⁻³, the concentration of O atoms and metastable oxygen (¹Δ_gO₂) molecules in the afterglow increased from 6×10^{15} to 1×10^{17} cm⁻³, while the concentration of ozone decreased from 5×10^{15} to 2×10^{15} cm⁻³. The oxygen atoms, metastable oxygen (¹Δ_gO₂) molecules and ozone were the principle reactive species present in the afterglow. Exposing the polymers to the plasma afterglow for up to 30 seconds led to surface activation and an increase in bond strength of the polymers to adhesives by as much as 16 times. X-ray photoelectron spectroscopy of PMMA revealed an 8% increase in the C 1s peak area attributed to carboxylic acid groups (288.9 eV). In

addition, the C 1s peak due to the methyl pendant groups (285.0 eV) decreased by 5%. The O:C ratio of PMMA increased from 0.4 to 0.7 after plasma treatment. Surface analysis of the polymers by internal reflection infrared spectroscopy confirmed the presence of carboxylic acid groups at 1710 cm⁻¹ and hydroxyl groups at 3100 to 3500 cm⁻¹ after activation. These results indicate that oxygen atoms and metastable O₂ molecules generated in the plasma rapidly oxidize the polymer chains. The experimental results as well as a detailed description of the reaction mechanism will be presented at the meeting.

3:40pm SE-MoA6 Coating Growth Behavior during the Plasma Electrolytic Oxidation Process, R.O. Hussein, D.O. Northwood, X. Nie, University of Windsor, Canada

In this study, aluminum oxide was deposited on an Al-alloy substrate to produce hard ceramic coatings using a Plasma Electrolytic Oxidation (PEO) process working at atmospheric pressure. Two different operation modes were used, namely a DC power mode and pulsed DC power mode with different frequencies. Optical Emission Spectroscopy (OES) was employed to study the species, electron temperature and densities of the plasma. The morphology, composition, and microstructure of the coatings on the Al substrate were investigated using Scanning Electron Microscopy (SEM) with energy dispersive X-ray (EDX) analysis, and X-ray diffraction. At the early stage of the PEO process the plasma electron temperature increased which shows the same trend as the output voltage. Aluminum emission line intensities (which are related to the spark behavior during the discharge) were higher for the pulsed DC mode than that from DC mode, causing different surface morphologies. It was also found that pulsed DC mode enhanced the coating growth during the early discharge stage, due to the strong ejection of aluminum from the substrate-oxide interface during the plasma discharges. The coating characteristics and OES analysis thus led to a better understanding of the ceramic coating growth behavior as influenced by the power operation modes.

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4:00pm SE-MoA7 Saddle-like ICP Antenna for RF Atmospheric Plasma Processes, Y. Glukhoy, American Advanced Ion Beam Inc.

A saddle-like ICP antenna with the several spiral coils distributed with an angular uniformity and enveloping a quartz tube of a plasma reactor was developed. It generates a transversal RF field directed normally to axis of this reactor. Due to such a design property of this antenna can be tuned between an initial capacitively coupled and a following inductively coupled state to facilitate a plasma ignition especially at atmospheric pressure. Unlike a conventional coil generating a filament-like ICP atmospheric discharge this antenna provides a larger high temperature area for evaporation of precursor as well as for a plasma-chemical reaction. This antenna was successfully tested for nanocoating by silicon dioxide of the different surfaces including the inner walls of the hollow articles.

I. Y. Glukhoy, I. Ivanov RF Atmospheric Plasma Systems for Nanopowder Production and Deposition of Nanocrystallines. AVS 53rd International Symposium, San Francisco, California, November, 2006 CA, USA.

4:20pm SE-MoA8 Diagnostic Study of an Arc Plasma Jet Under Atmospheric Pressure and Its Applications to Materials Processing, C.C. Hsu, C.Y. Wu, Y.W. Hsu, Y. Lin, Y.J. Yang, National Taiwan University

An atmospheric-pressure arc plasma jet was studied, and its use for material processing will be presented. This plasma jet was sustained by a DC pulsed power source of 20 kHz ~ 40 kHz using nitrogen. A voltage probe and a current probe were used to monitor the voltage and current (I-V) waveforms. The optical emission at the plasma jet downstream was monitored by an optical emission spectrometer. Multiple thermocouples were used to measure the downstream jet temperature. The I-V waveforms reveal that the jet undergoes abnormal glow to arc transition within each pulse power period. This transition is shown to be critical for sustaining a stable plasma jet and is primarily controlled by the power input to the plasma in the abnormal glow regime. Temperature and optical emission measurements show that the jet temperature decreases and the excited-state species densities increase with the increase of the gas flow rate, while both quantities increase with the increase of the applied voltage. These allow for the independent control of the temperature and the excited-state species densities by using these two operating parameters. The use of this plasma jet for materials processing, namely zinc oxide thin-film deposition and niobium oxide nanowire fabrication, will be presented. The correlation between the plasma behavior and the fabricated materials characteristics will be discussed.

Tuesday Morning, November 10, 2009

Advanced Surface Engineering

Room: C4 - Session SE-TuM

Hard and Nanocomposite Coatings

Moderator: P.H. Mayrhofer, Montanuniversitat Leoben, Austria

8:00am **SE-TuM1 AlTiN and AlCrN Hard Coatings - Alloying as an Approach to Improve Oxidation and Tribological Properties, C. Mitterer**, University of Leoben, Austria **INVITED**

Metastable transition metal aluminum nitride based hard coatings like AlTiN and AlCrN grown by plasma-assisted physical vapor deposition are nowadays widely used to protect high-performance tools against wear and oxidation. The excellent properties of these coatings arise from their ability to form protective Al₂O₃-based oxide scales and from the decomposition of their metastable face-centered cubic (fcc) lattice, resulting in age hardening.

The aim of this presentation is to give a survey of attempts to alloy AlTiN and AlCrN coatings, with the goals to improve hardness and wear resistance, oxidation resistance, toughness, and to reduce friction. Coatings were synthesized by reactive cathodic arc evaporation, and powder-metallurgically produced TiAl and CrAl targets with the alloying elements V, Si, B, Ta, and Ru have been used. Low Si, B and Ta contents are incorporated in the single-phase fcc solid solutions, enhancing both mechanical properties and oxidation resistance. In particular, for AlTiN coatings the onset temperature for oxidation is shifted to significantly higher values compared to AlTiN, which is related to a reduction of intrinsic stresses in the rutile layer formed underneath the top Al₂O₃ scale. B alloying of AlCrN results in the formation of a nanocomposite structure, with nanosized fcc grains surrounded by a BN-rich grain boundary layer, giving rise to extremely high hardness values and wear resistance. On the other hand, V alloying can be used to form self-lubricious V₂O₅ oxide layers, where their low friction coefficients in the temperature range between 550 and 700°C arise from liquid lubrication, due to the low melting temperature of this phase. Furthermore, low contents of Ru have been shown to increase the toughness of AlTiN coatings, which is assumed to formation of a metallic Ru phase within these coatings.

In summary, alloying of metastable transition metal aluminum nitride based hard coatings enables to design advanced quaternary and multiterinary hard coatings with property combinations meeting the requirements of severe machining processes.

8:40am **SE-TuM3 Pressure Dependence of the Al Ion Energy Distribution Functions during Filtered Cathodic Arc Thin Film Growth in an Ar, O₂ Ambient, A. Atiser, S. Mraz, J.M. Schneider**, RWTH Aachen University, Germany

Charge state resolved ion energy distribution functions (IEDFs) of Al⁺, Al²⁺ and Al³⁺ were measured as a function of Ar pressure in the range from 5.7 × 10⁻⁵ to 2.13 Pa (0.01 to 256 Pa cm). As the pressure distance product is increased, the annihilation of the Al²⁺ and Al³⁺ populations as well as the thermalization of the Al⁺ ion population is observed, resulting in the formation of a close to monoenergetic beam of Al⁺ ions at pressure distance product of 256 Pa cm. The average charge state was reduced from 1.58 to 1.00 as the pressure distance product was increased from 0.01 to 32 Pa cm. Thermalization is also observed in an Ar/O₂ mixture at 128 Pa cm, where stoichiometric γ -alumina films are grown. The IEDFs have been fitted by a shifted Maxwellian distribution. The plasma processing strategy presented here resulting in a monoenergetic Al⁺ plasma beam may through substrate bias potential variations enable effective tailoring of thin film properties such as density, elasticity and phase stability.

9:00am **SE-TuM4 Al-Si-N Thin Films: Nanocomposites and Solid Solutions, A. Pélisson, M. Parlinska-Wojtan, H.J. Hug, J. Patscheider**, EMPA, Switzerland

Thin films consisting of Al-Si-N were prepared by reactive magnetron sputtering from elemental targets in an Ar/N₂ reactive atmosphere at 200°C. The system shows a solubility limit for silicon at around 6 atomic %. Correspondingly the Al-Si-N system forms, as a function of the silicon content, either a solid solution or a two phase nanocomposite structure. To understand the properties and formation of the nanocomposite nanoscaled multilayers were used as a simplified model system. Coatings with a total thickness of about 1 micron and consisting of alternating layers of h-AlN or h-Al_{1-x}Si_xN (5 nm) and a-Si₃N₄ (from 0.25 nm to 2.0 nm) were prepared. The hardness as well as the residual stress state are strongly influenced by the thickness of the Si₃N₄ layer and the silicon content of the

crystalline Al-Si-N layer. Maximum hardness values of 33 GPa are reached for a Si₃N₄ layer thickness of 0.35 nm, whereas the stress state can be tuned between - 1.5 and + 1.5 GPa. Both High Resolution TEM and XRD showed that, for Si₃N₄ layer thicknesses below 1 nm, the Si₃N₄ layers grow heteroepitaxially on AlN. The implication for the hardness of isotropically deposited solid solution and nanocomposite thin films of Al-Si-N will be discussed.

9:40am **SE-TuM6 Development of Water Repellent Metal Oxide Thin Film as Like Organic Polymer, T. Watanabe, Y. Yokota, N. Yoshida**, The University of Tokyo, Japan, Y. Okura, Kogakuin University, Japan

Mechanically durable water repellent thin film composed of only metal oxides such like Al₂O₃, HfO₂, ZrO₂, TiO₂ and CeO₂ were successfully developed by sol-gel process. The key points to enhance dynamic hydrophobicity are reducing surface roughness and increasing chemical homogeneity. Surprisingly to say, developed films show 100 degree of water contact angle and sliding angles of water droplet is only around 20 degree. Water repellency has not been deteriorated even by 500 times abrasion tests of 0.1kg/cm². Water removability on these films is as like that of hydrophobic polymer surface. Fundamentally, intrinsic surface wettability of metal oxide is hydrophilic. However nanometer scale flatness and homogenous surface reduce activation energy of de-wetting process of water droplet. It is considered to cause of higher water removability. Durable hydrophobic surface composed only by inorganic oxide attracts much attention because it can be applied for water repellent automobile glass window and other applications which need higher mechanical strength and durability. Moreover, developed films show several unique properties which cannot be observed on organic polymer surfaces.

11:00am **SE-TuM10 Anti-Wear and Anti-Bacteria Behaviors of Rejuvenated TaN-Cu Nanocomposite Thin Films, J.H. Hsieh, P.C. Liu**, Ming Chi University of Technology, Taiwan, C. Li, Nanyang Technological University, Singapore

TaN-Cu nanocomposite films were deposited by reactive co-sputtering on Si and tool steel substrates. The films were then annealed using RTA (Rapid Thermal Annealing) at 400 °C for 2, 4, 8 minutes respectively to induce the nucleation and growth of Cu particles in TaN matrix and on film surface. Cu nano-particles emerged on the surface of TaN-Cu thin films were then removed after the samples were tested for their anti-wear and anti-bacterial behaviors. The samples were then re-annealed (rejuvenated), and re-tested for their anti-wear and anti-bacterial behaviors. The results reveal that the rejuvenated samples could have similar anti-wear and anti-bacterial behaviors so long as the annealing conditions were well adjusted. However, the hardness of the samples would decrease to a certain extent.

Thin Film

Room: B3 - Session TF1+SE-TuM

Glancing Angle Deposition I

Moderator: T. Karabacak, University of Arkansas at Little Rock

8:00am **TF1+SE-TuM1 Nanorod Structures for Energy Conversion, N.A. Koratkar**, Rensselaer Polytechnic Institute **INVITED**

Oblique angle deposition (OAD) is a technique which allows for fabrication of unique nanostructures, which cannot be grown by advanced lithographic techniques. OAD is simple, fast, cheap, has high mass production capability and can generate unique two- and three-dimensional nanostructures with large aspect ratio and controllable porosity, shape and symmetry. The fact that these nanostructures can be integrated onto a substrate platform makes them practical for many realistic applications. In this talk I will demonstrate the application of nanorods grown by OAD in various key device applications of today's energy starved society. The first is nanostructured Si anodes for rechargeable Li-ion batteries with higher capacity. The second is the development of Zinc Oxide (ZnO) and Indium Tin Oxide (ITO) nanorods by magnetron sputtering at low temperatures and their use as enhanced transparent conducting electrodes for polymeric photovoltaic cells. The third is the use of Pt nanorod based electrode architectures for proton exchange membrane fuel cells and the fourth is the use of Cu nanorods architectures for enhanced nucleate boiling which has strong implications for the management of thermal energy.

8:40am **TF1+SE-TuM3 Nanophotocatalysts Engineered by Glancing Angle Deposition Method.** *W. Smith, Y. Zhao*, University of Georgia

TiO₂ has long been used as an efficient and effective photocatalyst material, with applications in water purification, water splitting for hydrogen generation, clean windows, and many others. The photocatalytic efficiency of TiO₂ can be enhanced by increasing its surface area as well coupling it with another semiconductor which can create a charge separation effect. There are many methods to produce high surface area nano-sized TiO₂ such as sol-gel, hydrothermal, and ball-milling, but these techniques are governed by surface chemistry and random aggregation, and are difficult to control the overall size and morphology of the nanoparticles. These issues can be fixed by utilizing an oblique angle deposition (OAD) technique and glancing angle deposition (GLAD) technique, that can create ordered nanorod arrays with tunable height, separation, density and heterostructures. With these unique advantages, we systematically studied the photocatalytic rate of methylene blue versus the TiO₂ nanorod height, and found a scaling relationship that can be interpreted by a surface reaction model. We also created WO₃-TiO₂ two-layer thin film, tilted nanorods, and vertical nanorods by e-beam deposition, OAD, and GLAD. Two important factors played a role in the observed photocatalytic properties; the crystal phase of each material, and the interfacial area between TiO₂ and WO₃. The best sample was found to be the GLAD multi-layer nanorod array, which showed an enhancement up to 3 times over single layer TiO₂ GLAD nanorods. The GLAD structure had a higher interfacial area between TiO₂ and WO₃ than other samples. To maximize the interfacial area between the two materials, a dynamic shadowing growth (DSG) method was used to create a core-shell nanorod array. WO₃ nanorods were first grown on a bare substrate using GLAD to serve as the "core". A TiO₂ "shell" was then deposited such that the entire WO₃ "core" nanorod was covered. The photocatalytic decay rate for these core-shell samples again showed further improvement over single layer TiO₂ thin films and multi-layer c-TiO₂/a-WO₃ films by 13 and 3 times respectively.

These results show that the GLAD based nanofabrication technique is a versatile tool to design new photocatalytic nanostructures. With more structural and material engineering, better photocatalyst structures can be engineered.

9:00am **TF1+SE-TuM4 Enhanced Optical Absorption and Photoconductivity Response of Indium Sulfide Nanorod Arrays.** *M.F. Cansizoglu, T. Karabacak, H.W. Seo*, University of Arkansas at Little Rock, *R. Engelken*, Arkansas State University

Indium (III) sulfide is a wide bandgap and photoconductive material that has attracted attention due to its potential applications in optical sensors and in photovoltaic devices. High optical absorption in active regions of these devices is one of the key parameters that determine their performance especially in solar cell and photodetector applications. In this study, we show that indium sulfide nanorod arrays deposited by glancing angle deposition (GLAD) technique have superior optical absorption and low reflectance properties compared to conventional flat thin film coatings. Our GLAD nanorods had about 96% absorption in the sub-600 nm spectrum, while much thicker and denser thin films of indium sulfide was able to absorb only 80% of the incident light in the same spectrum. Due to the high optical absorption, a significant photoconductivity response was also observed in the nanorod samples, whereas no measurable photoresponse was detected in conventional thin films. In addition, we give a preliminary description of the enhanced light absorption properties of the nanorods by using Shirley-George Model that predicts enhanced diffuse scattering and reduced reflection of light due to the rough morphology.

9:20am **TF1+SE-TuM5 Oblique Angle Polymerization.** *M.C. Demirel*, Penn State University

The growth of spatially organized structures is of considerable fundamental interest, since it may provide us with important clues to the way in which organized structures form in Nature. A closer look at complex structures in insect wings and lizard toes reveal organized structured features at the microscopic scale. The organized structures in Nature are formed through evolutionary processes, and these complex molecules and features are built using molecular protein machinery. Synthetic polymers, that mimic biological materials in their designs, form organized structures too. We have demonstrated that nanostructured polymer thin films can be fabricated by an oblique angle polymerization method. [1-2] These structures are composed of approximately 40,000,000 aligned columns (approximately 100-150 nm in diameter) per square millimeter similar to the gecko footpad or insect wing. These structures have high aspect ratio and the production technique does not require any template, lithography method or a surfactant for deposition. This approach allows us to tune the chemical properties of nanostructured surfaces and film morphology to control the physicochemical properties of the resulting films, such as hydrophobicity, porosity, electrochemistry, chemical reactivity, surface energy and crystallinity. We have recently functionalized nanostructured polymer films

for controlled release and delivery of organics and synthetic molecules. Structured polymer brushes are envisioned to be useful in for specific controlled drug release, metallization (SERS and catalyst applications), tissue targeting as well as antifouling applications. [3-5]

Cetinkaya, M., Malvakdar, N., Demirel, M.C., "Power-Law Scaling of Structured Poly(p-xylylene) Films Deposited by Oblique Angle", JOURNAL OF POLYMER SCIENCE PART B: POLYMER PHYSICS, Vol. 46, pg 640-648, 2008.

Cetinkaya, M., Boduroglu, S., Demirel, M.C. "Growth of Nanostructured Thin Films of Poly(p-xylylene) Derivatives by Vapor Deposition", POLYMER, Vol.48, pg. 4130-4134, 2007

Demirel, M.C., Cetinkaya, M., Singh, A., Dressick W.J., "A Non-Covalent Method for Depositing Nanoporous Metals via Spatially Organized Poly(P-xylylene) Films", ADVANCED MATERIALS, Vol.19, pg.4495-4499, 2007

Boduroglu S., Cetinkaya, M., Dressick, W., Singh, A., **Demirel, M.C.**, "Controlling Wettability and Adhesion of Nanostructured Poly-(p-xylylene) Films", LANGMUIR, Vol.23,pg. 11391-11395, 2007

Kao, P., Malvakdar N., Wang, H. Allara, D., Demirel, M.C., "Surface Enhanced Raman Detection of Bacteria on Metalized Nanostructured Poly(p-xylylene) Films " Vol. 20, pg. 3562-3565, ADVANCED MATERIALS, 2008.

9:40am **TF1+SE-TuM6 Structural and Optical Properties of Metal Sculptured Thin Films on Large-Scale Prepatterned Substrates.** *D. Schmidt, T. Hofmann, E. Montgomery*, University of Nebraska-Lincoln, *B. Mbenkum*, Max Planck Institute for Metals Research, Germany, *M. Schubert, E. Schubert*, University of Nebraska-Lincoln

Three-dimensional (3D) metal nanostructures are of particular research interest in modern material science and engineering, due to their intriguing properties, which can differ considerably from their bulk counterparts. These size- and structure-driven properties in such 3D metal nanostructures credit themselves for potential implementation in optical, electro-mechanical, and electromagnetic systems.

We utilize glancing angle physical vapor deposition, which exploits physical shadowing and varying particle incidence azimuth for fabrication of 3D nanostructures from metals arranged in sculptured thin films (STFs). While such nanoscaffolds (typically in geometries of (slanted) columns, chevrons, screws, or spirals) are randomly distributed on untreated substrates, organized growth can be achieved on prepatterned surfaces. Self-assembled block copolymer nanolithography and nanosphere lithography are promising techniques to accomplish wafer-scale pre patterning. The desired spacing of the resulting hexagonal pattern can be tailored based on polymer chain length and nanosphere radius, respectively. Both methods are superior to conventional and electron beam lithography techniques because of small structure sizes achieved in the order of a few nanometers and large scale preparation.

This presentation elucidates our work on structure-related optical properties of different STFs from various metals grown on untreated as well as prepatterned silicon substrates by electron-beam evaporation at an oblique angle of incidence. Generalized spectroscopic ellipsometry is employed to determine the anisotropic optical constants (refractive index *n* and extinction coefficient *k*) of the thin films in the spectral range from 400 nm to 1650 nm. All investigated STFs show extreme birefringence as well as dichroism. We observe that optical properties depend rather on geometry than material [1,2].

[1] D. Schmidt, B. Booso, T. Hofmann, A. Sarangan, E. Schubert, and M. Schubert, Appl. Phys. Lett. **94**, 011914 (2009).

[2] D. Schmidt, B. Booso, T. Hofmann, A. Sarangan, E. Schubert, and M. Schubert, Opt. Lett. **34**, 992 (2009).

10:40am **TF1+SE-TuM9 On the Uniformity of Films Fabricated by Glancing Angle Deposition.** *N.G. Wakefield, J.C. Sit*, University of Alberta, Canada

Films fabricated using the glancing angle deposition technique are subject to significant variations in important film parameters across a sample due to varying geometric conditions at each point on the substrate. This is a serious fundamental problem, as non-uniformities in aspects such as film thickness or porosity can drastically change a film's properties across even a small sample size. This means that film properties can vary rapidly, and undesirably, with position over a substrate and attempting to scale technologies based on glancing angle deposition to large areas presents a major challenge. This paper presents a method to quantify the non-uniformities in these quantities, starting from a simple geometric framework, applicable to physical vapor deposition at low pressures. In this work, this method is applied to glancing angle depositions done at a fixed

deposition angle, but with arbitrary azimuthal substrate rotation. Quantities such as the effective deposition angle and the mass flux at any point on the substrate can be determined purely from the geometry of the deposition setup. Predicting further quantities such as the film porosity and thickness requires additional, material specific information that is easily obtainable. For a TiO₂ deposition at $\alpha = 70^\circ$ on a 10 cm substrate, dependent on the film's structure, porosity and thickness non-uniformities are found to range from $\pm 1.7\%$ to $\pm 8.2\%$ and $\pm 1\%$ to $\pm 30\%$ respectively. Experimental values were obtained using Mueller matrix spectroscopy and showed excellent agreement. The technique described here is general and can be applied to glancing angle deposition setups having arbitrary substrate size and throw distance. The ability to accurately model the gradients in quantities such as the film porosity, allows for a combinatorial approach to examine film properties such as refractive index, absorption or conductivity across a single substrate. Further improvements to the model should allow for the treatment of depositions done at varying deposition angles and with curved substrates.

11:00am **TF1+SE-TuM10 Nanostructured Tungsten and Tungsten Trioxide Films Prepared by Glancing Angle Deposition, D. Deniz, R.J. Lad, University of Maine**

The sensitivity of chemiresistive metal oxide gas sensors can be markedly increased by fabricating nanostructured films with very high surface to volume ratio. In this work, nanostructured tungsten (W) and tungsten oxide (WO₃) films were fabricated using pulsed direct current (DC) magnetron sputtering of a W target with a glancing angle deposition (GLAD) geometry. The major parameters that were varied included substrate temperature, deposition rate, substrate rotation, Ar/O₂ plasma composition, and post-deposition thermal treatments. The stoichiometry of the nanostructured films was characterized by X-ray photoelectron spectroscopy (XPS), and the structure and morphology were investigated using X-ray diffraction (XRD) and high resolution scanning electron microscopy (SEM). Metallic W nanorods were formed by sputtering in a pure Ar plasma at room temperature and they crystallized in a simple cubic β -phase with W(100) texture. Subsequent annealing at 500 °C in air transformed the nanorods to textured triclinic WO₃ structure but the nanorod morphology was retained. Stoichiometric WO₃ films grown in Ar/ O₂ plasma at room temperature had an amorphous structure and also exhibited a nanorod morphology. Post-deposition annealing at 500 °C in air induced crystallization to the triclinic WO₃ phase and also caused a morphological change into a very nanoporous network. The differences in the chemiresistive response to each of these high surface area nanoengineered films to CO₂ and CH₄ gas exposure will be presented.

11:20am **TF1+SE-TuM11 Dual Magnetron Oblique Sputtering of Biaxially Oriented ZnO Thin Films on Amorphous Substrates, B.L. Stevens, S.A. Barnett, Northwestern University**

This talk will describe results on deposition and characterization of biaxially oriented ZnO thin films on amorphous substrates. Biaxially-oriented ZnO thin films on low-cost substrates are of interest for ZnO-based devices and as "substrates" for subsequent growth of devices based on AlN, GaN, InN, and their alloys. Expensive single crystal substrates, which are typically used to achieve the requisite crystalline perfection of the epitaxial device layers, could be replaced by biaxially-textured ZnO substrates if sufficiently good orientation can be achieved.

The dual magnetron oblique sputtering (DMOS) geometry utilized two dc magnetron sputter sources, with metallic Zn targets, positioned opposite each other and at angles of 20 to 40° relative to the substrate normal. Sputtering was carried out in an oxygen-rich Ar-O₂ atmosphere. Substrates were Corning 7059 glass, Corning 1737F glass, or Si (001) that had been oxidized to produce an amorphous SiO₂ surface layer. Cross-sectional SEM showed reasonably dense as-deposited films even without substrate heating. The as-deposited films were under considerable compressive stress, as measured by x-ray peak position, in agreement with prior results on sputtered ZnO. Atomic-force microscopy measurements on as-deposited 1.5 μ m thick films showed relatively high rms roughnesses of 8.3 nm.

The ZnO films exhibited (002) out-of-plane orientation, as suggested by θ -2 θ x-ray scans and verified by x-ray pole figures that were completed for selected samples. Sputtering from a single target (instead of the usual dual-target geometry) caused a shift in the out-of-plane orientation, causing the (002) plane normal to be up to 10° off normal. X-ray scans as a function of azimuthal angle Φ were carried out to detect reflections from (101) planes. The strongest biaxial orientation was observed when the sputter sources were placed at 30° from the substrate normal, with Φ -scan peaks exhibiting a full width half maximum (FWHM) value of 23°. Elevated substrate temperature during deposition, up to 600°C, decreased the orientation in the films, yielding a ~17% increase in Φ FWHM. Post deposition annealing at up to 1000°C substantially improved the degree of biaxial orientation, decreasing the Φ -scan FWHM by ~60%. The effects of a range of

deposition and post-deposition annealing conditions on the film orientation will also be reported. The orientation mechanism also will be discussed.

11:40am **TF1+SE-TuM12 A Slice of GLAD: Use of Focused Ion Beam Tomography to Characterize Titania Thin Films, K.M. Krause, University of Alberta, Canada, D. Vick, NRC National Institute for Nanotechnology, Canada, M.J. Brett, University of Alberta, Canada**

Focused ion beam (FIB) tomography allows for the serial slicing and imaging of a sample volume on the order of several nanometers to microns thick. With this technique, a focused beam of ions rasters across the specimen surface, milling it layer-by-layer. In tandem, a scanning electron microscope (SEM) images the exposed surface at the removal of each individual slice. The series of SEM images can then be post-processed with custom or commercially available software to create a 3D reconstruction of the milled volume.

As FIB tomography has progressed over the years, the range of materials, structures, and size scales has been expanded. Various analysis have been carried out with FIB, including the study of how grain boundaries in Ni alloys influence crack propagation and how the geometry of buried Ge quantum dot superlattices depends on the growth of supporting materials layers [1 – 3]. In the present work we report on the use of ion beam milling and concurrent SEM imaging to probe the properties of titanium dioxide nanostructured thin films fabricated using the glancing angle deposition (GLAD) technique [4].

Our titania films are deposited at oblique angles, while substrate rotation is employed, on silicon wafers. The resultant films have a columnar structure with spacing between columns determined by the deposition angle and characteristics determined by the rotation speed and deposition rate. To support the porous GLAD films during FIB slicing, a photoresist is spun into the film and then baked, forming a heterogeneous solid. The photoresist not only provides support for the nanostructures as they are sliced, but also offers good atomic number (Z) contrast to the titania. The GLAD films are then sliced and imaged using a Zeiss NVision 40 Crossbeam® workstation. Captured images are post-processed using MATLAB™ and commercially available JEOL TEMography™ software packages.

While column morphology and geometric properties of GLAD films have been well studied, investigations of columnar structure have been limited to SEM and TEM. Here, we demonstrate that the FIB technique can be used to provide a spatially discrete view of GLAD intra-column and inner-column porosity and structure. Analysis of these properties is ongoing and current experimental results will be presented.

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Tuesday Afternoon, November 10, 2009

Advanced Surface Engineering

Room: C4 - Session SE+TF-TuA

Glancing Angle Deposition II

Moderator: K. Robbie, Queen's University, Canada

2:00pm **SE+TF-TuA1 Deposited Nanorod Films for Biosensor Applications**, **W. Zhang**, University of Illinois at Urbana-Champaign, *S.M. Kim*, Chung-Ang University, Korea, *N. Ganesh*, Intel, *I. Block*, *P. Mathias*, *B.T. Cunningham*, University of Illinois at Urbana-Champaign **INVITED**
Planar photonic crystals have been used as the basis of many biological sensing devices. Here, we successfully demonstrated that the combination of the photonic crystal structures and a dielectric nanorod coating prepared by the glancing angle deposition technique can lead to significant increases in the device sensitivity.

By incorporating a TiO₂ nanorod coating onto the label-free biosensor structure, the surface area of the device is increased. The sensitivity of high surface area sensors is compared with sensors without the high surface area coating. Results for detection of polymer films, proteins, and small molecules indicate up to a seven-fold enhancement of detected adsorbed mass density.

When a TiO₂ nanorod coating is applied on top of the high index layer of an enhanced fluorescence biosensor, the emission intensity of a fluorescent dye on the device is increased by over one hundred times compared to a reference glass slide. The increased sensitivity is due to the combined effects of enhanced near-fields and enhanced surface area. The sensitivity is further increased by close to two hundred times when a TiO₂ nanorod film is used as the high index layer of the photonic crystal structure.

The planar photonic crystal is also combined with a SiO₂-Ag "post-cap" nanostructure for applications in surface-enhanced Raman spectroscopy (SERS). It is demonstrated that the resonant near fields of the photonic crystal could be used to efficiently couple light from a laser to the Ag nanoparticles to achieve a high SERS enhancement factor.

2:40pm **SE+TF-TuA3 Surface Enhanced Raman Scattering from Silver Nanorod Array Substrates: Characteristics and Origin**, **Y. Liu**, **Z. Zhang**, **R.D. Dluhy**, **Y. Zhao**, University of Georgia

Surface-enhanced Raman scattering (SERS) has been a powerful analytical tool in chemical and biosensing applications. Silver nanorod array fabricated by oblique angle deposition can give a very strong SERS enhancement ($>10^8$). The SERS enhancement depends strongly on the length of nanorods, the incident angle of excitation light, the polarization states of excitation light, and the reflectance from substrate. A modified Greenler's model based on the reflection from a single Ag nanorod and the substrate as well as dipole radiation is proposed to explain these SERS characteristics. The theoretical calculation qualitatively agrees well with the experimental results. However, the location of the strongest SERS enhancement and the nature of such an enhancement are still unknown. To answer this question, we have designed another set of experiments, by taking the advantage of oblique angle deposition, to put Raman probe molecules on different locations of Ag nanorod array substrates and found that the apparent SERS enhancement factor is about 50 ~ 200 times from the surface of the nanorods than that from the Ag thin film surface under Ag nanorods array. These effects cannot be interpreted directly by the local electric field enhancement effect. By combining the local electric field effect calculated by three dimensional finite-difference time-domain method and the anisotropic optical absorbance of the SERS signal from the anisotropic Ag nanorod array, the numerical calculations are semi-quantitatively agree with the experimental results.

* This work is supported by National Science Foundation (NO. ECS-0701787) and US Army Research Laboratory (W911NF-07-2-0065).

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Y.-J. Liu, Z.-Y. Zhang, Q. Zhao, R. A. Dluhy, and Y.-P. Zhao, *The Surface Enhanced Raman Scattering from Ag Nanorod Array Substrate: the Site Dependent enhancement and Layer Absorbance Effect*, J. Phys. Chem. C, in press (2009)

3:00pm **SE+TF-TuA4 Local Plasmon Resonators Combinatorially-Multilayered by Oblique Angle Deposition Technique**, **M. Suzuki**, **R. Tabuchi**, **Y. Imai**, **S. Li**, **K. Nakajima**, **K. Kimura**, Kyoto University, Japan, **T. Fukuoka**, Archilys RP, Japan

We have successfully prepared multilayered sculptured thin films with various combinations of the layer thicknesses using a shutter system specially designed for the oblique angle deposition. A series of different thicknesses were realized on a single substrate by moving a step-shaped shutter incrementally across the sample during the oblique angle deposition, while an ordinary straight shutter was used during normal deposition. This deposition process has been applied to fabricate local plasmon resonators comprised of the sandwich of Au nanorod array (NRA)/structured dielectric layer/Ag mirror. The fundamental optical properties of the local plasmon resonators have been already reported [1]. Briefly, the reflectance in NIR region can be controlled between 10^{-4} and 1 due to the strong interference. At low reflectance conditions, Au nanorods absorb most of the incident light and are expected to enhance the local electric field in their close vicinity. However, detailed relation between the optical properties of the local plasmon resonators and the combination of the thicknesses of Au and dielectric layers has never been clarified. In this study, we prepared 4x6 arrays of the local plasmon resonators which have four and six different thicknesses of Au and the dielectric layers, respectively, on a single substrate of 50x50 mm². The surface enhanced Raman scattering intensity measured on the element with low reflectance is about 50 times stronger than that on the Au NRA prepared on the glass substrate (without Ag mirror). This indicates that the local electric field in the NIR region is controllable by using interference. Therefore, the NRA fabricated on the mirror with appropriate spacer layers is useful not only for improving conventional biochemical sensing but also for the novel applications using spatiotemporal control of the local plasmons. For optimization of the multilayered sculptured thin films, the combinatorial approach is quite useful.

[1] M. Suzuki et al., Journal of Nanophotonics 3, 031502 (2009).

4:00pm **SE+TF-TuA7 Influence of Substrate Temperature on Glancing Angle Deposited Ag Nanorods**, **C. Khare**, **C. Patzig**, **J.W. Gerlach**, Leibniz-Institut of Surface Modification, Germany, **B. Fuhrmann**, Martin-Luther-University Halle, Germany, **B. Rauschenbach**, Leibniz-Institut of Surface Modification, Germany

When Ag sculptured thin films (STFs) were grown with glancing angle deposition by ion beam sputtering at either room temperature or elevated substrate temperatures T_s , an enormous topographical difference could be observed. The incident particle flux reached the silicon substrate at a glancing angle $\beta \geq 80^\circ$ as measured to the substrate normal. A slit aperture was used in order to reduce the particle beam divergence. At room temperature, columnar structures were formed, irrespective of the presence of the slit aperture. At elevated temperatures (300° C, 350° C) and collimated particle flux in the presence of the slit aperture, however, accelerated surface diffusion causes the growth of nanorod- and nanowire-like structures. In the absence of the slit aperture, the flux beam divergence is higher, leading to island- and mountain-like crystalline structures that were found at elevated temperatures. The density of the nanorods and nanowires was observed to be higher on the planar Si substrates in comparison to honeycomb-like pre-patterned substrates with different pattern periods. On the patterned substrates, the nanorods are not necessarily found to be evolving on the seed points, but can rather also be observed in intermediate pre-pattern spaces. The glancing angle deposited films were observed to be polycrystalline, where the (111) crystal orientation of the film is dominant, while the presence of the less intense (200) reflection was noticed from XRD measurements. In contrast, the closed films deposited with $\beta \approx 0^\circ$ at high temperatures were found to be epitaxial with (200) orientation.

4:20pm **SE+TF-TuA8 Temperature Driven Anomalous Scaling during Glancing Angle Deposition**, **S. Mukherjee**, **D. Gall**, Rensselaer Polytechnic Institute

Ta, Nb, Cr and Al nanorod structures were grown by glancing angle physical vapor deposition on a continuously rotated Si(001) substrate at an incidence angle of 84° and at substrate temperatures $T_s = 300$ -1125 K. The width w of the self-affine nanorods increases with the height h according to $w \propto h^p$. The growth exponent p is a function of the homologous substrate temperature θ , which is the ratio of T_s to the melting point T_m . All studied

metallic systems exhibit the same $p(\theta)$ curve: p approaches a value of 0.5 for negligible surface diffusion ($\theta < 0.1$) and monotonously decreases to $p = 0.39$ for $\theta = 0.2$, as predicted by Meakin and Krug's model of nanorod growth with limited surface diffusion and by Mullins-Herring's model of 2+1 dimensional interface growth, respectively. However, p increases dramatically for $\theta = 0.22$ - 0.26 , to reach an anomalous value of 0.71. Above the transition temperature $\theta_c = 0.24 \pm 0.02$, the growth exponent decreases to reach $p = 0.3$ at $\theta = 0.42$.

We present a semi-analytical model using mean-field nucleation and non-linear chaos theory that relates p with the exponential divergence λ from a surface diffusion limited material independent morphology that is controlled by atomic shadowing. p is a function of the average island separation distance $\langle s \rangle$, which is a measure of the diffusion length scale and varies with θ , the activation energy E_m for surface diffusion, the critical island size i , and the dimensionality of adatom surface diffusion. The model predicts a transition from a 2-d to a 3-d island growth mode at θ_c . This transition, in turn, exacerbates the chaotic bifurcation associated with the atomic shadowing by the islands on the nanorod growth fronts, resulting in the higher growth exponents above θ_c . The model also provides a single homologous activation energy $E_m/kT_m = 2.46$ for surface diffusion on curved nanorod growth fronts, applicable to all studied metallic systems at all temperatures. p follows a linear function with $\langle s \rangle$, in both high and low temperature regimes and the slope correlates with the slope of λ vs $\ln(h)$, indicating that the growth exponent and hence the morphology is intricately related to both shadowing and surface diffusion.

4:40pm **SE+TF-TuA9 Investigation of Surface Sensitivity of Relative Humidity Sensors through ALD Coated GLAD**, *M.T. Taschuk*, University of Alberta, Canada, *K.D. Harris, J.M. Burtak, M.J. Brett*, NRC National Institute for Nanotechnology, Canada

We have been investigating the performance and optimization of nanostructured relative humidity (RH) sensors produced by glancing angle deposition (GLAD) [1 – 2]. GLAD offers significant advantages for sensor applications, including extremely large surface areas, response times as low as 50 ms, and the use of any material compatible with physical vapour deposition. However, there remain a number of open questions regarding the underlying physics of GLAD RH sensor performance and response time. Response time and magnitude varies with the size and nature of pores in our sensors, and the interaction between the analyte and deposited material. To better understand the analyte-surface interactions, we have studied the performance of RH sensors with a thin coating of TiO₂ deposited by atomic-layer deposition (ALD).

Columnar thin films of Si and TiO₂ were produced by GLAD on interdigitated electrode substrates, creating a RH sensor. The GLAD sensing layer was conformally coated with TiO₂ films by atomic layer deposition. In this process, the deposition chamber is evacuated and the reactive precursor, titanium isopropoxide (TIPO), is admitted. A thin layer of TIPO saturates the exposed substrate surfaces, and once complete, the deposition chamber is purged and oxygen is introduced. At the precursor-loaded substrate, this oxygen reacts with TIPO in a plasma-driven process to produce a thin layer of TiO₂ conformally surrounding the high surface area GLAD film. In this work, the ALD process is repeated cyclically to build up TiO₂ layers of different thicknesses.

Preliminary investigations have used 1.5 μm Si and TiO₂ GLAD films, coated with ALD TiO₂ films between 2 nm and 32 nm thick. The RH sensing properties of these devices were tested using a custom environmental chamber [1]. As expected, the uncoated Si and TiO₂ thin films exhibited different responsivities. However, once the different sensors were coated with ALD TiO₂ layers as thin as 2 nm, sensor response was very similar, indicating that sensor function is dominated by surface properties. To better investigate the transition between the GLAD post dominated response and ALD-layer dominated response, a series of films with thinner ALD coatings is underway. The sensor response will be characterized as a function of RH, electrical probe frequency, and ALD layer thickness. Current experimental results will be presented.

[1] J.J. Steele et al. IEEE Sensors Journal (2008) Vol 8. pp. 1422 - 1429

[2] M.T. Taschuk et al. Sensors and Actuators B (2008) Vol. 134, pp. 666 - 671.

5:00pm **SE+TF-TuA10 Direct Measurement of Porosity in Glancing Angle Deposited Thin Films**, *A.R. Gonzalez-Elipe*, ICMSE (CSIC - U. Seville), Spain, *F. Yubero*, CSIC, Spain, *J.R. Sanchez-Valencia*, ICMSE (CSIC - U. Seville), Spain

Porosity of thin films is generally estimated in an indirect way by looking to their refraction index. In the present communication we determine directly the porosity of a series of glancing angle deposited films by measuring the adsorption/desorption of water as a function of the partial pressure of water vapour in contact with the film. The method consists of measuring the changes in the vibration frequency of a quartz crystal monitor (QCM) with

its surface covered by the thin films. The analysis of the obtained curves permits to estimate the total porosity of the films, its partition between mesopores (pores larger than 2 nm) and micropores (pores smaller than 2 nm) and the pore size distribution function. Results are shown for a series of titanium oxide thin films prepared by evaporation at different glancing angles between 60° and 90°. It is shown that both the total porosity and the partition between meso and micropores change with the evaporation angle. A good correlation exists between these measurements and the optical constants of these films determined by ellipsometry. Analysis of the films by Scanning Electron Microscopy (SEM), and Atomic Force Microscopy (AFM) gives some hints to account for the evolution of porosity as a function of the evaporation angle.

1) A. Borrás, J.R. Sánchez-Valencia, J. Garrido-Molinero, A. Barranco, A.R. González-Elipe, Microporous and Mesoporous Materials 118 (2009) 314-324

5:20pm **SE+TF-TuA11 Monoclinic Magnetic Anisotropy and Hybridization of GLAD Sculptured Thin Films**, *A. Kjerstad, D. Schmidt, T. Hofman, M. Schubert, E. Schubert, R. Skomski, D. Sellmeyer*, University of Nebraska - Lincoln

We report on the magnetic monoclinic anisotropy behavior of cobalt sculptured GLAD structures. Exciting new physics are presented in a model showing the nanostructures result in a thin film with tunable properties dependent on orientation, tilt, and patterning of the slanted nanowires. These sculptured thin films can be further modified – non-magnetic structures are coated with ferroelectric polymers for novel surfaces. Alternatively, magnetic structures are modified using non-magnetic materials, once again creating hybridized structures with undiscovered properties.

Tuesday Afternoon Poster Sessions

Advanced Surface Engineering

Room: Hall 3 - Session SE-TuP

Advanced Surface Engineering Poster Session

SE-TuP1 Characterizations of Normal Incidence Polarizing Beam-Splitter Deposited by Glancing Angle Deposition, *Y.J. Park, K.M.A. Sobahan, J.J. Kim, C.K. Hwangbo*, Inha University, Republic of Korea

Glancing angle deposition (GLAD) is a sophisticated technique to fabricate engineered nanostructured thin films for next generation nano and micro devices. In this technique, oblique angle deposition and substrate rotation are employed to control the shapes and porosity of the films, caused by a self-shadowing effect and surface diffusion. Recently, the applications of the properties of the GLAD thin films become the basis of a wide array of industrial components including high-speed gas sensors, optical thin films or nanoporous coatings.

In this study, we investigate the optical and structural properties of normal incidence polarizing beam-splitter. It is realized as a combination of quarter-wave plate, Bragg reflector and opposite quarter-wave plate. The zigzag microstructures of the quarter-wave plates as well as the opposite quarter-wave plates and the helical structure of the Bragg reflector are fabricated by electron beam evaporation using GLAD technique and TiO₂ material is used in this purpose. The physical thicknesses of the opposite and quarter-wave plates are calculated using their anisotropy. It is found that the normal incidence polarizing beam-splitter reflects the p-polarized light while transmits the s-polarized light with wavelength lying in the Bragg regime. The structural and surface morphology of this device are also investigated using scanning electron microscope.

SE-TuP2 Modified Glancing Angle Deposition for Making Nanostructured High Porous SiO₂ Thin Films, *K.M.A. Sobahan, Y.J. Park, C.K. Hwangbo*, Inha University, Republic of Korea

Glancing angle deposition (GLAD) is a physical evaporation technique widely used to fabricate nanostructured thin-films materials with controllable shapes and porosity, which is achieved by a self-shadowing effect and surface diffusion. By taking advantage of the versatility of the GLAD technique, it is possible to engineer the materials with unique properties for added value in such areas as optical thin films or nanoporous coatings, high-speed gas sensors, and chemical devices. GLAD thin films can also serve as the foundation of many different types of nano and micro devices.

In this communication, we report the nanostructured porous SiO₂ thin films fabricated by modified GLAD technique. The optical properties of the SiO₂ films fabricated in this technique are investigated and as an application, the antireflection coating (AR) for visible wavelength is designed and fabricated. It is seen that the average reflectance of the AR coating is below 0.04%. The microstructures and the surface morphology are also investigated by using a scanning electron microscope (SEM).

SE-TuP3 Microstructure and Corrosion Resistance of Nano-Crystalline ZrTiN Films on AISI 304 Stainless Steel Substrate, *Y.W. Lin*, Instrument Technology Research Center, Taiwan, *J.H. Huang, G.P. Yu*, National Tsing Hua University, Taiwan

This study investigated the effect of ratio of Zr/(Zr+Ti) on microstructure and corrosion resistance of ZrTiN thin films. ZrTiN thin films were deposited by reactive magnetron sputtering based on our previous optimum coating conditions (substrate temperature, system pressure, nitrogen flow etc.) for TiN and ZrN thin films. The ratios of Zr/(Zr+Ti) were dominating by changing Ti and Zr target power, and found out the optimum composition with desired properties. The ratio of N/Ti/Zr and composition of ZrTiN thin film were analyzed by X-ray Photoelectron Spectroscopy (XPS) and Rutherford Backscattering Spectrometer (RBS). In terms of phase formation, there were two types of coatings were considered, single-phase solid solution of Zr_xTi_{1-x}N and interlacing nucleus of TiN or ZrN in the matrix of Zr_xTi_{1-x}N. The thickness of ZrTiN films measured by scanning electron microscope (SEM) was greater than 900 nm. The composition depth profiles measured by Auger electron spectrometer (AES) indicated that the compositions in the ZrTiN films were uniform from the film surface to the 304 stainless steel substrate. The crystal structure of the ZrTiN films was determined by X-ray diffraction (XRD) using a M18XHF-SRA diffractometer with Cu K_α radiation. Reflection line of ZrTiN (002) peak is observed between those of TiN (002) peak and ZrN (002) peak, similarly, reflection line of ZrTiN (111) peak is observed between those of TiN(111) peak and ZrN(111) peak, respectively. The corrosion resistance of ZrTiN films on commercial AISI 304 stainless steel has been investigated by

electrochemical measurement. The electrolyte, 0.5 M H₂SO₄ containing 0.05 M KSCN, was used for the potentiodynamic polarization. The potentiodynamic scan was conducted from - 800 to 800 mV (SCE) with scan rate ranging from 10 to 600 mV/min. The variation of Zr/(Zr+Ti) ratio on the microstructure and corrosion resistance of ZrTiN film was investigated.

SE-TuP4 Light Out-Coupling Characteristics Based-on the Interfacial Electronic Structure of MoO_x-doped Fullerene, a Potential Hole Ohmic-Contact Layer for Organic Semiconductor, *J.T. Lim, J.W. Kwon, G.Y. Yeom*, Sungkyunkwan University, Korea

Recently, the interest on the ohmic contact between the metal-organic interfaces has been actively increasing to inject charge carriers between electrodes and an adjoining organic layers more efficiently. Among those contact, the hole-injecting properties without a barrier height between anode and a hole-injecting layer are very important for driving the devices to a high brightness and a high luminous efficiency in organic semiconductors, such as the organic light-emitting diodes, organic solar cells, and organic thin film transistors. Here, we reported on the new ohmic-hole contact system of MoO_x-doped fullerene. The phosphorescent organic light-emitting diode with fullerene doped with 10% MoO_x showed the maximum brightness of 86500 cd/m² and the power efficiency of 15.6 lm/W at a luminance of 100 cd/m². The improvement of the light out-coupling property by inserting the MoO_x-doped fullerene layer between anode and a hole-transporting layer is due to the formation of an ohmic contact without the barrier height in a hole injection (Φ_B^h) as well as the raising of the band banding by pinning Fermi levels in the interfaces. The mechanism for the ohmic hole-injecting characteristic from anode to MoO_x-doped fullerene was proved from an ultraviolet photoemission spectroscopy (UPS) spectra. In UPS spectra, the highest occupied molecular orbital (HOMO) level of the interface formed between two materials nearly approaches to Fermi level of anode.

SE-TuP5 Novel Top-Down Fabrication Technique for Metallic Nanoparticles Using Microsphere Self-Assembly and Oblique Angle Thin Film Deposition, *M.A. Roddy, E.M. Kirkpatrick, S.R. Kirkpatrick*, Rose-Hulman Institute of Technology

Metallic nanoparticles are of significant interest to the biomedical, electronics, optical, and magnetic fields. We have worked to develop a novel technique to fabricate nanoparticles on the order of 100 – 1000 nm. The process uses a self-assembled planar array of polystyrene microspheres[1] as a structured template for oblique angle deposition of a thin film, such that the tops of the spheres are covered with ‘caps’ (see Attachment 1). The spheres provide mutual shadowing from deposition, which determines the nucleation sites for metallization resulting in semi-spherical and hemispherical caps. Nanoparticle caps of both SmCo and chrome were fabricated. Chrome caps were prepared by allowing a mixture of 800 nm microspheres and DI water to dry on a substrate (glass, oxidized silicon, or bare silicon). 100 nm of chrome was then sputtered on the microspheres at angles of 80, 75, and 70 degrees normal to the surface. The sputtering parameters were base pressure of 2E-8 torr, sputter gas pressure of 2E-3 torr, and power of 300 W. In order to characterize the resulting nanoparticles via SEM the polystyrene was removed either by methanol or oxygen plasma ashing. A similar method was used for the SmCo samples, however, both an underlayer and overlayer of 15 nm NiCr was deposited head-on in order to prevent oxidation of the SmCo. Morphology of the samples depended on deposition angle and the deposition direction compared to the orientation of the self-assembled template and the resulting particles ranged in size from 350-700 nm.

SE-TuP6 Tribological Behaviour of TiAlN/TiAlN/Pt Multilayers Deposited on Stainless Steels, *M. Flores, J. Garcia, E. Rodriguez*, Universidad de Guadalajara, Mexico, *L. Huerta*, Universidad Nacional Autonoma de México, *E. De las Heras*, Instituto Nacional de Tecnología Industrial, Argentina

In the present work we report the results of studies about the influence of Pt layers on the wear resistance of TiAl/TiAlN multilayers deposited on 316L stainless steel by magnetron sputtering using targets of TiAl and Pt. Coating types investigated included TiAlN, TiAlN/TiAl, TiAlN/TiAl/Pt and duplex coatings with substrates nitrided by pulse plasma nitriding. The thickness of the Pt layers was from 50 nm to 200 nm and the period of TiAlN/TiAl multilayer from 250 to 500 nm. The friction and wear tests were performed on a ball-on-flat tribometer and conducted in dry (unlubricated) conditions at room temperature. The loads used were from 2N to 10N and the oscillating frequency from 1 Hz to 5 Hz. The structure, composition and thickness of multilayers were studied by means of XRD, RBS and ellipsometry analysis. The surface topography and wore surface

were studied by means of optical microscopy and profilometry. The results indicate that coefficient of friction (COF) of TiAlN coatings decreased when metal layers are introduced.

SE-TuP7 Physical Processes for Low Temperature Plasma Activated Wafer Bonding. *T. Plach, K. Hingerl,* Johannes Kepler University, Austria, *V. Dragoi, G. Mittendorfer, M. Wimplinger,* EV Group, Austria

Low temperature plasma activated direct wafer bonding (LTPADWB) for Si-SiO₂ interfaces is a process that lowers the required annealing temperatures necessary for reaching high bond strength. Bulk strength can be realized by plasma activation with subsequent annealing at 300°C. The mechanism behind this improvement is still under discussion.

At this temperature, half of the bulk strength is reached already with conventional wafer bonding. The low temperature steps for the hydrophilic process are interpreted as follows: Up to 100°C the substrate surfaces are held together via van der Waals interaction which is mediated by a few monolayers of water. In the range of 100-200°C the water diffuses away from the interface both along the interface and through the oxide into the crystalline bulk, where it reacts with the silicon and forms oxide. The remaining half of the bond strength is usually attributed to a closing of gaps at the interface[1], which starts at the softening temperature of the thermal oxide at around 850-900°C.

To clarify the mechanism for this commercially available process, different bonding experiments were performed to evaluate the lifetime of the surface activation and the achievable bond strength when using substrates with various orientations. Interfaces of bonded wafer pairs were investigated by transmission electron microscopy (TEM). TEM images clearly show that there is no discernible interface between the native oxide on one side and the thermal oxide on the other side.

By covering half of the wafer during plasma activation, comparisons between the activated and non-activated region could be made by atomic force microscopy, by spectroscopic ellipsometry, by Auger analysis and by X-ray photoelectron spectroscopy.

It was found that the top surface stoichiometry is chemically changed, which favors bonding. Finally a model for the mechanism that explains the experimental results will be presented.

Keywords: wafer bonding; plasma; low temperature

References

[1] Q.-Y. Tong, U. Gösele, *Semiconductor Wafer Bonding: Science and Technology*, Wiley, (1998)

Wednesday Afternoon, November 11, 2009

Tribology Focus Topic

Room: C4 - Session TR+SE-WeA

Advances in Surface Engineering for Friction and Wear Control

Moderator: S.S. Perry, University of Florida

2:00pm **TR+SE-WeA1 The Deposition of Highly Adherent Fullerene-Like CN_x Coatings on Steel Substrates of Complex Geometry.** E. Broitman, Linköping University, Sweden & Carnegie Mellon University, S. Schmidt, G. Greczynski, Linköping University, Sweden, Zs. Czigany, Research Institute for Technical Physics and Materials Science, Hungary, C. Schiffers, CemeCon AG, Germany, L. Hultman, Linköping University, Sweden

Due to their superior wear resistance, high hardness, and low friction coefficient, carbon nitride (CN_x) coatings have been proposed as a candidate to replace diamond-like carbon (DLC) coatings. In this study we present the structural, morphological, and adhesive properties of fullerene-like (FL) and amorphous carbon nitride (CN_x) coatings synthesized by HIPIMS in an industrial CC-800/9 CemeCon equipment. The coatings were grown on steel substrates of complex geometry (including those with small diameter cavities and holes, and shapes such as bolts, nuts, and screws) to thickness of 2-3 μm . A novel HIPIMS pretreatment with two HIPIMS power supplies was used to increase the adhesion of the coatings: one power supply to establish the discharge and one to produce a pulsed substrate bias. The environment of the created Cr plasma sputter-cleans the surface and forms a Cr-containing gradual interface into the substrate. Subsequently, carbon nitride coatings were prepared by HIPIMS from a high purity graphite target in a N_2/Ar discharge at 3 mTorr with the N_2 fraction varied from 0 to 1, and the substrate temperature varied from ambient to 300 °C. X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), scanning transmission microscopy (STEM), and high resolution transmission electron microscopy (HRTEM) have been used to study the coating and the steel/Cr/ CN_x interfaces. Identification of coating adhesion failures was done by the Daimler-Benz Rockwell-C adhesion test.

2:20pm **TR+SE-WeA2 Tribological and Mechanical Properties of Nanostructured Hydrogenated Amorphous Carbon and TiB₂ Films.** B. Zhao, Y.W. Chung, Northwestern University

Hydrogenated amorphous carbon films (CH_x) are known to attain ultra-low friction performance only in dry environments. Our work demonstrated that sulfur doping of hydrogenated carbon films (CH_x+S) results in ultra-low friction performance in both dry and humid environments. However, these films have a hardness of 7 - 10 GPa and an elastic modulus around 80 GPa, which are too low for some high stress applications. Formation of nanostructured coatings is known to improve hardness. With the aim to produce hard, low-friction coatings, we synthesized nanostructured films of CH_x (or CH_x+S) and titanium diboride using dual-target magnetron sputtering. Titanium diboride deposited by this method had a hardness >30 GPa. This paper will discuss the film structure as well as tribological and mechanical properties. Nanolayered films with a majority titanium diboride composition showed hardness improvement around rule-of-mixtures values with favorable low friction performance in humid air.

2:40pm **TR+SE-WeA3 Tribological Characteristics of a Tungsten Tip/Au-Ni Alloy Interface, Studied by Means of Combined STM-QCM.** L. Pan, J. Krim, North Carolina State University

A two-phase Au-Ni (20 at.% Ni) alloy has recently been suggested as a potential contact material for RF switch microelectromechanical systems (MEMS) switches. Tribological properties impact switch closure behaviour and heating at the interface impacts both the electrical and mechanical properties of the switch. We have thus performed a QCM STM study of heating and wear at the interface between a tungsten tip and a range of gold nickel alloys with varying compositional percentages. The comparison of nano heating generated via friction and surface response to the tip crash would be shown here.

3:00pm **TR+SE-WeA4 Quantitative Measurements of Adhesion Forces in Polycrystalline Silicon Surfaces via a Doubly Clamped Beam Test Structure.** I. Laborante, B. Bush, G. Li, C. Carraro, R. Maboudian, University of California - Berkeley

Current state of knowledge indicates that the prevalence of static adhesion in microstructures remains one of the major hurdles preventing a larger number of MEMS-based products from entering the mainstream, and quantitative understanding of this phenomenon is currently lacking. This is

due to the fact that contact mechanics at the micro-/nanoscale are a complicated multiscale problem, in particular when one is dealing with rough and rigid impacting surfaces. The results of investigations aimed at elucidating the adhesion force between co-planar, impacting polycrystalline silicon surfaces will be presented using a microfabricated doubly clamped cantilever beam test structure. The effect of apparent area of contact will be examined via microfabricated dimples of varying size. Determination of adhesion forces through systematic optical interferometric measurements will be presented. The data reveal a weak dependence of adhesion on the apparent contact area, instead of scaling with the contact area. Possible mechanisms leading to this behavior will be discussed.

4:00pm **TR+SE-WeA7 Nanoscale Control and Understanding of Friction at High-Speeds for Future Disk Drive Head-Disk Interfaces.** C.M. Mate, Hitachi San Jose Research Center **INVITED**

Tremendous progress has been made over the past several decades towards understanding the nanoscale origins of tribological phenomena [1], leading to numerous breakthroughs in friction and wear control. The impact of these breakthroughs has been particularly striking in the disk drive industry, where improved tribological engineering of the head-disk interface has led to the magnetic spacing being reduced from ~100 nm in 1995 to ~10 nm in 2009, enabling a 10^3 increase in storage areal density. In today's drives, recording head sliders fly reliably at incredibly small clearances (~2 nm during read-write operations) for many years at speeds > 10 m/s. As the industry moves to even smaller spacings, however, head-disk contact will become more frequent and improved surface engineering to control friction and wear will become more paramount.

In this talk, I will first review the key surface engineering features (slider air bearing surface, disk topography, overcoat, lubricant, etc.) that enable today's disk drive sliders to fly at nanometer clearances over disk surfaces. I will then describe work going on in our laboratory both to determine the nanoscale origins of friction and to use this understanding to develop future head-disk interfaces that are expected to run in continuous contact.

To determine the nanoscale origins of friction at high-speed sliding contacts (> 1 m/s), we have developed a *high shear rate apparatus* using technology from the disk drive industry [2]. With this new instrument, friction, adhesion, and wear can be studied at high sliding speeds (1 to 100 m/s) for nanometer thick lubricant films sandwiched between atomically smooth surfaces. Recently, this instrument has been modified to incorporate optical microscopy for in-situ visualization when a slider runs in contact with a transparent rotating disk. This technique has been particularly useful for studying the formation of nanoscale, non-equilibrium menisci at high speed contacts.

[1] C.M. Mate, *Tribology on the Small Scale: A Bottom up Approach to Friction, Lubrication, and Wear*, Oxford University Press, Oxford, 2008.

[2] C. M. Mate, R.N. Payne, Q. Dai, K. Ono, *Phys. Rev. Lett.* 97 (2006) 216104.

4:40pm **TR+SE-WeA9 The Effects of Humidity on the Tribological Properties of Nanocrystalline Diamond.** N. Theodore, K.J. Wahl, Naval Research Laboratory

The tribological response of nanocrystalline diamond (NCD) coatings to variations in moisture content of the environment was examined under reciprocating sliding conditions. Surface roughness, structure, composition, and carbon chemistry were determined by atomic force microscopy (AFM), X-ray diffraction (XRD), and Raman spectroscopy. All coatings were nanocrystalline with crystallite sizes ranging from 4 to 60 nm as measured by XRD. Visible wavelength Raman spectroscopy of the NCD coatings revealed various carbon chemistries. The NCD coatings could be classified in three subsets by Raman microscopy: (1) coatings exhibiting a single strong peak at 1332 cm^{-1} typical of crystalline diamond bonding; (2) coatings possessing broad peaks at 1340 cm^{-1} and 1550 cm^{-1} characteristic of the *D* and *G* peaks in sp^2 hybridized carbon along with the diamond 1332 cm^{-1} peak; and (3) coatings displaying additional peaks at 1135 cm^{-1} and 1470 cm^{-1} , commonly attributed to trans-polyacetylene bonding, along with the three previously described peaks. Reciprocating sliding tests using sapphire counterfaces in controlled humid environments resulted in low friction values for all coatings, between 0.02 and 0.09. Decreasing the humidity caused an increase in the number of cycles to run-in to low friction. These observed differences in run-in and counterface wear as a function of environment will be presented and related to NCD coating composition and microstructure.

5:00pm **TR+SE-WeA10 Crystallography-Dependent Self-Lubrication on Nickel Surfaces During Wear**, *C.C. Battaile, S.V. Prasad, J.R. Michael, P.G. Kotula*, Sandia National Laboratories

Wear experiments on Ni surfaces show that stable, nanocrystalline tribofilms can form under appropriate tribological conditions, even on single crystals. The presence of these nanocrystalline layers is qualitatively dependent on the crystallography of the surface and wear orientations, and are responsible for a marked reduction in friction on bare contact, suggesting numerous surface engineering possibilities. For example, when a 1 N normal load and 3.75 mm/s tangential speed are applied to a 1/8" diameter Si₃N₄ ball in contact with electropolished single-crystal Ni in a dry nitrogen environment, the measured friction coefficient is usually in the range 0.6 to 0.8. However, when the Ni surface is of the {110} type and the sliding direction is <211>, the friction coefficient abruptly drops to 0.3 after about 500 cycles, where it remains indefinitely. Modeling of this phenomenon, based on crystal plasticity, microstructure formation, and grain boundary sliding, suggests that the self-lubrication is due to the capacity of ultra-fine-grained microstructures to support grain rotation. Wear experiments on bulk nanocrystalline Ni deposits support this hypothesis by demonstrating low friction coefficients (around 0.3) and virtually no wear-in under low loads and sliding speeds, and higher friction (around 0.6) under high loads and speeds. We will provide an overview of the experiments and modeling of nanocrystalline film formation on single-crystal Ni, detail the results from friction experiments on bulk nanocrystalline Ni, and discuss model validation of the phenomenon's strain rate sensitivity.

5:20pm **TR+SE-WeA11 NEXAFS Characterization of Vapor Deposited Monolayer and Submonolayer Films on Si and Al₂O₃ for MEMS Friction Control**, *C. Jaye, D.A. Fischer*, National Institute of Standards and Technology, *B.M. DeKoven*, Surface and Interface Consulting, *J.D. Chinn*, Integrated Surface Technologies

Most microelectromechanical systems (MEMS) are fabricated using semiconductor and ceramic materials such as Si, and SiO₂, and Al₂O₃ which are hard, brittle materials and are not commonly used for mechanical devices. MEMS components are very small and lack power or much inertia when in motion, so they are highly susceptible to the influence of adhesive and surface forces. MEMS lubrication schemes involving vapor phase lubrication have been proposed as a means of continuously replenishing lubricant films on MEMS surfaces.

We present synchrotron based near edge x-ray absorption fine structure (NEXAFS) spectroscopy results of vapor deposited monolayers and submonolayers on SiO₂ and Al₂O₃ substrates under different process conditions. NEXAFS is a powerful non-destructive method in which soft x-rays are absorbed followed by the excitation (transition) of electrons from a core K- or L-level to partially filled into empty low-lying antibonding molecular states. Bond orientation information is deduced from the changes in the intensity of the resonances upon rotating the substrate normal in the plane of incidence of the polarized synchrotron beam.

Carbon K-shell NEXAFS performed at different incidence angles revealed that the vapor deposited fluorodecyltrichlorosilane (FDTS) molecules on silicon and alumina substrates produced self-assembled monolayered films that have high surface coverage and can be highly oriented. Using the NEXAFS technique, dichroic ratios (based on the σ^* C-F resonance) of the order of 0.5 have been obtained, thus revealing that these FDTS films have a high degree of molecular orientation. Orientation and coverage comparisons for water wiped and isopropylalcohol wiped FDTS as well as directly vapor deposited FDTS will be presented. The implications for the design of surfaces and interfaces for stiction control in MEMS devices will also be discussed.

Authors Index

Bold page numbers indicate the presenter

— A —

Abraham, B.: SE2-MoM4, 2
Anders, A.: SE2-MoM8, **3**
Anpo, M.: SE1-MoM1, 1
Arens, E.: SE1-MoM9, 2
Atiser, A.: SE-TuM3, 6

— B —

Barankin, M.: SE-MoA4, 4
Barankova, H.: SE-MoA3, 4
Bardos, L.: SE-MoA3, **4**
Barnett, S.A.: TF1+SE-TuM11, 8
Battaile, C.C.: TR+SE-WeA10, **14**
Block, I.: SE+TF-TuA1, 9
Brenning, N.: SE2-MoM6, 3
Brett, M.J.: SE+TF-TuA9, 10; TF1+SE-TuM12, 8
Broitman, E.: SE2-MoM3, 2; TR+SE-WeA1, **13**
Buriak, J.M.: SE+TF-TuA9, 10
Bush, B.: TR+SE-WeA4, 13

— C —

Cai, G.: SE1-MoM4, 1
Calle, C.: SE1-MoM9, 2
Cansizoglu, M.F.: TF1+SE-TuM4, **7**
Carraro, C.: TR+SE-WeA4, 13
Chang, H.T.: SE1-MoM5, 1
Chen, Y.: SE1-MoM4, **1**
Cheng, C.: SE1-MoM4, 1
Chinn, J.D.: TR+SE-WeA11, 14
Chistyakov, R.: SE2-MoM4, 2
Chung, Y.W.: TR+SE-WeA2, 13
Cloud, A.N.: SE2-MoM11, **3**
Cremer, R.: SE2-MoM1, **2**
Cunningham, B.T.: SE+TF-TuA1, 9
Czigany, Zs.: TR+SE-WeA1, 13

— D —

Davis, K.: SE1-MoM9, 2
De las Heras, E.: SE-TuP6, 11
DeKoven, B.M.: TR+SE-WeA11, 14
Demirel, M.C.: TF1+SE-TuM5, **7**
Deniz, D.: TF1+SE-TuM10, **8**
DeSario, P.A.: SE1-MoM3, **1**
Dluhy, R.D.: SE+TF-TuA3, 9
Dragoi, V.: SE-TuP7, 12

— E —

Engelken, R.: TF1+SE-TuM4, 7

— F —

Fischer, D.A.: TR+SE-WeA11, 14
Flauta, R.E.: SE2-MoM11, 3
Flores, M.: SE-TuP6, **11**
Fuhrmann, B.: SE+TF-TuA7, 9
Fukuoka, T.: SE+TF-TuA4, 9

— G —

Gall, D.: SE+TF-TuA8, 9
Ganesh, N.: SE+TF-TuA1, 9
Garcia, J.: SE-TuP6, 11
Gerlach, J.W.: SE+TF-TuA7, 9
Glukhoy, Y.: SE-MoA7, **4**
Gonzalez, E.: SE-MoA4, **4**
Gonzalez-Elipe, A.R.: SE+TF-TuA10, 10
Graham, M.E.: SE1-MoM3, 1
Gray, K.A.: SE1-MoM3, 1
Greczynski, G.: SE2-MoM3, 2; TR+SE-WeA1, 13
Guschl, P.: SE-MoA4, 4

— H —

Harris, K.D.: SE+TF-TuA9, 10
Helmerson, U.: SE2-MoM6, 3
Hickman, N.: SE1-MoM9, 2
Hicks, R.: SE-MoA4, 4
Hingerl, K.: SE-TuP7, 12
Hofman, T.: SE+TF-TuA11, 10
Hofmann, T.: TF1+SE-TuM6, 7
Hoshi, Y.: SE1-MoM6, **1**

Hsieh, J.H.: SE-TuM10, **6**
Hsing, H.C.: SE1-MoM5, 1
Hsu, C.C.: SE-MoA8, **4**
Hsu, Y.W.: SE-MoA8, 4
Huang, J.H.: SE-TuP3, 11
Huerta, L.: SE-TuP6, 11
Hug, H.J.: SE-TuM4, 6
Hultman, L.: SE2-MoM3, 2; TR+SE-WeA1, 13
Hussein, R.O.: SE-MoA6, **4**
Hwangbo, C.K.: SE-TuP1, 11; SE-TuP2, 11

— I —

Imai, Y.: SE+TF-TuA4, 9
Ishihara, D.: SE1-MoM6, 1

— J —

Jaye, C.: TR+SE-WeA11, **14**
Jhan, G.: SE1-MoM4, 1
Jones, J.: SE2-MoM10, 3

— K —

Karabacak, T.: TF1+SE-TuM4, 7
Khare, C.: SE+TF-TuA7, **9**
Kikuchi, M.: SE1-MoM8, 2
Kim, J.J.: SE-TuP1, 11
Kim, S.M.: SE+TF-TuA1, 9
Kimura, K.: SE+TF-TuA4, 9
Kirkpatrick, E.M.: SE-TuP5, 11
Kirkpatrick, S.R.: SE-TuP5, 11
Kjerstad, A.: SE+TF-TuA11, 10
Koratkar, N.A.: TF1+SE-TuM1, **6**
Kotula, P.G.: TR+SE-WeA10, 14
Krause, K.M.: TF1+SE-TuM12, **8**
Krim, J.: TR+SE-WeA3, 13
Kwon, J.W.: SE-TuP4, 11

— L —

Laboriante, I.: TR+SE-WeA4, **13**
Lad, R.J.: TF1+SE-TuM10, 8
Lange, M.: SE2-MoM10, **3**
Lei, H.: SE1-MoM6, 1
Li, C.: SE-TuM10, 6
Li, G.: TR+SE-WeA4, 13
Li, S.: SE+TF-TuA4, 9
Lim, J.T.: SE-TuP4, **11**
Lin, J.: SE2-MoM4, 2
Lin, T.: SE1-MoM4, 1
Lin, Y.: SE-MoA8, 4
Lin, Y.W.: SE-TuP3, **11**
Liu, P.C.: SE-TuM10, 6
Liu, Y.: SE+TF-TuA3, **9**
Lu, T.Y.: SE1-MoM5, 1
Lundin, D.: SE2-MoM6, **3**

— M —

Maboudian, R.: TR+SE-WeA4, 13
Mate, C.M.: TR+SE-WeA7, **13**
Mathias, P.: SE+TF-TuA1, 9
Matsuoka, M.: SE1-MoM1, 1
Mbenkum, B.: TF1+SE-TuM6, 7
McFall, J.: SE1-MoM9, 2
Michael, J.R.: TR+SE-WeA10, 14
Mishra, B.: SE2-MoM4, 2
Mittendorfer, G.: SE-TuP7, 12
Mitterer, C.: SE-TuM1, **6**
Mo, C.C.: SE1-MoM5, 1
Montgomery, E.: TF1+SE-TuM6, 7
Moore, J.J.: SE2-MoM4, 2
Mraz, S.: SE-TuM3, 6
Mukherjee, S.: SE+TF-TuA8, **9**
Murata, A.: SE1-MoM8, **2**
Muratore, C.: SE2-MoM10, 3

— N —

Nakajima, K.: SE+TF-TuA4, 9
Nakamura, S.: SE1-MoM8, 2
Nason, S.: SE1-MoM9, 2
Neumann, M.J.: SE2-MoM11, 3

Nie, X.: SE-MoA6, 4
Northwood, D.O.: SE-MoA6, 4

— O —

Oka, N.: SE1-MoM8, 2
Okura, Y.: SE-TuM6, 6

— P —

Pan, L.: TR+SE-WeA3, **13**
Park, Y.J.: SE-TuP1, **11**; SE-TuP2, 11
Parlinska-Wojtan, M.: SE-TuM4, 6
Patscheider, J.: SE-TuM4, **6**
Patzig, C.: SE+TF-TuA7, 9
Péllisson, A.: SE-TuM4, 6
Plach, T.: SE-TuP7, **12**
Prasad, S.V.: TR+SE-WeA10, 14

— R —

Raadu, M.A.: SE2-MoM6, 3
Rauschenbach, B.: SE+TF-TuA7, 9
Reed, A.: SE2-MoM10, 3
Rees, J.A.: SE2-MoM4, 2
Roddy, M.A.: SE-TuP5, **11**
Rodriguez, E.: SE-TuP6, 11
Rohde, S.L.: SE2-MoM11, 3
Ruzic, D.N.: SE2-MoM11, 3

— S —

Sakai, T.: SE1-MoM6, 1
Sanchez-Valencia, J.R.: SE+TF-TuA10, 10
Sato, Y.: SE1-MoM8, 2
Schiffers, C.: TR+SE-WeA1, 13
Schmidt, D.: SE+TF-TuA11, 10; TF1+SE-TuM6, 7
Schmidt, S.: SE2-MoM3, 2; TR+SE-WeA1, 13
Schneider, J.M.: SE-TuM3, **6**
Schubert, E.: SE+TF-TuA11, 10; TF1+SE-TuM6, 7
Schubert, M.: SE+TF-TuA11, **10**; TF1+SE-TuM6, 7
Sellmeyer, D.: SE+TF-TuA11, 10
Selwyn, G.S.: SE-MoA1, **4**
Seo, H.W.: TF1+SE-TuM4, 7
Shigesato, Y.: SE1-MoM8, 2
Sit, J.C.: TF1+SE-TuM9, 7
Skomski, R.: SE+TF-TuA11, 10
Smith, W.: TF1+SE-TuM3, **7**
Sobahan, K.M.A.: SE-TuP1, 11; SE-TuP2, **11**
Sproul, W.D.: SE2-MoM4, **2**
Stevens, B.L.: TF1+SE-TuM11, **8**
Suzuki, M.: SE+TF-TuA4, **9**

— T —

Tabuchi, R.: SE+TF-TuA4, 9
Takeuchi, M.: SE1-MoM1, **1**
Taschuk, M.T.: SE+TF-TuA9, **10**
Theodore, N.: TR+SE-WeA9, **13**

— V —

Vick, D.: TF1+SE-TuM12, 8
Voevodin, A.: SE2-MoM10, 3

— W —

Wahl, K.J.: TR+SE-WeA9, 13
Waite, A.: SE2-MoM10, 3
Wakefield, N.G.: TF1+SE-TuM9, 7
Wang, J.: SE2-MoM4, 2
Watanabe, T.: SE-TuM6, **6**
Wimplinger, M.: SE-TuP7, 12
Wong, M.S.: SE1-MoM4, 1; SE1-MoM5, 1
Wu, C.Y.: SE-MoA8, 4
Wu, Z.L.: SE2-MoM4, 2

— Y —

Yamaguchi, H.: SE1-MoM8, 2
Yang, Y.J.: SE-MoA8, 4
Yeom, G.Y.: SE-TuP4, 11
Yokota, Y.: SE-TuM6, 6
Yoshida, N.: SE-TuM6, 6
Yu, G.P.: SE-TuP3, 11

Yubero, F.: SE+TF-TuA10, **10**

— **Z** —
Zhang, W.: SE+TF-TuA1, **9**

Zhang, Z.: SE+TF-TuA3, **9**
Zhao, B.: TR+SE-WeA2, **13**
Zhao, Y.: SE+TF-TuA3, **9**; TF1+SE-TuM3, **7**