

# Monday Morning, October 18, 2010

## Advanced Surface Engineering

Room: Cimmaron - Session SE+PS-MoM

## Atmospheric Pressure Plasmas

Moderator: H. Barankova, Uppsala University, Sweden

8:20am **SE+PS-MoM1 Plasmajet Atmospheric Pressure Plasma: Effects of H<sub>2</sub> Addition in N<sub>2</sub> Main Plasma Gas on the Optical and Electrical Plasma Characteristics and on Si-based Film Composition**, *D. Debrabandere, X. Vanden Eynde*, CRM (Centre for Research in Metallurgy), Belgium, *F. Reniers*, Université Libre de Bruxelles, Belgium  
Si-based coatings were deposited with a cold plasma jet (Plasmabrush® PB1 from Reinhausen Plasma) at atmospheric pressure with nitrogen as main plasma gas and hexamethyldisilazane (HMDSN) as precursor. Effects of hydrogen addition on the plasma characteristics and the coating composition have been evidenced with optical emission spectroscopy (OES), power measurements and XPS in-depth analyses of deposited coatings. The evolution of the nitrogen line (at 315.9 nm) intensity with the applied voltage (ranging from 3.0 kV to 4.5 kV) has a sigmoid shape for the pure nitrogen plasma but it is quite linear with hydrogen addition (up to 3%). Based on OES spectra, the presence of the NH specie in the nitrogen-hydrogen plasmas has been evidenced (around 336.0 nm) but not in the pure nitrogen plasma. The power measured showed the same evolution with the applied voltage as the nitrogen line optical emission intensity: sigmoid shape for the pure nitrogen plasma and straight line for the nitrogen-hydrogen mixture. Although the plasma power is in similar range for both gases (except for applied voltages from 3.2 to 3.6 kV), the nitrogen concentrations in the films as evidenced by XPS were lower with the nitrogen-hydrogen plasma than with the pure nitrogen plasma indicating a chemical effect of the presence of hydrogen in the plasma.

### Acknowledgements

The authors would like to thank the Walloon Region (Belgian authorities) for financial support in the framework of a FIRST DOCA program.

8:40am **SE+PS-MoM2 Plasma Polymerization at Atmospheric Pressure: an Environmental Friendly Approach to Synthesize (ultra)hydrophobic, Biocompatible, Hybrid, Barrier or Ion – Exchange Coatings**, *D. Merche, J. Hubert, F. Dabeux, B. Nisol, A. Batan, N. Vandencastele, F. Reniers*, Université Libre de Bruxelles, Belgium

Plasma treatments are widely used in various applications, such as surface modification (etching, grafting, cross-linking...), cleaning, pollutant removal, and thin films deposition. They are advantageous since they have a low energy cost, they do not release toxic organic solvents into the environment, they are easy to control (the main parameters to control the plasma are the current, voltage, frequency and the gas pressure and composition) and they can be run at room temperature. The plasma polymerization technologies at atmospheric pressure were developed more recently. They allow avoiding expensive vacuum set up, and can be easily implemented in a continuous production line. Two major configurations were used for the deposits: direct (in a DBD system) and remote mode (atmospheric torch). The synthesis conditions (in one step, starting from a liquid precursor, and using an atmospheric pressure plasma) of various types of coatings will be presented and discussed: PEG[1] and PTFE-like coatings [2] (for biocompatible coatings), multifunctional hybrid coatings for barrier properties [3]; sulfonated polystyrene membranes for fuel cell applications [4,5]. The chemical structures of the various coatings were studied by XPS, FTIR and SIMS spectrometry. Correlations between the chemical structure and composition of the coatings and the plasma parameters were established.

[1] B. Nisol, C. Poleunis, P. Bertrand, F. Reniers, "Poly(ethylene glycol) Films Deposited by Atmospheric Pressure Plasma Liquid Deposition and Atmospheric Pressure Plasma-Enhanced Chemical Vapour Deposition: Process, Chemical Composition Analysis and Biocompatibility", Plasma processes and polymers, (2010) under press

[2] N. Vandencastele, O. Bury, F. Reniers "Process to deposit a fluorinated layer on a support", WO/2009/030763

[3] A. Batan, F. Brusciotti, I. De Graeve, J. Vereecken, M. Wenkin, M. Piens, J.J. Pireaux, F. Reniers and H. Terryn, "Comparison between wet deposition and plasma deposition of silane coatings on aluminium", Progress in Organic Coatings, (2010) under press

[4] D. Merche, C. Poleunis, P. Bertrand, M. Sferrazza, F. Reniers, "Synthesis of PS thin films by means of an atmospheric pressure plasma

torch and a dielectric barrier discharge", IEEE trans. on plasma science, 37 (2009), 951-960.

[5] Delphine Merche, Julie Hubert, Claude Poleunis, Patrick Bertrand, Philippe De Keyzer, François Reniers "Synthesis of sulfonated PS films using a Dielectric Barrier Discharge high pressure plasma" plasma processes and polymers, submitted

9:00am **SE+PS-MoM3 Surface Treatment of Energy Conversion Device Components by Cold Atmospheric Plasma**, *L. Bardos, H. Barankova*, Uppsala University, Sweden

Advantage of virtually unlimited substrate sizes makes the cold atmospheric plasma very attractive for treatments of surfaces e.g., for improving the lifetime and performances of renewable energy conversion systems. Samples of fiberglass-reinforced vinyl ester with a vinyl ester based gelcoat from windmill turbine blades and steel sheets used for ocean buoys in the linear wave energy converters have been treated by the Fused Hollow Cathode (FHC) and Hybrid Hollow Electrode Activated Discharge (H-HEAD) atmospheric plasma, generated in Ar, Ne and a mixture of air with water. The resulting surface energy has been examined by contact angle measurements. Turbine blade surface becomes hydrophilic after the treatment, sticking of the water droplets is reduced and the surface dries fast after rain, snow or icing. An increased surface tension after plasma treatment of steel relaxes within about 60 min. However, the SEM observations of paint-steel interfaces after an immediate application of the protective paint on treated surfaces have confirmed a considerable improvement of the paint adhesion that can provide better corrosion resistance and lifetime of buoys. Results of tests under different plasma parameters are presented and discussed.

9:20am **SE+PS-MoM4 Smooth and Self-Similar SiO<sub>2</sub>-like Layers on Polymers Synthesized using Dielectric Barrier Discharge Assisted CVD at Atmospheric Pressure**, *P. Antony Premkumar, S.A. Starostin*, Eindhoven University of Technology, Netherlands, *H. de Vries*, FUJIFILM Manufacturing Europe BV, Netherlands, *M. Creatore, M.C.M. van de Sanden*, Eindhoven University of Technology, Netherlands

High quality inorganic oxide thin films applied over polymers are of significant technological interest in the field of optics, vapour barrier coatings, microelectronics, flat panel displays and protective coatings. The layers prepared by PECVD at atmospheric pressure (AP-PECVD) is considered as a promising technology due to its economical and technological advantages. Despite these benefits, the major challenge of this coating technology is the usually reported poor film quality which arises mainly due to the intrinsic instabilities of the plasma as well as from the complex reactions of the deposition process.

In this investigation, we demonstrate the remarkable SiO<sub>x</sub> film properties synthesized using AP-PECVD in a roll-to-roll configuration [1]. The depositions were performed, in He free gas mixtures, using uniform glow-like dielectric barrier discharge as the electrical sources to assist CVD at atmospheric pressure. As a generic characteristic of the developed technology, it is observed that, irrespective of precursors (TEOS or HMDSO) and process gases (Ar, N<sub>2</sub> or air) employed, the films are smooth, both in short and long range length scales, and of near stoichiometric silica with very low carbon content (<2%). Detailed AFM morphology description and surface statistical analysis on SiO<sub>2</sub> dynamics showed that no dynamical film roughening in growth front and lateral directions are observed and the synthesized layers (~350 nm) follow the topology of the substrate, mimicking its surface texture characteristics. The value of the roughness exponent ( $\alpha$ ), close to 1, determined from the height-height correlation function analysis, indicates a self-similar scaling of the SiO<sub>2</sub>-like film morphology with the polymer substrate. The films are uniform with no defects or particle being incorporated during the deposition process and exhibit excellent barrier performances towards O<sub>2</sub> and H<sub>2</sub>O permeation.

[1] P. Antony Premkumar, S.A. Starostin, M. Creatore, H. de Vries, R.M.J. Paffen, P.M. Koenraad, M.C.M. van de Sanden, *Plasma. Proc. Polym.* (2010) In Press

9:40am **SE+PS-MoM5 Atmospheric-pressure Plasma Activation of Silicon and Glass Surfaces for Low-Temperature Direct Bonding**, *C.-P. Klages, M. Eichler*, Fraunhofer Institute for Surface Engineering and Thin Films (IST), Germany, *B. Michel*, Technische Universität Braunschweig / Institut für Oberflächentechnik (IOT), Germany **INVITED**

Low-temperature direct bonding of silicon wafers has been industrially established for several years now. To achieve a lowered annealing temperature required for sufficient bond strength from about 1000 °C to a few 100 °C only, low-pressure plasma treatment came into use more than 20 years ago. As shown at Fraunhofer IST more recently, also plasma

activation at 1 bar is capable of reducing required annealing temperatures to around 100 °C while still achieving bond energies 2 to 3 times higher compared to RCA-cleaned reference wafer pairs.

Many questions concerning the key effects, responsible for lowering the required annealing temperature, are still under investigation, especially for the attractive atmospheric-pressure method. At IOT and IST, the effects of dielectric barrier discharge (DBD) treatments performed under a wide range of conditions at 1 bar pressure on the properties of native or thermal SiO<sub>2</sub> layer on silicon wafers and on the achieved bond strength have been investigated in the recent years. The presentation will give an overview of the results from these investigations which were obtained using several surface analytical methods.

Recently, main interest has shifted from silicon to other materials and to alternative atmospheric-pressure plasma processes. With special gases used for the plasma activation, an increased bonding strength is also achievable for borosilicate glass bonding. However, while the mechanism of bonding enhancement in case of native oxide layers on Si can clearly be attributed to a surprisingly rapid growth of a porous oxide film, a convincing explanation for the effects achieved with glasses is still missing.

A common attribute of surface activation by DBD and low-pressure plasmas is a direct access of the plasma to the surface. By contrast, corona discharge makes use of the inhomogeneity of the electric field near a needle tip. Plasma zone and wafer are spatially separated and the electric field stress at the wafer surface is greatly reduced. Promising results of corona discharge treatment as an activation method for low-temperature wafer bonding have been obtained, indicating that relatively stable charged species play an important role. On the other hand, excimer UV radiation was virtually ineffective.

New insights into the kinetics of silanol condensation were also made possible by continuous measurements of the bonding strength *in situ* during annealing. Results of these studies show that the bond strength increase can be attributed to the expansion of bonded micro regions instead of statistical formation of siloxane bridges between the wafers.

10:40am **SE+PS-MoM8 Atmospheric Pressure Microcavity Plasma Arrays for Spatial Surface Modification**, R.D. Short, S. Al-Bataineh, E. Szili, C. Priest, Ph. Gruner, University of South Australia, E. Anglin, Flinders University, Australia, H.J. Griesser, University of South Australia, N. Voelcker, Flinders University, Australia, D. Steele, University of South Australia

*Microplasmas*, a rapidly growing technology, are normally operated at or near atmospheric pressure with dimensions ranging from microns to millimetres. [1] We are developing this technology for surface modification without using a physical mask or additional processing steps to increase the versatility and cost-effectiveness of the technology. Micropatterning of various chemistries and biomolecules is seen as vital to the successful development of new and emerging technologies, such as microfluidics and high throughput cell screening tools. [1, 2] In this presentation, the fabrication process of microcavity plasma array devices will be introduced, followed by a demonstration of the utility of these devices for generating specially well-controlled micron-scale surface treatment and polymer deposition. Two issues regarding the utility of these devices for localised surface modification were investigated: 1) Can these devices be used to modify a surface with micron-scale features without having the substrate pressed against the array? 2) Can this be achieved with control over diffusion of the plasma reactive components? We explored this through XPS imaging and small spot analysis, which gave insights into the surface chemistry of the micron-scale modified areas. Finally, we demonstrate the utility of microcavity plasma array surface engineering in the development of biological cell arrays.

1. Iza, F., et al., *Microplasmas: Sources, particle kinetics, and biomedical applications*. Plasma Processes and Polymers, 2008. 5(4): p. 322-344.
2. Klages, C.-P., et al., *Microplasma-Based Treatment of Inner Surfaces in Microfluidic Devices*. Contributions to Plasma Physics, 2007. 47(1-2): p. 49-56.

11:00am **SE+PS-MoM9 Electrical Characterization of Dielectric Barrier Discharges of Various Electrode Geometries**, V. Rodriguez-Santiago, J.K. Hirvonen, B.E. Stein, U.S. Army Research Laboratory, D.R. Boris, S.G. Walton, U.S. Naval Research Laboratory, D.D. Pappas, U.S. Army Research Laboratory

The increased use of atmospheric-pressure plasmas for the surface modification of materials has drawn particular interest in understanding the basic phenomena underlying dielectric barrier discharges (DBDs). One of

the main advantages of using DBDs is the generation of cold, non-equilibrium plasma at atmospheric pressure conditions without the need of vacuum equipment. A typical DBD setup consists of one or both electrodes covered with a dielectric material with a sufficiently high applied voltage to ignite the plasma. The plasma can be either filamentary or spatially uniform depending on parameters such as dielectric and electrode material, interelectrode gap, carrier and reactive gas mixture, and the type of applied voltage among others. Another important aspect is the geometry of the electrode assembly, which will determine the electric field configuration and thus influence the discharge characteristics.

In this study, we investigate the electrical characteristics of He and He-O<sub>2</sub> dielectric barrier discharges using a pulsed, sinusoidal signal in the kHz frequency range with a (1-10) kV peak-to-peak amplitude. Full characterization of the plasma will be carried out using rod, sheet and planar electrode assemblies, while materials of various dielectric constants such as mica, quartz and polyethylene will be employed. Voltage, current and power distributions will be analyzed aiming to identify the optimal electrode geometries and dielectric materials needed to produce uniform and large scale plasmas for materials processing.

11:20am **SE+PS-MoM10 ICP Atmospheric Plasma Torch with Saddle-like Antennas for Yttrium Oxide Nanocoating**, Y. Glukhoy, H. Schiesser, American Advanced Ion Beam Inc.

ICP atmospheric plasma torch is the most powerful electrode-less heat generating system with relatively small dimensions and a reasonable consumption of power and gases. It serves as an universal tool for nanocoating of surfaces where the gaseous, liquid as well as powder precursors can be used. A total melting, evaporation and plasma chemical reaction of precursor can be achieved with torches that provide a sufficient residential time a high temperature plasma fluid. But a conventional torches are supplied by a coil inductor pinching this fluid due to an axial magnetic field. In result, a high temperature area is reduced and a sufficient part of precursor is converted in dust. In order to broaden and lengthen this area for a sufficient increasing of a residential time the inductor has been replaced with two saddle-like ICP antennas with the different frequencies, i.e. 27.12 and 13.56 MHz. Each antenna comprises two or more spiral coils in a mirror position and in series or parallel connection. These coils are distributed with an angular uniformity and envelop a quartz tube of a plasma reactor. Such a non-axisymmetric design allows generation of a transversal RF field directed normally to axis of this reactor. But a plasma fluid is fixed on the axis due to buoyancy in the centrifugal force field created by a swirling injection of a discharge and sheath gases. However, the temperature gradient and a pressure drop caused by a cold carrier gas injected with a high velocity axially into a plasma bulk generate turbulence disrupting and distorting the plasma fluid. In result, a heat transfer from plasma to the wall is increased, becomes non-uniform and creates a hot spot melting the quartz wall. Mechanisms of the non-axisymmetric coupling, torch generation, contribution of different factors in distortion of the plasma fluid and method elimination of the hot spot have been investigated. In addition, we will discuss recent effort to extend applications such a torch in different areas including fabrication of yttrium oxide anti-corrosive nanocoating of focusing rings used in plasma etching processes in semiconductor industry.

1. 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 .
2. Y. Glukhoy, Saddle-like ICP Antenna for RF Atmospheric Plasma Processes. AVS 56th International Symposium, San Jose, California, November, 2009 CA, USA .

# Monday Afternoon, October 18, 2010

## Advanced Surface Engineering

Room: Cimmaron - Session SE+PS-MoA

### Pulsed Plasmas in Surface Engineering

Moderator: J. Patscheider, EMPA, Switzerland

2:00pm SE+PS-MoA1 2010 AVS Peter Mark Award Lecture - High Power Impulse Magnetron Sputtering (HIPIMS) - Fundamentals and Applications, A.P. Ehiarian\*, Sheffield Hallam University, UK  
INVITED

High power impulse magnetron sputtering (HIPIMS) is one of the youngest magnetron sputtering technologies. It provides new parameter space and new level of control of deposition parameters which are unattainable by conventional sputtering or cathodic arc evaporation technologies.

HIPIMS utilises a short (impulse) gas discharge with duration of ~100  $\mu$ s and duty cycles of <1% allowing it to access high peak power densities of 3000  $\text{Wcm}^{-2}$  at voltages of several hundred volts and current density of 1-4  $\text{Acm}^{-2}$ . Within each HIPIMS pulse the discharge is ignited through a hot electron ionisation wave and then develops into a cold metal plasma. The properties of the target material such as sputter yield, secondary electron emission coefficient, atomic mass and ionisation potential determine the power dissipated in the discharge, the density of plasma and the transport from the target to the substrate. The lifetime of both gas and metal ions spans over several milliseconds after the pulse often extending to the next pulse, thus creating a constant bombardment of ions at the substrate.

The degree of metal ionisation is controlled by the peak power density dissipated at the target and reaches 50% for Ti and 70% for Ta. The high metal ionization fraction of the HIPIMS technology has been utilised in applications for metalizing high-aspect vias with depth-to-width ratio of 30:1 achieving 10% bottom coverage for Ti, Ta and Cu films. The technology has been upscaled to a production cycle for through-silicon via (TSV) interconnects on 200 mm wafers.

HIPIMS pretreatment can implant metals and rare earths in substrates whilst maintaining the crystalline character, promoting local epitaxial growth over large lateral areas and excellent adhesion. This enables the introduction of oxidation- and corrosion- barriers at the coating-substrate interface.

Reactive sputtering in Ar and N<sub>2</sub> atmosphere in HIPIMS are characterised with a strong dissociation of the nitrogen molecule. In conditions of high power density, the N<sup>1+</sup> : N<sub>2</sub><sup>+</sup> ratio and Ti<sup>1+</sup>:Ti<sup>0</sup> ratio can exceed 1 thus promoting a fully dense intercolumnar boundaries in TiN films and increase their hardness. A preferred growth orientation of (200) is observed even without substrate biasing.

Nanoscale multilayer (superlattice) structured coatings based on CrAlYN/CrN have been grown with very low waviness and strongly improved density. These coatings provide excellent oxidation resistance and reduced fatigue deficit of aerospace turbine blades.

Nanocomposite coatings based on CrAlSiN were also deposited by HIPIMS for applications in high-temperature oxidation protection. Closer packing and reduced misorientation of nanocrystals as well as increased size of nanoclusters in which they are grouped are crucial mechanisms crucial in enhancing the film hardness.

The technology is finding new applications in the deposition of Cu(InGa)Se<sub>2</sub> in industrial photovoltaic cell coaters where a 3% improvement in efficiency over conventional sputtering has been achieved.

2:40pm SE+PS-MoA3 Influence of Plasma Conditions on the Properties of Hafnium and Titanium Films Deposited using HIPIMS, A.N. Reed, Air Force Research Laboratory, M.A. Lange, Air Force Research Laboratory/Universal Technology Corp., J.G. Jones, C. Muratore, J.J. Gengler, A.A. Voevodin, Air Force Research Laboratory

The orientation of a film can have a significant effect on its physical properties, for example the thermal conductivity of hexagonal materials. There has been a significant amount of work in the area of controlling the microstructure of films using deposition parameters. High power impulse magnetron sputtering, HIPIMS, is a PVD technique that produces a sputtered flux with a higher ion content than conventional DC magnetron sputtering. The ionization fraction of material upon the substrate permits some control of the film characteristics. In this study films were grown at pressures ranging from 5-30 mTorr, and pulse duration from 20-200 $\mu$ s. The resulting films exhibited pressure dependent deposition rates as well as

changing crystalline structure based on pulse duration. Energy resolved mass spectrometry and optical emission spectroscopy allowed correlation of ion energy distributions to deposition rates. Material characterization techniques, such as XRD, XPS, and SEM, have been used to correlate film structure to processing conditions for hafnium, titanium, and their nitrides. Time-domain thermal reflectance was used to measure the films' thermal conductivities. Differences in these values were related to the film microstructure.

3:40pm SE+PS-MoA6 High Power Impulse Magnetron Sputtering for the Growth of Functional Amorphous and Nanocrystalline Films, K. Sarakinos, A. Aijaz, M. Samuelsson, U. Issaksson, U. Helmersson, Linköping University, Sweden  
INVITED

Growth of films by condensation from the vapor phase frequently proceeds far from thermodynamic equilibrium giving rise to metastable configurations with unique attributes which are largely determined by the energy of the film forming species. One way of transferring energy to the growing film is via bombardment by ionized species which are present in plasma assisted physical vapor deposition (PVD) techniques. High power impulse magnetron sputtering (HiPIMS) is a novel plasma assisted PVD technique in which large fluxes of energetic ions are made available at the growing film. This is achieved by applying the power to the target in short unipolar pulses of low duty cycle (<10%) and frequency (<10 kHz). This mode of operation results in the generation of ultra dense plasmas (electron densities 10<sup>18</sup>-10<sup>19</sup> m<sup>-3</sup>) and a subsequent high degree of ionization for both gas atoms and sputtered material. HiPIMS has been extensively used for the deposition of polycrystalline elemental and compounds films facilitating control over their microstructure, phase composition, optical, mechanical and electrical properties. In the present talk the use of HiPIMS for the deposition of amorphous and nanocrystalline carbon and metal nitride based films is demonstrated. Discharges are generated using a variety of experimental parameters with respect to the pulse width, pulsing frequency, composition and pressure of the gas atmosphere. Time-averaged and time-resolved plasma diagnostics reveal that the variation of the above mentioned process parameters allows for control over the flux, the energy and the nature of the bombarding ionized species. Growth of films at those conditions enables to tune their bonding properties, their microstructure and their crystallinity and through this tailor important functional attributes such as their mechanical performance and high temperature stability.

4:20pm SE+PS-MoA8 New Development in Modulated Pulse Power Sputtering of Aluminum Oxide, Aluminum Nitride and Carbon Films, R. Chistyakov, Zond Inc, B. Abraham, Zpulser LLC

Modulated pulse power (MPP) sputtering is a versatile high power pulse magnetron sputtering technique in which there can be multiple voltage steps within a pulse. In this study, multiple voltage steps have high amplitude voltage oscillations. It was found that at certain level of voltage oscillations amplitude and frequency it is possible to sustain near arc free discharge in reactive gas environment. A special plasma generator with adjustable voltage oscillations amplitude and frequency was developed. The maximum output voltage is 1400 V. Aluminum oxide and aluminum nitride films have been reactively deposited with new approach in near arc free mode. The deposition rate, film structure, orientation, and mechanical properties were analyzed and measured, and the results of the film property measurements will be presented. Carbon films were sputtered with high average and peak power. It was found that with particular voltage pulse shapes there is no cones formation on the target surface during the deposition

\* Peter Mark Memorial Award Winner

# Tuesday Morning, October 19, 2010

## Advanced Surface Engineering

Room: Cimmaron - Session SE-TuM

### Hard and Nanostructured Coatings

Moderator: I. Petrov, University of Illinois at Urbana-Champaign

#### 8:00am SE-TuM1 PVD-Oxide Coatings for Tribological Applications, H. Rudigier, J. Ramm, OC Oerlikon Balzers AG, Liechtenstein INVITED

In the past, oxide coatings for tribological applications were almost exclusively deposited using chemical vapour deposition technology. The synthesis of corundum type Al-Cr-O coatings at temperatures of the order of 500°C using physical vapour deposition - cathodic arc evaporation in the case of Al-Cr-O - has triggered research activities to explore the potential of oxide materials for wear protection and other tribological applications. An overview of the various attempts to deposit oxides will be given, as well as a discussion of their properties and applications.

#### 8:40am SE-TuM3 Nanostructure, Bonding, and High Temperature Oxidation of SiZrON Thin Films, M.S. Byrne, R.J. Lad, University of Maine

SiZrON thin films have potential applications as hard high temperature coatings since they combine the oxidation resistance and hardness of oxides with the toughness of nitrides. In this study, a range of  $\text{Si}_x\text{Zr}_y\text{O}_z\text{N}_{1-x-y-z}$  thin films with a nominal thickness of 200 nm were deposited onto r-cut sapphire and fused silica substrates at 200°C using reactive RF magnetron co-sputtering of Zr and Si targets in  $\text{N}_2/\text{O}_2/\text{Ar}$  gas mixtures. The films were characterized using high resolution scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) in the as-deposited state as well as after annealing treatments up to 1000°C both in air and in vacuum. Grazing incidence XRD indicates that the as-deposited are amorphous for oxygen-rich and Si-rich film stoichiometries, but nanocrystalline ZrN or  $\text{ZrO}_2$  phases form within an amorphous matrix for N-rich and Zr-rich films. XPS shows a decrease in the Si, Zr, O, and N Auger parameters as the chemical bonding becomes more ionic with increasing O+Si content. For the different films, the N1s XPS lineshape indicates different states involving Si-N-O, Zr-N-O, and/or O-N bonding. When annealed to 1000°C in vacuum, negligible changes in stoichiometry or nanostructure are observed. However, when the films are heated to 1000°C in air, N depletion and Si enrichment at the film surface is observed, accompanied by the formation of tetragonal phase  $\text{ZrO}_2$  nanocrystallites and changes in nanomorphology as observed by SEM. Argon ion depth profiling with XPS was used to investigate the kinetics of the high temperature oxidation process.

#### 9:00am SE-TuM4 Spinodal Decomposition of $\text{Ti}_{0.33}\text{Al}_{0.67}\text{N}$ Thin Films Studied by Atom Probe Tomography, L.J.S. Johnson, Linköping University, Sweden, M. Thuvander, K. Stiller, Chalmers University of Technology, Sweden, M. Odén, L. Hultman, Linköping University, Sweden

#### 9:20am SE-TuM5 Structure, Mechanical Properties and Thermal Stability of Zr-Al-N Thin Films, P.H. Mayrhofer, L. Chen, D. Holec, D. Luef, R. Rachbauer, University of Leoben, Austria, Y. Du, Central South University

$\text{Zr}_{1-x}\text{Al}_x\text{N}$  thin films were synthesized by magnetron sputtering with AlN mole fractions  $x$  ranging from 0 to 0.9. We reveal, via X-ray diffraction (XRD) and transmission electron microscopy (TEM) that the films crystallize in the cubic NaCl (c) structure with  $x \leq 0.32$  and the wurtzite ZnS (w) structure with  $x \geq 0.75$ . For AlN mole fractions between 0.32 and 0.75 the films crystallize with multiple phases and contain a fully percolated disordered phase. This is in agreement with *ab initio* calculations suggesting that within a broad  $x$  range of 0.38–0.75 the cubic, wurtzite and hexagonal (BN structure) are equally preferred with respect to their energy of formation. Lower AlN mole fractions prefer the cubic structure whereas higher AlN fractions favor the wurtzite structure. The maximum hardness of  $H \sim 36$  GPa with an indentation modulus of  $E \sim 303$  GPa is observed for the single-phase cubic  $\text{Zr}_{0.68}\text{Al}_{0.32}\text{N}$  coating. For higher Al contents the hardness rapidly decreases to  $\sim 22$  GPa with  $x \sim 0.45$  and then slightly decreases further to  $\sim 21$  GPa for even higher Al contents. This is in perfect agreement with the structural investigations. During thermal annealing to 1500 °C in inert atmosphere the supersaturated phases of the films decompose towards their stable constituents c-ZrN and w-AlN. This is connected with a change in their mechanical properties where two major differences can be observed. The hardness of as deposited single-phase cubic  $\text{Zr}_{1-x}\text{Al}_x\text{N}$  slightly increases with annealing to  $T_a \sim 1000$  °C due to the formation of cubic Zr- and Al-rich

domains. Contrary to this observation the hardness of as deposited multi-phase  $\text{Zr}_{1-x}\text{Al}_x\text{N}$  coatings with  $x$  values between 0.38 and 0.5 increases by  $\sim 10$  GPa during annealing to  $\sim 900$  °C. Here, the observed hardness increase is mainly based on the structural rearrangement during annealing which results in the formation of crystalline areas with compact interface boundaries. As soon as w-AlN is formed, at around 1100 °C, the hardness decreases for as deposited single-phase cubic and multi-phase  $\text{Zr}_{1-x}\text{Al}_x\text{N}$  coatings.

#### 9:40am SE-TuM6 Growth and Microstructure Analysis of Hafnia-Based Nanostructured Coatings, M. Noor-A-alam, C.K. Roy, C.M. Bradely, A.R. Choudhuri, C.V. Ramana, University of Texas at El Paso

The aim of this work is to develop nano-structured Hafnia-based coating which can withstand with high temperature environment. Yttria stabilized hafnia (YSH) coatings have been fabricated on Nickel-based super alloy Inconel-738 and stainless steel using PVD method. The coatings have been produced at various temperatures. The thickness of the coating was about 500 nm as demonstrated in the cross-sectional imaging by Scanning Electron Microscopy (SEM). The structural characterization performed by X-ray diffraction (XRD) indicates the cubic crystal structure of YSH coating. Columnar structure has been noticed in all the coatings. The microhardness investigated by using a diamond tip microhardness testing machine indicates 3 Gpa hardness coatings. The temperature stability of these coatings has been examined. The result will be discussed in detail.

#### 10:40am SE-TuM9 Low Temperature Synthesis of $\alpha\text{-Al}_2\text{O}_3$ Films, K. Jiang, F. Nahif, RWTH Aachen University, Germany, K. Sarakinos, Linköping University, Sweden, S. Konstantinidis, University of Mons, Belgium, D. Music, J.M. Schneider, RWTH Aachen University, Germany

In this study, we deposit  $\text{Al}_2\text{O}_3$  films using plasma assisted chemical vapor deposition (PACVD) in an  $\text{Ar-H}_2\text{-O}_2\text{-AlCl}_3$  atmosphere and by filtered cathodic arc.

During PACVD a novel generator is employed delivering four times larger power densities than those obtained in conventional PACVD approaches. This mode of operation enables the increase of the efficiency of the  $\text{AlCl}_3$  dissociation in the gas phase, as well as a more intense energetic bombardment of the growing film. We demonstrate that these deposition conditions allow for the growth of dense films  $\alpha\text{-Al}_2\text{O}_3$  with negligible Cl incorporation and elastic properties similar to those of the bulk  $\alpha\text{-Al}_2\text{O}_3$  at a temperature of  $560 \pm 10$  °C.

$\alpha\text{-Al}_2\text{O}_3$  films are deposited employing a monoenergetic  $\text{Al}^+$  beam generated by a filtered cathodic arc. A critical  $\text{Al}^+$  ion energy of 40 eV for the formation of the  $\alpha\text{-Al}_2\text{O}_3$  phase at a substrate temperature of 720 °C is determined. This energy is used as input for classical molecular dynamics and Monte-Carlo based simulations of the growth process, as well as *ab initio* calculations. The combination of theory and experiment indicates that in addition to the well known surface diffusion the previously non considered diffusion in sub-surface regions is an important atomistic mechanism in the phase formation of  $\text{Al}_2\text{O}_3$ .

#### 11:00am SE-TuM10 Al-Si-N-O Hard Coatings Prepared by Reactive Magnetron Sputter Deposition from Composite Targets, J. Patscheider, M. Parlinska-Wojtan, A. Pélisson, Empa, Switzerland, P. Polcik, Plansee Composite Materials GmbH, Germany, P. Pecher, Glas Troesch AG, Switzerland

The applicability of hard nitride coatings on a large industrial scale often depends on the sensitivity of their properties on oxygen contaminations. Following the experience of reactive magnetron sputter deposition of optically transparent Al-Si-N thin films by co-sputtering from two elemental targets in a confocal arrangement, the possibility to prepare similar films from powder metallurgical Al-Si targets of different Al/Si ratios in mixed  $\text{Ar-N}_2\text{-O}_2$  is investigated. This arrangement is especially interesting when such coatings have to be prepared on an industrial scale. In this work, the effect of oxygen on the coating properties is examined, as reactive elements like Al often cause oxygen to be incorporated as a contamination. It is shown that hardness values up to 28 GPa are reached at oxygen concentrations of several atomic percent. The deliberate addition of  $\text{O}_2$  to the reactive gas mixture of  $\text{Ar/N}_2$  leads to the incorporation of oxygen up to 20 atomic %. Despite these very high concentrations hardness values of 25 GPa are reached. Similar to silicon, oxygen additions cause grain refinement and a gradual disappearance of the columnar structure with increasing oxygen content. It is shown that the hardness is primarily influenced by the plasma density and to a lower extent by other factors like silicon content and preferred orientation.

11:20am **SE-TuM11 A New Approach to the Synthesis of Adherent Hard Coatings with High Toughness**, *A.N. Ranade*, Northwestern University, *L.R. Krishna*, International Advanced Research Centre (ARCI), India, *Y.W. Chung*, Northwestern University

Traditional ceramic coatings provide abrasive wear protection due to high hardness. However, these coatings have low fracture toughness, making them susceptible to surface or internal flaws and failure under high impact loads. In addition, when ceramics are deposited onto metal substrates, lower thermal expansion coefficients compared to those of metals can cause thermal stress that may result in delamination. This paper explores a new approach to the synthesis of adherent hard coatings with high toughness. The approach begins with a metal matrix identical to that of the substrate, followed by the incorporation of nanoscale hard particles to increase hardness by Orowan strengthening. Theoretical estimates indicate that incorporation of 10 vol. % of such nanoscale particles can raise the hardness by as much as 20 GPa. The coating matrix is identical to that of the substrate, resulting in maximum adhesion and minimum thermal stress. Furthermore, by choosing nanoscale particles whose structure is semi-coherent with the metal matrix, local stress at the particle-matrix interface may activate the motion of screw dislocations, thus preserving the high fracture toughness of the matrix. This paper will present initial results of this exploration, using Ti as the matrix and semi-coherent TiB<sub>2</sub> nanoparticles as the strengthening agent. Characterization tools include x-ray diffraction (structure), AFM (surface roughness), SEM/TEM (size and distribution of nanoparticles), nanoindentation (elastic modulus, hardness, and fracture toughness), and scratch testing (adhesion), as a function of nanoparticle concentration. These studies should provide a general strategy for designing adherent hard coatings with high toughness.

11:40am **SE-TuM12 Oxidation and Diffusion Study on AlCrVN Hard Coatings using Oxygen Isotopes <sup>16</sup>O and <sup>18</sup>O**, *R. Franz*, University of Leoben, Austria, *J. Schnoeller*, *H. Hutter*, Vienna University of Technology, Austria, *C. Mitterer*, University of Leoben, Austria

In the commonly applied procedure to study the oxidation behavior of hard nitride and carbide coatings, the sample is heated to a certain temperature and exposed to an oxygen-containing atmosphere during a defined period of time. Subsequently, the oxidized specimen is analyzed as to the thickness and morphology of the oxide layer or the composition and chemical nature of the oxides. In order to gain more information about the mechanisms active during oxidation the procedure can be split into two stages where different isotopes, <sup>16</sup>O and <sup>18</sup>O, are introduced in each step. An analysis by means of secondary ion mass spectrometry depth-profiling with its inherent isotope selectivity allows for an investigation of the general oxidation behavior as well as the oxygen diffusion during the oxidation process. In the present case, two AlCrVN coatings of equal composition but different crystal structure were studied. The single-phase coating with its face-centered cubic (fcc) structure presents a higher oxidation resistance as compared to the dual-phase coating containing a wurtzite and a fcc phase. After the annealing treatment, the surface of the latter is entirely covered by VO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub> as evidenced by Raman spectroscopy. The single-phase coating, on the other hand, reveals unoxidized coating material and AlVO<sub>4</sub> crystals. However, even though exhibiting a significantly different oxidation resistance, the oxygen diffusion is similar. In both cases peak values of <sup>18</sup>O, which was introduced in the second stage, were found near the oxide-nitride interface indicating that O atoms diffused through the already formed oxides. Additional experiments using a gas mixture comprising natural water vapor H<sub>2</sub><sup>16</sup>O and <sup>18</sup>O<sub>2</sub> revealed that mainly the molecular oxygen serves as source for the formation of oxides as with increasing water vapor partial pressure the oxide layer thickness was significantly reduced.

# Tuesday Afternoon, October 19, 2010

## Advanced Surface Engineering

Room: Cimmaron - Session SE-TuA

### Surface Engineering for Thermal Management

Moderator: A.A. Voevodin, Air Force Research Laboratory

2:00pm **SE-TuA1 Nanometer-Scale and Interfacial Thermal Transport and Thermal Properties Characterization, W.P. King, University of Illinois at Urbana-Champaign** **INVITED**

This talk discusses recent work on measurements of nanometer-scale and interfacial heat transfer as well as measurements of nanometer-scale thermophysical properties of solid materials. The research combines atomic force microscope (AFM)- based measurements, nanometer-scale thermal processing, and nanometer-scale infrared spectroscopy.

In the first research thrust, an AFM cantilever probe can be used to measure thermomechanical expansions with spatial resolution smaller than 10 nm and out-of-plane displacements as small as 3 pm. Such displacements correspond to about 10 mK temperature changes. We use this technique to measure temperature distributions in graphene and carbon nanotube devices. It is possible to make a quantitative measurement of temperature rise in carbon nanoelectronic devices that are one atom thick.

In the second research thrust, we use AFM cantilever probes with integrated heaters. When the AFM tip is in contact with a solid substrate, the tip-substrate contact is an ultrasmall hotspot with a diameter as small as 1 nm. This tip can be used to measure nanometer-scale temperature-dependent mechanical, chemical, and electronic properties of surfaces.

2:40pm **SE-TuA3 Determination of Thermal Accommodation Coefficients from Heat Transfer Measurements Between Parallel Plates, W.M. Trott, J.R. Torczynski, M.A. Gallis, D.J. Rader, J.N. Castañeda, Sandia National Laboratories**

Thermal accommodation coefficients have been derived for a variety of gas-surface combinations using an experimental apparatus developed to measure the pressure dependence of the conductive heat flux between parallel plates at unequal temperature separated by a gas-filled gap. The heat flux is inferred from temperature-difference measurements across the plates in a configuration where the plate temperatures are set with two carefully controlled thermal baths. Temperature-controlled shrouds provide for environmental isolation of the opposing test plates. Since the measured temperature differences in these experiments are very small (typically 0.3° C or less over the entire pressure range), high-precision thermistors are used to acquire the requisite temperature data. High-precision components have also been utilized on the other control and measurement subsystems in this apparatus, including system pressure, gas flow rate, plate alignment, and plate positions. The apparatus also includes the capability for *in situ* plasma cleaning of the installed test plates. Measured heat-flux results are used in a formula based on Direct Simulation Monte Carlo (DSMC) code calculations to determine the thermal accommodation coefficients. Thermal accommodation coefficients have been determined for three different gases (argon, nitrogen, helium) in contact with various surfaces. Materials include metals and alloys such as aluminum, gold, platinum, and 304 stainless steel. A number of materials important to fabrication of Micro Electro Mechanical Systems (MEMS) devices have also been examined. For most surfaces, coefficient values are near 0.95, 0.85, and 0.45 for argon, nitrogen, and helium, respectively. Only slight differences in accommodation as a function of surface roughness have been seen. Surface contamination appears to have a more significant effect: argon plasma treatment has been observed to reduce thermal accommodation by as much as 0.10 for helium. Mixtures of argon and helium have also been examined, and the results have been compared to DSMC simulations incorporating thermal-accommodation values from single-species experiments. Sandia National Laboratories is a multi-program laboratory operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

3:00pm **SE-TuA4 The Nanoscale Surface Modification of the Wettability on Enhancements of Two Phase Change Heat Transfer Coefficient and Critical Heat, C.H. Li, The University of Toledo, G.P.B. Peterson, Georgia Institute of Technology**

4:00pm **SE-TuA7 Surface Engineering for Thermoelectric Energy Conversion, D.S. Dudis, M. Check, J. Ferguson, Air Force Research Laboratory** **INVITED**

Thermoelectric energy conversion encompasses both the conversion of thermal energy to electricity (energy harvesting and power generation), as well as the conversion of electrical energy to thermal energy (refrigeration and heat pumping). Since 1993 a renaissance has taken place in quest for better thermoelectric materials offering improved thermoelectric energy conversion efficiencies. An obstacle to achieving improved thermoelectric properties is to increase the electrical conductivity to thermal conductivity ratio ( $\sigma/k$ ), while not negatively impacting thermopower (Seebeck coefficient). Surface engineering has proven particularly important in this quest, as the transport of thermal energy across boundaries is intimately tied to surface effects. This talk will review recent progress in thermoelectric materials research and highlight some challenges tied to surface and materials engineering.

4:40pm **SE-TuA9 Thermal Conductance of Pt/VO<sub>2</sub>/Pt Heterointerfaces, D.-W. Oh, D.G. Cahill, University of Illinois at Urbana-Champaign**

5:00pm **SE-TuA10 Synthesis and Thermoelectric Properties of RuO<sub>2</sub> Nanorods, D. Music, F.H.-U. Basse, RWTH Aachen University, Germany, J.J. Gengler, A.A. Voevodin, Air Force Research Laboratory, J.M. Schneider, RWTH Aachen University, Germany**

We have explored the effect of the O/Ru ratio on the morphology and the Seebeck coefficient of RuO<sub>2</sub> nanorods (space group *P4<sub>2</sub>/mmm*) synthesized by reactive sputtering. At an O/Ru ratio of 1.69, a faceted surface is observed, while nanorod formation occurs at O/Ru ratios of 2.03 and 2.24. Using classical molecular dynamics with the potential parameters derived in this work, we show that volatile species enable nanorod formation. Based on *ab initio* calculations, two effects of the nanorod formation on the Seebeck coefficient are observed: (i) increase due to additional states in the vicinity of the Fermi level and (ii) decrease due to oxygen point defects (volatile species). These two competing effects give rise to a moderate increase of the Seebeck coefficient upon nanorod formation.

5:20pm **SE-TuA11 Thermal Conductivity Measurements of RuO<sub>x</sub> Thin Films, J.J. Gengler, A.A. Voevodin, Air Force Research Laboratory, D. Music, F.H.-U. Basse, J.M. Schneider, RWTH Aachen University, Germany**

Thermal conductivity trends in RuO<sub>x</sub> thin films of varying stoichiometry were characterized with a time-domain thermoreflectance (TDTR) technique. At an O/Ru ratio of  $x = 1.69$ , a faceted film surface is observed with a measured thermal conductivity value of  $28.8 \pm 0.8 \text{ W m}^{-1} \text{ K}^{-1}$ . With an O/Ru ratio of  $x = 2.24$ , nanorod formation occurs. These films were grown by a reactive magnetron sputtering technique with nonrotating substrates oriented 20° normal to the Ru target. Such material synthesis conditions resulted in a gradient sample structure at the onset of nanorod formation. As a result, the RuO<sub>2.24</sub> samples exhibited gradually changing surface roughness (rms of 12 nm – 200 nm) and thermal conductivity values ( $22 \text{ W m}^{-1} \text{ K}^{-1} - 5 \text{ W m}^{-1} \text{ K}^{-1}$ ), respectively. The thermal conductivity of the thin film samples studied here are all well below that of single crystal RuO<sub>2</sub> with tetragonal rutile structure ( $50 \text{ W m}^{-1} \text{ K}^{-1}$  [1]). The samples also have an inverse relationship of thermal conductivity with Seebeck coefficient [2], which is desirable for improving the figure of merit for thermoelectric performance.

#### References

- [1] Ferizovic D, Hussey LK, Huang Y-S, Munoz M. Determination of the room temperature thermal conductivity of RuO<sub>2</sub> by the photothermal deflection technique. *Appl Phys Lett* 2009;94:131913.
- [2] Music D, Basse F H-U, Haddorf R, Schneider JM. Synthesis and thermoelectric properties of RuO<sub>2</sub> nanorods. *J Appl Phys*, submitted for review.

5:40pm SE-TuA12 Heat Transport at Water Interfaces in the Proximity of Micro- and Nano-Structured Surfaces, S.A. Putnam, J.G. Jones, Wright Patterson Air Force Base

Breakthroughs in many of today's advanced technologies depend on the ability to reliably dissipate enormous amounts of thermal energy (heat) from very small areas. The most demanding applications are managed with nucleate boiling-based cooling schemes (e.g. spray cooling, heat pipes, thermosyphons, flow boiling, and jet impingement), where the cooling effectiveness is dictated by both the cooling configuration and the coolant itself. Surface features can also play a crucial role in boiling/cooling processes because they can, for example, i) increase the total wettable surface area, 2) control the bubble nucleation dynamics at the surface (e.g. vapor bubble release rate and size), and iii) change the effective surface energy (i.e., the intrinsic driving mechanism for wetting the hot surface with a coolant). Here we present our studies on thermal transport at liquid interfaces, focusing on 1) our recent experimental data and corresponding numerical simulations of water microdroplets evaporating, wetting, and bouncing on micro- and nano-structured surfaces and 2) our time-domain thermoreflectance (TDTR) experiments for the interfacial thermal conductance ( $G$ ) of evaporating water microdroplets on aluminum thin-films as a function of surface temperature.

# Tuesday Afternoon Poster Sessions

## Advanced Surface Engineering

Room: Southwest Exhibit Hall - Session SE-TuP

### Advanced Surface Engineering Poster Session

**SE-TuP1 Effect of NiCr-based Bondcoat and Post Treatment Process on the Adhesion of Air Plasma Sprayed WC-Co Coatings, F. Ghadami, University of Tehran, Iran, S. Ghadami, University of Semnan, Iran**

In this study WC-12wt%Co and NiCr-based powders were sprayed by the Air Plasma Spray (APS) method to form conventional WC-Co and double-layer NiCr-based/WC-Co coatings on steel substrates. The microstructure of as-sprayed samples with and without NiCr-based bondcoat were analyzed and found WC, W<sub>2</sub>C carbides and an amorphous phases. The single layer WC-Co coating samples were also heat-treated at 650, 900 and 1150°C for 1 hr. Heat treatment at all temperatures examined resulted in phase changes within the coating layer by formation of W<sub>x</sub>Co<sub>y</sub>C, η-carbides. Adhesive strength as well as microhardness of the as-sprayed and heat-treated coatings were also investigated. Results indicated that, adhesive strength has improved by using NiCr-based bondcoat in WC-Co deposits. The results also showed that heat treatment at 900 and 1150°C improves adhesive strength and hardness in conventional WC-Co coating samples. In this case, heat treatment process at 900°C gave the highest adhesive strength among the WC-Co coatings, which was due to the formation of η-carbides in interface of coating and substrate and formation of chemical bonding.

**SE-TuP2 Nanostructured Surfaces for Electrodes Prepared by Glancing Angle Deposition, U.B. Jensen, E. Ferapontova, D.S. Sutherland, Aarhus University, Denmark**

There are many potential applications for nanostructured surfaces. The aim of this work is making better electrodes for use in bio sensors and biofuel cells. One possible application is implantable medical devices, which could be a valuable tool for diagnosis and treatment of certain diseases, e.g. diabetes. If a biofuel cell could be made to deliver enough power, the signal from a bio sensor could be transmitted wirelessly to a computer capable of analysing and acting in response to the data. [1] Furthermore, if a bio sensor was functional and accurate for long times, an implantable medical device could work for months or longer.

The present approach to this challenge is to develop nanostructured surfaces on electrodes, onto which enzymes can be attached. Since the enzymes catalyze specific reactions, this can be used for sensing of a particular bio molecule. The proposition is that by changing the nanostructures one can improve and/or tailor electrodes for any bio sensing application.

The nanostructured surfaces were prepared by a combination of two techniques: colloidal lithography and glancing angle deposition [2]. This combination allows for control of critical parameters such as porosity, curvature and shape of the nanostructures. An example of nano-scale objects is shown in the figure – gold pillars protruding from a flat surface. This surface can be of almost any material, and the nano-scale objects uniformly covers large surface areas.

In terms of applications various enzymes will be immobilised on nanostructured surfaces. After changing various surface properties prior to enzyme immobilisation the efficiency of biofuel cells and bio sensors will be determined. This will make it possible to establish which properties are optimal, and it is therefore likely that better electrodes for bio sensing and fuel cells can be developed.

[1] C. Gomez, S. Shipovskov and E. E. Ferapontova, *J. Renewable Sustainable Energy* 2, 013103, (2010)

[2] K. Robbie and M. J. Brett, *J. Vac. Sci. Technol. A* 15(3), 1460–1465, (1997)

**SE-TuP3 Spatially Controlled Heat Generation by Local Plasmon Resonator, K. Namura, M. Suzuki, R. Tabuchi, K. Nakajima, K. Kimura, Kyoto University, Japan**

Heat generation from noble metal nanoparticles due to their local plasma resonance is attracting much attention because of the fast response and the flexibility to choose heating area. The conventional nanoparticle heaters are fabricated by simple lithography of Au thin films on glass or Si substrate so that they absorb only a few 10 % of the incident light even at the wavelength of the local plasma resonance. Therefore, they are ineffective from the viewpoints of not only the fabrication cost but also photothermal conversion. In addition, it is difficult to spatially control the generated heat

because photothermal conversion efficiency is constant for all nanoparticles.

Recently, we demonstrated the self-assembling of Au nanoparticles/dielectric layer/ Ag mirror sandwiches, namely, the local plasmon resonator, by using a dynamic oblique deposition technique<sup>1</sup>. Due to strong interference, their optical absorption can be controlled between 0.1% and 100% by changing the thickness of the dielectric layer. Although we focused our attention only on the local field enhancement in that work, now we notice that photothermal conversion efficiency can be spatially tuned by using the local plasmon resonators. This work is the feasibility study of application of the local plasmon resonator to the spatially controlled nanoheaters.

We prepared combinatorial local plasmon resonator chips which have different thicknesses of Au and the dielectric layers on a single substrate of 50×50 mm<sup>2</sup> by oblique deposition and measured the absorption spectrum on each element. In order to evaluate the heat generation from Au nanoparticles, we measured the temperature of the water, with which a small cell created on a local plasmon resonator was filled, irradiating the laser of the wavelength of 785 nm. The temperature of the water on the element with high absorption becomes higher than that on the element with low absorption. The change in temperature proportional to absorption of the element in the local plasmons resonator chips. This suggests that the photothermal conversion efficiency can be controlled by the interference. Consequently, local plasmon resonator can be applied to the nanoheaters, which can spatially control the heat generation.

This work was supported by KAKENHI 21656058 and by the Iketani Science Foundation.

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

**SE-TuP4 Multifrequency Atomic Force Microscopy with Heated Cantilever Tips, J.L. Remmert, Universal Technology Corporation, J.G. Jones, A.A. Voevodin, Air Force Research Laboratory, W.P. King, University of Illinois at Urbana-Champaign**

Multifrequency drive capabilities have recently been implemented on the atomic force microscope (AFM) to enhance imaging contrast and retrieve information about the material properties of the sample surface<sup>1</sup>. Common to each technique is the use of a complex (amplitude-modulated) waveform to oscillate the cantilever tip in proximity to the substrate at two or more of its flexural resonances. Simultaneous measure of the amplitude and phase of the cantilever ac deflection is used to characterize the tip-sample coupling and may, for example, relay mechanical and chemical information through the separation of short- and long- range forces between distinct resonance modes<sup>2,3</sup>. In this way, bimodal imaging has also advanced magnetic<sup>3</sup> and electrostatic<sup>4</sup> force mapping with the application of appropriate fields. Related techniques track spatial variations in the contact resonance by evaluating the cantilever response across either a frequency band (band excitation, BE) or at fixed limits bracketing the peak (dual ac resonance tracking, DART). Resonance tracking also reduces crosstalk between the surface topography and frequency-dependent material properties, and has been employed to measure energy dissipation<sup>5</sup>, as well as for piezoelectric domain characterization<sup>6</sup> and local thermal analysis<sup>7</sup> with drive signals modulating the local electrical bias and temperature gradient, respectively. This work focuses on the latter approach: the use of dual frequency excitation to resistively heat and actuate an AFM tip for thermomechanical imaging of sample surfaces. Evaluation of the ac deflection at two frequency limits provides the amplitude and phase data required to extract the quality factor (dissipation) by the simple harmonic oscillator model<sup>1</sup>. The experimental procedure (thermal DART) has been demonstrated along with data post-processing to establish a temperature-dependent study of surface mechanical properties.

<sup>1</sup>R. Proksch and C. Callahan, United States Patent Application Publication US 2009/0013770 A1 (2009).

<sup>2</sup>R. Proksch, *Applied Physics Letters* **89**, 113121 (2006).

<sup>3</sup>J.W. Li, J.P. Cleveland, and R. Proksch, *Applied Physics Letters* **94**, 163118 (2009).

<sup>4</sup>R. W. Stark, N. Naujoks, A. Stemmer, *Nanotechnology* **18**, 065502 (2007).

<sup>5</sup>S. Jesse, S.V. Kalinin, R. Proksch, A.P. Baddorf, and B.J. Rodriguez, *Nanotechnology* **18**, 435503 (2007).

<sup>6</sup>B. J. Rodriguez, C. Callahan, S. V. Kalinin, and R. Proksch, *Nanotechnology* **18**, 475504 (2007).

<sup>7</sup>M.P. Nikiforov, S. Jesse, A.N. Morozovska, E.A. Eliseev, L.T. Germinario and S.V. Kalinin, *Nanotechnology* **20**, 395709 (2009).

**SE-TuP5 Time Domain Thermoreflectance and 3-Omega Comparison Studies of Polymer-Metallic-Ceramic Nanolaminate Coatings,** *A.R. Waite*, Air Force Research Laboratory/Universal Technology Corp., *J.J. Gengler*, Air Force Research Laboratory/Spectral Energies, LLC, *J.G. Jones*, *C. Muratore*, *A.A. Voevodin*, Air Force Research Laboratory

Multilayered polymer-metal-ceramic nanolaminate coatings were grown by room temperature plasma enhanced chemical vapor deposition (PECVD) and magnetron sputtering processes in a dual chamber PVD-CVD system to examine optical coatings with tailored, through-thickness thermal conductivity. Highly cross-linked fluoropolymer films were grown by PECVD from an octafluorocyclobutane gas precursor. High refractive index ceramic layers were deposited by pulsed DC magnetron sputtering of a TiO<sub>2</sub> target. Thin (5-20 nm) silver interlayers with thicknesses on the order of phonon mean free paths were also integrated into the nanolaminate stack. The thickness and position of the layers with high and low refractive index layers could be adjusted to develop optical coatings with desired functionality for different wavelengths of incident light, while metal layers were integrated to distribute heat and eliminate decomposition of the polymer films during heating by incident light. The through-thickness thermal conductivity of the films with and without the integrated silver layers was compared by time domain thermoreflectance (TDTR) and 3-Omega techniques. The 3-Omega analysis provides the bulk thermal conductivity of the nanolaminate stack which was compared to the constructed thermal transport model from the TDTR analysis of each film material and their respective interfaces.

**SE-TuP6 Water Adsorption on TiN and TiCN Hard Coatings,** *E. Broitman*, Carnegie Mellon University, *M. Rebelo de Figueiredo*, University of Leoben, Austria, *W. Michalak*, Carnegie Mellon University, *R. Franz*, University of Leoben, Austria, *G. Zanini Gadioli*, Carnegie Mellon University, *C. Mitterer*, University of Leoben, Austria

It is known that ceramic coatings with substantial amounts of structurally incorporated carbon show low-friction behavior, in particular at intermediate temperatures. However, the mechanisms behind activation, formation and modification of the required free carbon in the friction contact are still not fully understood, especially in the case of Ti<sub>x</sub>CN<sub>y</sub>, a widely used commercial coating. In a previous study the importance of the presence of water vapor for the formation of a friction-reducing layer has been revealed by tribological tests at different water vapor pressures in the surrounding atmosphere. In the present work, water adsorption studies on titanium nitride (TiN) and titanium carbon nitride (TiCN) coatings are carried out in order to gain a new insight about the active chemical processes on the coating surface.

The TiN and TiCN coatings were prepared by dc magnetron sputtering of a TiN and Ti<sub>2</sub>CN compound target, respectively, in a lab-scale deposition system. X-ray diffraction was used to study the crystal structure and the obtained patterns show a face-centered cubic structure with a [111] texture for TiCN and a [200] texture for TiN. Both X-ray Photoelectron Spectroscopy (XPS) and Temperature Program Desorption (TPD) experiments in the range 110-700 K were conducted in an Ultra High Vacuum chamber with a base pressure of  $\sim 3 \times 10^{-10}$  Torr. Also, the water adsorption on the coatings as a function of % relative humidity was measured using a quartz crystal microbalance.

XPS measurements reveal the presence of a surface oxide, with the composition of the coatings being Ti<sub>2.0</sub>N and Ti<sub>1.73</sub>CN<sub>1.35</sub>. TPD experiments show that water adsorption has a zero-order desorption mechanism. After low coverage and temperature of exposure of 110 K, the spectra yield calculated desorption energies of  $22.96 \pm 4.17$  kJ/mol and  $18.42 \pm 4.73$  kJ/mol for the TiN and TiCN surfaces, respectively, based on a leading-edge analysis. Measurements from higher coverage indicate the strength of the water-water attractive interactions which cause clustering of H<sub>2</sub>O into 2-D islands and then multilayers. The desorption energies from this regime are calculated to be  $47.45 \pm 2.31$  kJ/mol and  $41.73 \pm 4.06$  kJ/mol for the TiN and TiCN surfaces, respectively. These values are higher than the water's combined heats of vaporization and fusion:  $\Delta H_v + \Delta H_f = 9.72$  kcal/mol + 1.44 kcal/mol. The water adsorption results can be correlated to the microstructure, composition and tribological properties.

**SE-TuP7 Effects of Ag/Cu Ratios on the Annealing Temperature and Mechanical Properties of TaN-(Ag,Cu) Nanocomposite Thin Films,** *J.H. Hsieh*, *S.Y. Hung*, Ming Chi University of Technology, Taiwan, Republic of China, *S.Y. Chang*, *C.C. Tseng*, National Chung Hsing University, Taiwan, Republic of China

TaN-(Ag,Cu) nanocomposite films were deposited by reactive co-sputtering on Si(110) substrates. The samples were then annealed using RTA (Rapid Thermal Annealing) at various temperature (200 °C ~ 400 °C) for 2, 4, 8 minutes respectively to induce the nucleation and growth of Ag/Cu particles in TaN matrix and on film surface. This study was attempted to find out if annealing temperature and mechanical properties

were affected by Ag/Cu ratios. C-AFM (Conductive Atomic Force Microscopy) and FESEM (Field Emission Scanning Electron Microscopy) were used to confirm the emergence of Ag/Cu nano-particles on the surface of TaN-(Ag,Cu) thin films. Nano-indenter was used to examine the mechanical properties of the films. The results reveal that annealing temperature could be as low as 200 °C for the sample with Ag/Cu ratio at 4:6, while the hardness values could be at their highest. Accordingly, the films may be applied on polymeric substrate in the future for the purpose of anti-wear and anti-bacteria.

# Wednesday Morning, October 20, 2010

## Thin Film

Room: San Miguel - Session TF+SE-WeM

### Glancing Angle Deposition (GLAD) I

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

#### 8:00am TF+SE-WeM1 Soft Nanostructured Films for Biomedical Applications, M.C. Demirel, Pennsylvania State University INVITED

Anisotropic textured surfaces represent key structural components utilized by various animals and plants to gain a competitive advantage for survival. For example, a closer look at complex structures in insect wings and lizard toes reveal organized structured features at the microscopic scale. These structures are composed of millions of aligned columns per square millimeter, which create novel anisotropic properties. We have demonstrated that these structures can be fabricated synthetically by an oblique angle polymerization (OAP) method. OAP 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. In this talk, we will describe unique anisotropic physicochemical properties (i.e. morphing/folding, wetting, and friction) of well-ordered arrays of nano-rods/tubes, which mimic biological structures at the microscopic scale. We will also present results concerning the use of these films for biomedical and biosensors applications.

#### 8:40am TF+SE-WeM3 Growth Temperature Controlled Morphology of Ge Nanocolumns, C. Khare, J. Bauer, J.W. Gerlach, Leibniz Institute of Surface Modification (IOM), Germany, B. Fuhrmann, Martin-Luther-University Halle, Germany, T. Höche, B. Rauschenbach, Leibniz Institute of Surface Modification (IOM), Germany

#### 9:00am TF+SE-WeM4 Glancing Angle Deposited Platinum Nanorod Arrays with Enhanced Electrocatalytic Activity for Oxygen Reduction Reaction in PEM Fuel Cells, W.J. Khudhayer, A.U. Shaikh, T. Karabacak, University of Arkansas at Little Rock

In this work, we have investigated the electrochemical properties of vertically aligned, single-layer, low loading, carbon-free and single crystal Pt nanorod arrays as a potential cathode material in polymer electrolyte (PEM) fuel cells. These nanorods of different lengths in the range of 20-600 nm were produced by glancing angle deposition (GLAD) technique with Pt loading values of 0.016-0.5 mg/cm<sup>2</sup>. Electrodes of conventional carbon supported Pt nanoparticles (Pt/C) were also prepared for comparison with Pt nanorods for their electrochemical properties. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were utilized to study the morphology and crystallography of Pt nanorods. SEM and XRD results reveal that Pt nanorods are well-isolated, vertically aligned, and single-crystal with atomically sharp tips. The single-crystal property allows enhanced electrochemical activity and reduced surface oxidation, while the isolated nature of the rods in lateral directions can provide a channeled porosity for effective transportation of gases in a PEM fuel cell. The electrochemical activity of Pt nanorods as well as Pt/C was evaluated using cyclic voltammetry (CV). CV results show that Pt nanorod electrocatalysts reduce oxygen to water at a more positive potential than Pt/C, indicating that our catalyst has a lower oxygen overpotential due to the enhanced electrode porosity, single-crystal property, and the dominance of the preferred crystal orientation for oxygen reduction reaction (ORR). In addition, a series of CV scans show that our catalyst is more stable than Pt/C in the acidic environment. Finally, in order to get a fair comparison for high surface area catalysts, detailed thin-film rotating disk electrode measurements at room temperature were performed on 200 nm long Pt nanorods as well as Pt/C for comparison to calculate the most important kinetics parameters (Tafel slopes, exchange current density, Pt mass-specific activity and area-specific activity), which are the accepted measures of true catalysts activity towards ORR. These results reveal the enhanced mechanism and kinetics of ORR on Pt nanorods compared to Pt/C.

#### 9:20am TF+SE-WeM5 Hydrogen Storage Properties of Magnesium Nanotrees by Glancing Angle, M.F. Cansizoglu, T. Karabacak, University of Arkansas at Little Rock

Among many solid state materials for hydrogen storage, magnesium hydride (MgH<sub>2</sub>) combines a hydrogen capacity of 7.6 wt % with the benefit of the low cost of production and abundance. The main difficulties for implementing MgH<sub>2</sub> are slow absorption/desorption kinetics and high reactivity towards air and oxygen, which are also common issues in most

lightweight metal hydrides. Previously, improvements in hydrogen storage and release properties have been reported by using nanostructured magnesium that can be obtained through various fabrication methods including ball-milling, mechanical alloying, and vapor transport. In this study, we investigate the hydrogen absorption and desorption properties of magnesium "nanotrees" fabricated by glancing angle deposition (GLAD) technique, and also conventional Mg thin films deposited at normal incidence. Mg nanotrees are about 15 μm long, 10 μm wide, and incorporate "nanoleaves" of about 20 nm in thickness and 1.2 μm in lateral width. A quartz crystal microbalance (QCM) gas absorption/desorption measurement system has been used for our hydrogen storage studies. Nanostructured and thin film Mg have been deposited directly on the surface of the gold coated unpolished quartz crystal samples. QCM hydrogen storage experiments have been performed at temperatures ranging between 100-300°C, and at H<sub>2</sub> pressures of 10 and 30 bars. QCM measurements revealed that Mg nanotrees have better storage characteristics compared to Mg thin films. They can reach hydrogen storage values of about 4.80 wt% at 100°C, and up to about 6.71 wt% (which is close to the theoretical maximum storage value of Mg) at temperatures lower than 150°C. The significant enhancement in hydrogen absorption properties of Mg nanotrees is believed to originate from novel physical properties of their nanoleaves. These structures are very thin (~20 nm) and both surfaces are exposed to hydrogen enhancing the diffusion of hydrogen together with a decreased diffusion length. In addition, nanostructured Mg have been observed to be quite resistant to surface oxidation, which is believed to be due to the single crystal property of the Mg nanoleaves.

#### 9:40am TF+SE-WeM6 Fabricating Crystalline ZnO Nanorods by Glancing Angle Deposition, J.M. LaForge, M.T. Taschuk, M.J. Brett, University of Alberta, Canada

Zinc oxide possesses a combination of properties, including semiconductor electronic behaviour, optical transparency, and piezoelectricity, that make it an interesting candidate for energy scavenging, photovoltaics, and chemical sensing applications (1, 2). Several unique nanostructures may be formed with ZnO, with a variety of growth methods that exploit the difference in surface energy between the low-index crystal faces of the wurtzite ZnO crystal leading to preferential growth along the c-axis.

Glancing angle deposition (GLAD) is assumed to operate effectively under conditions of limited surface diffusion so that growth occurs from geometric shadowing of an incoming particle flux. While amorphous GLAD films are typical, there are numerous crystalline films reported in the literature, including ZnO (3). This suggests that in certain material systems growth kinetics play a role in GLAD growth. However, the conditions under which GLAD produces crystalline films has not been thoroughly investigated or explained.

We have selected ZnO to investigate these issues for two reasons: first, the technological applications outlined above, and second, to explore the material growth properties which can produce crystalline structures. This makes it an ideal candidate for studying nanostructure morphology and crystal properties as a function of process parameters, including deposition rate, pitch and throw distance. Optimal growth conditions for zinc oxide nanorod films occurred for pitch values in the vicinity of 1 nm to 10 nm. Study of the post aspect ratio and areal post density suggests that typical GLAD growth occurs for deposition rates <0.005 nm sec<sup>-1</sup> and that growth kinetics begin to contribute significantly at deposition rates >0.01 nm sec<sup>-1</sup>. Films deposited at pitch values between 0.001 nm to 6.5 μm are crystalline and textured, and greater texturing is achieved for conditions of decreased surface diffusion.

(1) Wang, Z. L. *Journal of Physics: Condensed Matter*. **2004**, *16*, R829-R858.

(2) Ye, C.; Fang, X.; Hao, Y.; Teng, X.; Zhang, L. *The Journal of Physical Chemistry. B*. **2005**, *109*, 19758-65.

(3) Teki, R.; Parker, T.; Li, H.; Koratkar, N.; Lu, T.-M.; Lee, S. *Thin Solid Films*. **2008**, *516*, 4993-4996.

#### 10:40am TF+SE-WeM9 Optical, Magnetic, Magneto-Optical and Electrochemical Properties of Sculptured Thin Films, E.B. Schubert, D. Schmidt, T. Hofmann, A.C. Kjerstad, E. Montgomery, S. Schöche, M. Schubert, University of Nebraska - Lincoln

Bottom-up and self-organized three-dimensional (3D) structure design on the nanoscale opens a new field in nanostructure based thin film engineering with a broad range of practical applications for sensors, optical coatings, photovoltaic devices or biomaterials, for example. Sculptured thin films (STFs) belong to this group of thin films and current research creates exciting new knowledge about the unique material properties that are related to shape, dimension, and distribution of the nanostructures within

the thin film ensemble. The following paper presents new sculptured thin film properties obtained from material analysis using optical, magnetic, magneto-optical and electrochemical characterization techniques. [1-5] Material properties have been quantified from model analysis and results from our investigations lead to original device designs for applications such as highly-sensitive mass balances, subwavelength antireflection coatings, magneto-optical memory and chemical sensors.

- [1] E. Schubert, Contributions to Plasma Physics **47**, 545 (2007).
- [2] D. Schmidt, B. Booso, T. Hofmann, E. Schubert, A. Sarangen, and M. Schubert, Appl. Phys. Lett. **94**, 011914 (2009).
- [3] D. Schmidt, B. Booso, T. Hofmann, E. Schubert, A. Sarangan, and M. Schubert, Opt. Lett. **34**, 992 (2009).
- [4] D. Schmidt, A. C. Kjerstad, T. Hofmann, R. Skomski, E. Schubert, and M. Schubert, J. Appl. Phys. **105**, 113508 (2009).
- [5] D. Schmidt, T. Hofmann, E. Schubert, and M. Schubert, Appl. Phys. Lett. **96**, 091906 (2010).

11:00am **TF+SE-WeM10 Stress Behavior of Obliquely Sputtered Ta Films on Glass Substrates**, S.U. Jen, P.H. Chiang, Academia Sinica, Taiwan, Republic of China

Ta films were obliquely deposited on glass substrates by magnetron sputtering method using the parameters: deposition angle  $\alpha = 60^\circ$ ; deposition temperature  $T_s = 298, 373, 473, \text{ and } 573 \text{ K}$ ; Ar working gas pressure  $P_{AR} = 2, 7.5, \text{ and } 15 \text{ mTorr}$ ; film thickness  $t_f = 100 \text{ nm}$ . From X-ray diffraction, atomic force microscopy, cross-section transmission electron microscopy, and Auger depth profile analysis, we conclude that: [1] the axis of each columnar grain is inclined at an angle  $\beta \approx 35^\circ$  with respect to the film normal; [2] in-plane grain aggregates show some vestiges of the chain-like structure, whose long axis is perpendicular to the plane of incidence (i.e. the transverse or width direction of the sample); [3] oxygen atoms are found inside the film; especially located in the columnar gaps (or microvoids) between neighboring grains. The stress of each film was measured via Stoney equation. The main results in regard to the stress behavior of this series of Ta films are summarized below: [a] the intrinsic stress  $S_i$  is always tensile and dominant over the thermal stress  $S_T$ ; [b] the total stress is anisotropic with the longitudinal stress being larger than the transverse stress; [c] as  $T_s$  increases,  $S_i$  becomes less tensile. Result [a] is reasonable because Ta is a high melting point material.<sup>1</sup> Especially, in the oblique-deposition case, the formation of gaps becomes more obvious. Hence, much larger tensile stress (than in the normal-deposition case) arises from the attractive interaction of oxygen atoms across the gaps. Result [b] is a consequence of the self shadowing effect, which is already manifested in the conclusion [2] above. Result [c] is due to the fact that as  $T_s$  is higher, there is a structure transition from zone I to zone T, and oxygen atoms are less likely to be incorporated into the film.

<sup>1</sup> G. Guisbiers, O. Van Overschelde, M. Wautelet, Acta Materialia **55**, 3541(2007).

11:20am **TF+SE-WeM11 Role of Columnar Nanostructures on Static and Dynamic Wetting Properties of Silver Film**, D. Singh, J. Singh, IIT Delhi, India

The study of wetting has always been a very active field of research. In recent years, the interest in this field is stimulated by nanoengineering the surface to meet the requirements of various biological, chemical and industrial applications by modifying their wetting properties. In the present study, we have investigated the effect of silver nanocolumns on the static as well as dynamic wettability of surface. The nanocolumns of about 400 nm length and 150 nm diameter ( $\alpha = 85^\circ$ ) were grown by oblique angle deposition method over the Si(100) substrate. The effect of these nanocolumns on static wetting behavior was studied by performing sessile drop contact angle measurements using de-ionized water. A significant enhancement in the hydrophobicity of silver surface with contact angle value of  $108^\circ$  was observed (see supplement file, Fig. 1). To ensure that the observed changes in wetting behavior are due to the influence of nanocolumns, the measurements were carried out for different surface features ranging from plane to nanocolumnar film (grown for  $\alpha = 0^\circ, 65^\circ, 75^\circ$  and  $85^\circ$ , see SEM images in supplement file, Fig.2). Contact angle was observed to increase gradually from  $94^\circ$  to  $96^\circ$  with increase in oblique angle ( $\alpha$ ) from  $0^\circ$  to  $75^\circ$ . A drastic increase in contact angle was observed for nanocolumnar surface grown at  $\alpha = 85^\circ$ . For these silver samples the rms (root mean square) surface roughness was found to follow almost the same pattern as that of contact angle with  $\alpha$ , suggesting the dependence of wettability on surface roughness. The observed results were explained following the Cassie-Baxter model considering the silver nanocolumns to form a silver-air composite surface. To investigate the effect of nanocolumns on dynamic wetting property, the contact angle measurements for higher sample surface temperature ( $T_s = 80^\circ\text{C}$ ) were performed and the rate of change of contact angle of water drop for an interval of 10 sec was

measured. This transition rate of contact angle values was found to increase drastically for the nanocolumnar surface (see the supplement file, Fig.3). It shows that the nanocolumnar growth affects not only the static contact angle by making the surface hydrophobic but also greatly influences the surface temperature dependent dynamic wetting behavior of water drop. This study provides a basic understanding of the wetting behavior of nanocolumnar surface as well as shows the possibility to tune the surface wettability for meeting the requirements of various industrial applications.

# Wednesday Afternoon, October 20, 2010

## Advanced Surface Engineering

Room: San Miguel - Session SE+TF-WeA

### Glancing Angle Deposition (GLAD) II

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

2:40pm SE+TF-WeA3 Nanorods by Extreme Shadowing: New Pictures and New Physics, *D. Gall*, Rensselaer Polytechnic Institute

INVITED

Glancing angle deposition (GLAD) uses an oblique deposition angle to exacerbate atomic shadowing during physical vapor deposition to create underdense layers consisting of nanorods with engineered shapes and three-dimensional composition variations. This growth process is intrinsically chaotic. However, initial substrate patterning combined with temporal changes in the deposition fluxes yield surprisingly regular nanostructure arrays. The questions about the theoretical minimum feature size as well as rod branching, merging, and broadening is discussed by presenting statistical morphology data from various metals deposited over a large temperature range. The rod width follows a power law scaling where the growth exponent depends linearly on the island nucleation length scale, but exhibits a discontinuity at 20% of the melting point, associated with a transition from a 2D to a 3D island growth mode. Different metals show excellent quantitative agreement when scaled to the melting point, yielding a single homologous activation energy of 2.46 for surface diffusion on curved nanorod growth fronts, applicable to all metallic systems at all temperatures. The onset of bulk diffusion near 50% of the melting point during such growth under exacerbated shadowing conditions leads to a direct transition from an underdense (zone I) structure to a dense (zone III) structure. Applications include nanostructured fuel cell electrodes, active components of nano pressure sensors, and lubricant transport channels for high-temperature self-lubrication.

4:00pm SE+TF-WeA7 Quasi-periodic Pattern Formation on Columnar Thin Films by Ion Beam Erosion at Oblique Incidence, *M. Suzuki, H. Moriwaka, K. Nakajima, K. Kimura*, Kyoto University, Japan

4:20pm SE+TF-WeA8 Shadowing Effect of Patterned Seeds in Glancing Angle Deposition, *D. Soma, D.-X. Ye*, Virginia Commonwealth University

Glancing angle deposition (GLAD) technique has been developed by several groups including us in the past few years to produce three-dimensional nanostructures of a large variety of material. This technique combines oblique angle deposition with substrate manipulations in a physical vapor deposition system. The shadowing effect is the dominant growth mechanism resulting in the formation of various nanostructure arrays by programming the substrate rotation in polar and/or azimuthal direction. On patterned seeds, the shadowing effect strongly depends on the geometric parameters of the seed arrays, i.e. the aspect ratio of individual seeds, and the separation and arrangement of the seeds. In this talk, we will study those geometric parameters using a (2+1)-dimensional Monte Carlo simulation. In our simulation, we couple the shadowing effect and ballistic aggregation with rotating oblique incident particles. The uniformity of the nanostructures grown on the seeds will be investigated. The results of this study will provide a guideline for the design of seeds to achieve uniform size nanostructures by using GLAD.

4:40pm SE+TF-WeA9 Control of Phase Formation in Metal Oxide GLAD Films, *R.T. Tucker*, University of Alberta, Canada, *A.E. Schoeller, M.D. Fleischer*, NRC - National Institute for Nanotechnology, Canada, *M.J. Brett*, University of Alberta, Canada

Glancing angle deposition (GLAD) has found application in a wide range of fields requiring porous, high surface area thin films, including sensors, optics, and energy devices. [1] This diversity is due in large part to the wide range of compatible materials, including metals, semiconductors, and organic compounds. Metal oxides are of particular interest for energy storage and conversion applications since they can be tuned for a combination of transparency, electrical conductivity, and chemical and thermal stability. Achieving the desired stoichiometric phase is essential for controlling desirable metal oxide properties. Here we discuss the challenges associated with achieving phase control in porous GLAD films.

Metal oxide GLAD films typically deposit in an amorphous state, so post-deposition processing is one route used to access a particular crystallinity and stoichiometry. Thermal annealing conditions depend on the desired phase: anatase TiO<sub>2</sub> readily forms at a few hundred degrees Celsius in air; Ti<sub>4</sub>O<sub>7</sub> generally requires longer anneals at high temperatures (1000 °C) in a

reducing atmosphere (eg. H<sub>2</sub> in carrier gas). [2] Annealing temperature, duration, and environment (e.g. oxidizing vs. reducing atmosphere) can all have an impact on film morphology, since coalescence or softening of structures is greatly enhanced at temperatures near the melting point of the metal oxide. Both the porosity of the film and the strength of the reducing atmosphere affect the extent of oxygen removal and morphology changes at relatively high temperatures, while still allowing access to a wide range of compositions (e.g. Ti<sub>n</sub>O<sub>2n-1</sub>, n = 2 - 9), phases (e.g. monoclinic, tetragonal, or orthagonal Nb<sub>2</sub>O<sub>5</sub>) and the associated optical, electronic, and thermal properties.

We will present methods to retain the porosity and structure of GLAD thin films while achieving desired stoichiometry and phase via post-deposition annealing, with a specific focus on phase and crystallinity characterization using x-ray diffraction. We will attempt to correlate results from the Ti-O and Nb-O systems with results from other systems of interest (e.g. W-WO<sub>3</sub>) [3] as part of a better understanding of phase formation in porous thin films.

[1] M.M. Hawkeye and M.J. Brett, *J. Vac. Sci. & Tech. A*, **25**, 1317 (2007).

[2] J.R. Smith *et al.*, *J. Appl. Electrochem.*, **28**, 1021 (1998).

[3] D. Deniz *et al.*, *Thin Solid Films*, **518**, 4095 (2010).

We thank NSERC, iCORE, Micralyne, and the National Research Council - Technology Development Program for financial support.

5:00pm SE+TF-WeA10 A Fan-Shadowing Model in Oblique Angle Deposition, *B. Tanto*, Rensselaer Polytechnic Institute, *G.A. Ten Eyck*, Sandia National Laboratories, *T.-M. Lu*, Rensselaer Polytechnic Institute

Recently oblique angle deposition has been used in a wide range of important, unique applications. The column angle of the obliquely deposited columnar structures is an important parameter that determines their mechanical, optical, and chemical properties. Unfortunately this angle can be greatly affected by materials and processing conditions which are too complex to model and predict. Existing models such as the tangent rule and cosine rule are independent of materials and processing conditions and therefore in general have a limited ability to predict the column angle. We present a semi empirical model that includes the effects of materials and processing conditions. We show that our model is able to accurately predict column angle analytically for a wide range of obliquely deposited amorphous Ge for two different sets of processing conditions. We also show how this model can be used to predict other useful quantities, such as porosity and column width.

The model uses the fact that the deposition on a line (or wire) results in a fan structure due to a self-shadowing effect with a fan angle that depends on materials and processing conditions. We first show how columnar structures can be generated by analytically applying global shadowing between the fan structures growing on adjacent lines. The columnar structures obtained possess geometrical properties (such as column width and column merging) that are consistent with columnar structures observed in experiment and simulation. We show how the exact shape and time evolution of the columnar structure can be calculated based on the knowledge of the fan shape. Once the exact shape of the columnar structure is known, various useful quantities can also be obtained: column angle, porosity, and column width. We experimentally verified our model by depositing amorphous Ge on line seeded substrate and on a flat substrate. The model agrees with experiments done on both substrates.

Finally, we describe relatively simple experimental setups that can be used for fast and convenient measurement of the fan geometry at various processing conditions, such as flux rates and temperatures. These fan geometry data obtained on normal incident flux can then be used to predict the columnar structure geometries for the whole range of incident flux angles and for all the various processing conditions.

5:20pm SE+TF-WeA11 Investigation of the Nanorod-Structuring Threshold in Glancing Angle Deposition (GLAD), *D. Deniz, R.J. Lad*, University of Maine

Thin films of tin (Sn), aluminum (Al), gold (Au), ruthenium (Ru), tungsten (W), ruthenium dioxide (RuO<sub>2</sub>), tin dioxide (SnO<sub>2</sub>) and tungsten trioxide (WO<sub>3</sub>) were grown by glancing angle deposition (GLAD) to determine whether a nanostructuring threshold condition can be quantified as a function of both substrate temperature and melting point of the material. Films were grown using both DC and pulsed DC magnetron sputtering with continuous substrate rotation over the temperature range from 18 - 800°C. Film morphologies, structures, and compositions were characterized by high resolution scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Films were also grown in non-GLAD configurations for comparison. For the elemental metals, it is found that nanorod-structuring occurs for materials with

melting points higher than that of Al (660°C) when films are grown at room temperature with a relatively small rotation rate of ~5 rpm. For the oxide materials, our results indicate that a critical substrate temperature (TS) to melting point (TM) ratio exists, above which GLAD nanorod-structuring becomes ineffective because the adatom mobilities become large enough for non-kinetically limited film nucleation and growth processes to occur, similar to those operative in a non-GLAD growth configuration.

# Authors Index

**Bold page numbers indicate the presenter**

## — A —

Abraham, B.: SE+PS-MoA8, 3  
Aijaz, A.: SE+PS-MoA6, 3  
Al-Bataineh, S.: SE+PS-MoM8, 2  
Anglin, E.: SE+PS-MoM8, 2  
Antony Premkumar, P.: SE+PS-MoM4, 1

## — B —

Barankova, H.: SE+PS-MoM3, 1  
Bardos, L.: SE+PS-MoM3, 1  
Basse, F.H.-U.: SE-TuA10, 6; SE-TuA11, 6  
Batan, A.: SE+PS-MoM2, 1  
Bauer, J.: TF+SE-WeM3, 10  
Boris, D.R.: SE+PS-MoM9, 2  
Bradely, C.M.: SE-TuM6, 4  
Brett, M.J.: SE+TF-WeA9, 12; TF+SE-WeM6, 10  
Broitman, E.: SE-TuP6, 9  
Byrne, M.S.: SE-TuM3, 4

## — C —

Cahill, D.G.: SE-TuA9, 6  
Cansizoglu, M.F.: TF+SE-WeM5, 10  
Castañeda, J.N.: SE-TuA3, 6  
Chang, S.Y.: SE-TuP7, 9  
Check, M.: SE-TuA7, 6  
Chen, L.: SE-TuM5, 4  
Chiang, P.H.: TF+SE-WeM10, 11  
Chistyakov, R.: SE+PS-MoA8, 3  
Choudhuri, A.R.: SE-TuM6, 4  
Chung, Y.W.: SE-TuM11, 5  
Creatore, M.: SE+PS-MoM4, 1

## — D —

Dabeux, F.: SE+PS-MoM2, 1  
de Vries, H.: SE+PS-MoM4, 1  
Debrabandere, D.: SE+PS-MoM1, 1  
Demirel, M.C.: TF+SE-WeM1, 10  
Deniz, D.: SE+TF-WeA11, 12  
Du, Y.: SE-TuM5, 4  
Dudis, D.S.: SE-TuA7, 6

## — E —

Ehiasarian, A.P.: SE+PS-MoA1, 3  
Eichler, M.: SE+PS-MoM5, 1

## — F —

Ferapontova, E.: SE-TuP2, 8  
Ferguson, J.: SE-TuA7, 6  
Fleischauer, M.D.: SE+TF-WeA9, 12  
Franz, R.: SE-TuM12, 5; SE-TuP6, 9  
Fuhrmann, B.: TF+SE-WeM3, 10

## — G —

Gall, D.: SE+TF-WeA3, 12  
Gallis, M.A.: SE-TuA3, 6  
Gengler, J.J.: SE+PS-MoA3, 3; SE-TuA10, 6; SE-TuA11, 6; SE-TuP5, 9  
Gerlach, J.W.: TF+SE-WeM3, 10  
Ghadami, F.: SE-TuP1, 8  
Ghadami, S.: SE-TuP1, 8  
Glukhoy, Y.: SE+PS-MoM10, 2  
Griesser, H.J.: SE+PS-MoM8, 2  
Gruner, Ph.: SE+PS-MoM8, 2

## — H —

Helmersson, U.: SE+PS-MoA6, 3  
Hirvonen, J.K.: SE+PS-MoM9, 2  
Höche, T.: TF+SE-WeM3, 10  
Hofmann, T.: TF+SE-WeM9, 10  
Holec, D.: SE-TuM5, 4

Hsieh, J.H.: SE-TuP7, 9

Hubert, J.: SE+PS-MoM2, 1  
Hultman, L.: SE-TuM4, 4  
Hung, S.Y.: SE-TuP7, 9  
Hutter, H.: SE-TuM12, 5

## — I —

Issaksson, U.: SE+PS-MoA6, 3

## — J —

Jen, S.U.: TF+SE-WeM10, 11  
Jensen, U.B.: SE-TuP2, 8  
Jiang, K.: SE-TuM9, 4  
Johnson, L.J.S.: SE-TuM4, 4  
Jones, J.G.: SE+PS-MoA3, 3; SE-TuA12, 7; SE-TuP4, 8; SE-TuP5, 9

## — K —

Karabacak, T.: TF+SE-WeM4, 10; TF+SE-WeM5, 10  
Khare, C.: TF+SE-WeM3, 10  
Khudhayer, W.J.: TF+SE-WeM4, 10  
Kimura, K.: SE+TF-WeA7, 12; SE-TuP3, 8  
King, W.P.: SE-TuA1, 6; SE-TuP4, 8  
Kjerstad, A.C.: TF+SE-WeM9, 10  
Klages, C.-P.: SE+PS-MoM5, 1  
Konstantinidis, S.: SE-TuM9, 4  
Krishna, L.R.: SE-TuM11, 5

## — L —

Lad, R.J.: SE+TF-WeA11, 12; SE-TuM3, 4  
LaForge, J.M.: TF+SE-WeM6, 10  
Lange, M.A.: SE+PS-MoA3, 3  
Li, C.H.: SE-TuA4, 6  
Lu, T.-M.: SE+TF-WeA10, 12  
Luef, D.: SE-TuM5, 4

## — M —

Mayrhofer, P.H.: SE-TuM5, 4  
Merche, D.: SE+PS-MoM2, 1  
Michalak, W.: SE-TuP6, 9  
Michel, B.: SE+PS-MoM5, 1  
Mitterer, C.: SE-TuM12, 5; SE-TuP6, 9  
Montgomery, E.: TF+SE-WeM9, 10  
Moriwaka, H.: SE+TF-WeA7, 12  
Muratore, C.: SE+PS-MoA3, 3; SE-TuP5, 9  
Music, D.: SE-TuA10, 6; SE-TuA11, 6; SE-TuM9, 4

## — N —

Nahif, F.: SE-TuM9, 4  
Nakajima, K.: SE+TF-WeA7, 12; SE-TuP3, 8  
Namura, K.: SE-TuP3, 8  
Nisol, B.: SE+PS-MoM2, 1  
Noor-A-Alam, M.: SE-TuM6, 4

## — O —

Odén, M.: SE-TuM4, 4  
Oh, D.-W.: SE-TuA9, 6

## — P —

Pappas, D.D.: SE+PS-MoM9, 2  
Parlinska-Wojtan, M.: SE-TuM10, 4  
Patscheider, J.: SE-TuM10, 4  
Pecher, P.: SE-TuM10, 4  
Pélisson, A.: SE-TuM10, 4  
Peterson, G.P.B.: SE-TuA4, 6  
Polcic, P.: SE-TuM10, 4  
Priest, C.: SE+PS-MoM8, 2  
Putnam, S.A.: SE-TuA12, 7

## — R —

Rachbauer, R.: SE-TuM5, 4  
Rader, D.J.: SE-TuA3, 6  
Ramana, C.V.: SE-TuM6, 4  
Ramm, J.: SE-TuM1, 4  
Ranade, A.N.: SE-TuM11, 5  
Rauschenbach, B.: TF+SE-WeM3, 10  
Rebello de Figueiredo, M.: SE-TuP6, 9  
Reed, A.N.: SE+PS-MoA3, 3  
Remmert, J.L.: SE-TuP4, 8  
Reniers, F.: SE+PS-MoM1, 1; SE+PS-MoM2, 1  
Rodriguez-Santiago, V.: SE+PS-MoM9, 2  
Roy, C.K.: SE-TuM6, 4  
Rudigier, H.: SE-TuM1, 4

## — S —

Samuelsson, M.: SE+PS-MoA6, 3  
Sarakinos, K.: SE+PS-MoA6, 3; SE-TuM9, 4  
Schuesser, H.: SE+PS-MoM10, 2  
Schmidt, D.: TF+SE-WeM9, 10  
Schneider, J.M.: SE-TuA10, 6; SE-TuA11, 6; SE-TuM9, 4  
Schnoeller, J.: SE-TuM12, 5  
Schöche, S.: TF+SE-WeM9, 10  
Schoeller, A.E.: SE+TF-WeA9, 12  
Schubert, E.B.: TF+SE-WeM9, 10  
Schubert, M.: TF+SE-WeM9, 10  
Shaikh, A.U.: TF+SE-WeM4, 10  
Short, R.D.: SE+PS-MoM8, 2  
Singh, D.: TF+SE-WeM11, 11  
Singh, J.: TF+SE-WeM11, 11  
Soma, D.: SE+TF-WeA8, 12  
Starostin, S.A.: SE+PS-MoM4, 1  
Steele, D.: SE+PS-MoM8, 2  
Stein, B.E.: SE+PS-MoM9, 2  
Stiller, K.: SE-TuM4, 4  
Sutherland, D.S.: SE-TuP2, 8  
Suzuki, M.: SE+TF-WeA7, 12; SE-TuP3, 8  
Szili, E.: SE+PS-MoM8, 2

## — T —

Tabuchi, R.: SE-TuP3, 8  
Tanto, B.: SE+TF-WeA10, 12  
Taschuk, M.T.: TF+SE-WeM6, 10  
Ten Eyck, G.A.: SE+TF-WeA10, 12  
Thuvander, M.: SE-TuM4, 4  
Torczynski, J.R.: SE-TuA3, 6  
Trott, W.M.: SE-TuA3, 6  
Tseng, C.C.: SE-TuP7, 9  
Tucker, R.T.: SE+TF-WeA9, 12

## — V —

van de Sanden, M.C.M.: SE+PS-MoM4, 1  
Vanden Eynde, X.: SE+PS-MoM1, 1  
Vandencastele, N.: SE+PS-MoM2, 1  
Voelcker, N.: SE+PS-MoM8, 2  
Voevodin, A.A.: SE+PS-MoA3, 3; SE-TuA10, 6; SE-TuA11, 6; SE-TuP4, 8; SE-TuP5, 9

## — W —

Waite, A.R.: SE-TuP5, 9  
Walton, S.G.: SE+PS-MoM9, 2

## — Y —

Ye, D.-X.: SE+TF-WeA8, 12

## — Z —

Zanini Gadioli, G.: SE-TuP6, 9