Tuesday Afternoon, October 21, 2008

Advanced Surface Engineering
Room: 204 - Session SE-TuA

Photocatalytic Coatings
Moderator: P.H. Mayrhofer, Montanuniversität Leoben, Austria

2:40pm **SE-TuA4 Wettability Controlled Surface of Photocatalytic Coatings : Application for Dynamic hydrophoboicity**, ***T. Watanabe***, *N. Yoshida*, The University of Tokyo, Japan **INVITED**

Highly hydrophobic coating attracts much attention for long time as antifouling surface because it provides low energy surface whose interaction with contamination is smaller. Especially hydrophobic coating with photocatalytic oxidation capability is expected to become an ideal antifouling surface. According to Young, Dupre and Girifalco-Good equations, substances that can be highly hydrophobic are restricted to polymer material. Therefore it is usually hard to obtain highly hydrophobic thin film with TiO2 photocatalyst because polymer material is oxidized by photocatalysis. Moreover TiO2 photocatalyst itself is hydrophilicized by photo illumination. Due to such reasons, there are not many reports of hydrophobic coating with photocatalyst. However the situation can be dramatically changed when the concept of dynamic hydrophobicity is introduced. Parameter of dynamic hydrophobicity such like sliding speed or sliding angle does not depend on not only thermodynamic stable parameters but it strongly depends on surface microstructure. In fact, we have been investigating the dynamic hydrophobicity on self-assembled monolayer surfaces and found that the dynamic hydrophobicity is strongly affected by the surface roughness of only a few nanometers. Therefore if we focus on dynamic hydrophobicity, the inorganic substances can become potential candidates for having higher hydrophobicity by controlling surface roughness. Inorganic materials are hardly oxidized by TiO2 photocatalysis, and this is a great advantage. Of course even though a high flat surface is obtained, a water droplet cannot form on the surface and the liquid does not slide off as a droplet. Therefore, we have to choose an inorganic material with the lowest possible hydrophilicity. Although most of the inorganic materials exhibit a higher surface energy as compared to organic materials, it was reported that HfO2 is less hydrophilic. Therefore, we have prepared HfO2 combined with a TiO2 composite film and examined the water sliding angle of the surface. The result shows that the surface processed by the optimized preparation procedure shows a water contact angle of around 70° and a sliding angle of 30° are observed. This surface also shows high photocatalytic decomposability against IPA. Also very recently, we have obtained TiO2 with highly dynamic hydrophobic surface by physical deposition process. It shows sliding angle of 17 ° and at the same time show fairly well photocatalytic activity.

4:00pm **SE-TuA8 The Role of Carbon in Anatase as Visible Light Photocatalyst**, ***Y.J. Chen***, *G.Y. Jhan, M.S. Wong*, National Dong Hwa University, Taiwan

Titania is known as the favorable material as photocatalyst. However, the wide bandgap of titania limits its efficient utilization of solar light with most photon energies below the bandgap of titania. In this paper, we report that titania powders synthesized by low-pressure flat-flame metalorganic chemical vapor deposition shows high photocatalytic efficiency under visible light illumination. Using acetylene and oxygen as fuel and oxidizer for the flame, the titanium isopropoxide was decomposed and oxidized, and the nanoparticles of titania were formed. The phase of titania powder can be manipulated by carrier gas flow rate such that the higher the carrier gas flow, the higher the rutile content. From the methylene blue decomposition study we found that the powder with almost pure anatase phase synthesized under slightly oxygen deficient environment possesses best photocatalytic efficiency under illumination of visible light. The reaction rate constant is even higher than that of ST-01 titania powder, which is commercially available for photocatalytic applications. The visible light absorption is resort to the presence of carbon since no other chemical bonds not associated with carbon are chromophores. It also suggest that carbon species are associated with catalytic site on anatase surface so that carriers generated by photon absorption by the carbon species can transfer quickly onto catalytic sites and perform the subsequent catalytic reactions. Evidence will be provided to show that the carbon species does evolve with annealing, and the presence of carbon species is in coincident with the presence of visible light absorption.

4:20pm **SE-TuA9 Nb-doped TiO_2 Thin Films for Solar Energy Conversion**, ***P.A. DeSario***, *K.A. Gray, M.E. Graham*, Northwestern University

A deeper understanding of synthesis, structure and function is needed to improve the design of materials tailored to solar energy conversion and storage. This study highlights the efficacy of reactive sputtering as a means to fabricate cation-doped TiO_2 films having controlled properties tailored to the generation of energy rich fuels such as CH_4 or CH_3OH by photoreduction of CO_2. It is our hypothesis that cation substitution in the TiO_2 lattice is an effective way to shift the photoresponse of the material further into the visible light region without deleteriously modifying its photochemical properties. Unbalanced reactive dc magnetron sputtering (UBMS) with partial pressure control of oxygen was utilized to synthesize a series of pure and mixed phase TiO_2 films. Films were doped with Nb to evaluate the effect of cation doping on optical, chemical and physical properties. Nb doping was achieved by altering a pure Ti target in a pieced manner by adding slugs of dopant material at regular intervals. The films were interrogated structurally and functionally using SEM, EDS, XPS, XRD and UV-vis spectroscopy. The ability of these materials to selectively and efficiently reduce CO_2 to energy rich fuels was evaluated in a gas phase reactor coupled with a GC/FID. While earlier work established the relationships between sputtering process parameters and the film structure, including phase identity and distribution in pure TiO_2[1], this work is focused on how the addition of Nb cations in the range of 0-20%Nb change the film growth and phase formation relative to the pure material. The work also tries to characterize the cation valence and location in the TiO_2 lattice, but this is still under investigation. The parametric response of film structure still suggests that in the mixed phase system, greater energy input favors the formation of rutile and lower energy favors anatase, but the Nb additions shift the regions of phase stability compared to the pure TiO_2 case. The shift in optical absorption to the visible wavelength range as a function of Nb concentration and anatase-rutile phase distribution is also presented.

[1] L. Chen, et al., Fabricating Highly Active Mixed Phase TiO_2 Photocatalysts by Reactive DC Magnetron Sputter Deposition. Thin Solid Films, 2006. 515(3): p. 1176-1181.

4:40pm **SE-TuA10 Effect of Phase, Crystallinity and Carbon Content on Photocatalysis of Carbon-Doped Titania Films**, *P.W. Chou, Y.S. Wang,* ***M.S. Wong***, National Dong Hwa University, Taiwan

Amorphous pure and carbon-doped titania films were prepared by reactive sputtering of titanium metal target and co-sputtering of Ti and carbon targets, respectively, in Ar and oxygen plasma. The as-deposited films were subsequently annealed in vacuum and in air. The influence of annealing atmosphere and temperature on the composition, phase and crystallinity of the films was systematically studied to understand their effects on photocatalytic activity. Both the pure and the carbon-doped films annealed in air transformed into anatase phase at 300℃ and retained pure anatase phase even at 800℃; while those annealed in vacuum transformed into rutile/anatase mixed phase at 300℃ and into pure rutile at 600℃. Carbon incorporation and oxygen deficient environment seem to favor phase transformation of amorphous titania to rutile at low temperatures in post-annealing.

5:00pm **SE-TuA11 Rules for Efficient Titania Coatings. Applications to Water, Air and Material Cleaning**, ***J.-M. Herrmann***, CNRS-Université de Lyon, France **INVITED**

Photocatalysis concerns Fine, Green and Environmental Chemistry. Titania coatings must follow the rules of photocatalysis with the influence of 5 basic parameters governing the activity (mass of catalyst, wavelength, concentrations or partial pressure of reactants, temperature and radiant flux). Besides mild selective oxidations obtained by generating active neutral atomic O* species in the absence of water, photocatalysis can detoxify inorganics in water by oxidizing them in their harmless upper oxidized state. Similarly, organic pollutants are totally oxidized in CO2. Complex molecules (pesticides, dyes, herbicides, insecticides) are totally destroyed as well as bacteriae (E.Coli, streptococcus faecalis) in water without re-growth. Air pollutants (VOC's, odors) can also be destroyed by cracking OH° radicals produced by UV-irradiated titania-coated supports. The applications concern domestic anti-odor refrigerators, electronics with a "molecular" purity of the ambient working atmosphere, the destruction of odors emitted by water treatment plants and solid waste landfills. Eventually, Virus H5N2, a model virus close to H5N1, responsible for the aviar flu, was totally destroyed in a contaminated air flux of 40 m^3/h with a 99.93% efficiency in a single pass. Photocatalytic self-cleaning technology consists in depositing sub-micronic thin layers of titania at the surface of glass, metals, concrete, etc, whose photocatalytic activities are calibrated by test-reactions. In the real world, dirty materials, such as glasses, to be "selfcleaned" are soiled by greasy and sticky deposits, which, in addition, induce a strong adherence of ambient dusts. The mechanism of self-cleaning glasses was elucidated by the mineralization of palmitic acid (n-$C_{15}H_{31}$-COOH), present in the human sebum and in the natural varnish of plants. It disappeared by successive "photo-Kolbe" reactions with photo-produced holes h^+. The linear hydrophobic aliphatic chains are progressively "peeled off," carbon atom after carbon atom, via successive photo-Kolbe reactions. Palmitic acid degradation would require 16 of them. Fortunately, the overall self-cleaning glass process can be strongly accelerated by by-passing many intermediates via the release of several VOC's in the atmosphere, quite innocuous for the environment. The efficiency of titania demands two requirements: (i) a good cristallinity (anatase phase) and (ii) a high (cationic) purity.

Advanced Surface Engineering
Room: 204 - Session SE-WeM

Atmospheric Pressure Treatments and Hard and Nanocomposite Coatings
Moderator: H. Baránková, Uppsala University, Sweden, P.H. Mayrhofer, Montanuniversität Leoben, Austria

8:00am **SE-WeM1 Controlling Plasma Deposition with Liquid Aerosol Precursors**, ***L. O'Neill***, *J.D. Albaugh*, Dow Corning, Ireland **INVITED**

Recent studies have clearly demonstrated that numerous precursors can be used to produce thin film coatings by injecting liquid aerosol droplets into a non-thermal equilibrium atmospheric pressure plasma. The deposition appears to proceed via a controlled free radical polymerisation with controlled precursor fragmentation. It has recently been reported that several different siloxane products and intermediates can be used to prepare thin films by this method and the resultant coatings can be tailored to produce deposits which vary from hydrophobic siloxane to cross-linked silica thin films. Linear, cyclic, dimethyl and Si-H containing siloxanes have been deposited with equally high deposition rates. However, under certain conditions, coatings deposited from linear and dimethyl structures can appear "wet" and have a presumably low cross-link density compared to their cyclic or Si-H counterparts. Therefore, a more detailed study has been undertaken to investigate which factors control deposition rate and cross-link density in liquid aerosol – plasma polymerisation processes. A series of liquids have been nebulised and introduced into a purpose built RF atmospheric pressure plasma jet operating with helium as the main process gas. The resultant coatings have been thoroughly characterised to determine which chemical properties of the precursor directly impact upon the chemistry and morphology of the coatings.

8:40am **SE-WeM3 Deposition of Metallic Nanoparticles using Atmospheric Plasma**, *F. Demoisson,* Universite Libre de Bruxelles, Belgium, *J.J. Pireaux,* Facultés Universitaires Notre Dame de la Paix, Belgium, *H. Terryn,* Vrije Universiteit Brussel, Belgium, ***F. Reniers***, Universite Libre de Bruxelles, Belgium

The deposition of metal nanoparticles on various substrates is of high interest in surface science, as they can induce new chemical properties on surfaces. Applications can be found in catalysis, for gas sensor applications, in environmental science,.... however, the deposition of metal nanoparticles is facing many challenges such as : difficulty to have a strong binding on various surfaces (polymer, carbon, glass,...), technological difficulty of the deposition process, bad dispersion of the particles on the surface, bad particle size distribution,.... Usual processes require today high vacuum evaporation of the metal onto preactivated surfaces, or the use of hazardous organometallic compounds as precursors. In this work we present a new process[1] to deposit, in one step, easily, metal nanoparticles (Au, Rh, Pt) onto various surfaces (HOPG, glass, polymer, metal), using an atmospheric plasma torch (AtomFlo, SurX Technologies). The resulting surfaces are characterized by FEG-SEM and XPS. The results show an excellent particle size distribution, and a very good homogeneity of the particle distribution on the surfaces. Surface coverages in the range of 10-15% were obtained. The adhesion of the particles on the surface was tested using ultrasonication and proved to be very good.

[1] F. Demoisson, JJ Pireaux, F. Reniers, "process to deposit nanoparticles on a substrate" patent pending 08151463.0-1215.

9:00am **SE-WeM4 Design and Applications of the Atmospheric Pressure Hollow Cathodes**, *H. Baránková,* ***L. Bárdos***, Uppsala University, Sweden

The hollow cathode cold atmospheric plasma sources, similarly as hollow cathode plasma sources at the moderate and low pressures, exhibit the Hollow Cathode Effect (HCE). The atmospheric pressure, however, requires reduction of dimensions, so that a typical structure inside the hollow cathode, i.e. the space charge sheath - common negative glow - space charge sheath, is preserved. The experimental results on the hollow cathode generation, using a special construction with a tunable wall separation, are presented. The influence of the gas and the type of generation on the optimum size is investigated. The experimental results are supported by the hollow cathode model. The applications of the hollow cathodes operating at the atmospheric pressure are given.

9:20am **SE-WeM5 Advanced Atmospheric Pressure Microplasma Sources for Surface Treatment**, ***K.-D. Weltmann***, *R. Brandenburg, R. Foest, E. Kindel, M. Stieber, T.V. Woedtke*, Leibniz-Institute for Plasma Science and Technology e.V. (INP Greifswald), Germany **INVITED**

Compact miniaturized atmospheric plasmas exhibit very promising technological potential for surface treatment. Basically, there are two features which make them unique: (I) the tool-like, small size and light weight plasma generation unit allows fast and almost arbitrary 3D movements and (II) the contracted and comparably cold plasmas allow focused small-spot treatments, even of heat sensitive small size objects with temperature loads to the surface between 35°°C and 90°C. Especially in the area of biomedical applications these opportunities triggered significantly increasing research and development of plasma application directly to living objects. But also industrial surface treatment processes such as activation, functionalization, passivation, coating and etching gain importance. Here, an overview of different tailor-made miniaturized atmospheric pressure plasma sources is presented which can be used for specific purposes of surface coating, functionalization and decontamination. Actually, plasma assisted processes for biological decontamination up to the level of sterilization are becoming an alternative to conventional methods especially for heat sensitive materials. However, the realization of industrial plasma-based decontamination or sterilization technology still remains a great challenge. This is due to the fact that antimicrobial treatment processes needs to consider all properties of the product to be treated as well as the requirements of the complete procedure, e.g. a reprocessing of medical instruments. Here the applicability of plasma-based processes for the antimicrobial treatment on selected, heat sensitive products with special geometries is demonstrated. Modular and selective plasma sources, developed at INP are used which match the specific requirements of a variety of complex 3-dimensional structures. Measurements of relevant plasma properties (optical emission in the VIS, UV, and VUV region, along with substrate temperatures) are reported. Following this, a discourse is given about possible treatment processes and the state of the art in the new field of plasma medicine, i.e. about expected benefits of localized plasma treatment of living tissue for healing purposes. In the last part of the presentation the use of different RF-driven plasma atmospheric pressure microplasma-jets for deposition of dense SiO$_x$ films with potential for barrier layers will be described. Measurements of relevant film properties (chemical composition and morphology) are reported and the state of the art of an advanced source tuning regime named "locked mode" is described. This mode leads to improvements of film quality and lateral homogeneity in the deposition spot.

10:40am **SE-WeM9 Stress and Strain in Polycrystalline Thin Films**, ***G.C.A.M. Janssen***, TU Delft, The Netherlands **INVITED**

Polycrystalline thin films on substrates usually are in a "stressed" state. In the presentation the two main methods for stress measurements, wafer curvature and X-ray lattice parameter measurements will be presented. Special attention will be given to the information that can be obtained by applying both techniques. This discussion will be followed by a discussion of recent results on stress in hard polycrystalline films. For Cr and CrN films, it has been shown that the stress is not uniform over the thickness of the film. High tensile stresses are observed near the substrate-film interface. Lower tensile stresses are observed further away from the interface. Moreover, it has been shown that the tensile stress is generated at the grain boundaries. In the case for which the deposition of the film is accompanied by an ion bombardment, a compressive stress is generated. The tensile- and compressive stresses in these films are independent and additive. For TiN films the situation is even more complicated. For TiN higher compressive stresses are observed close to the substrate-film interface. This effect is explained form the observation that for TiN, the evolution of the grain boundary density is accompanied by an evolution of the texture. Various texture components exhibit a different sensitivity to compressive stress generation by ion-peening.

11:20am **SE-WeM11 The Location and Effects of Si in Arc-Evaporated (Ti$_{1-x}$Si$_x$)N$_y$ Thin Solid Films**, *A. Flink, M. Beckers, B. Alling, J. Bareno,* Linköping University, Sweden, *J. Sjölen,* Seco Tools AB, Sweden, *I. Abrikosov,* ***L. Hultman***, Linköping University, Sweden

Arc-Evaporated (Ti$_{1-x}$Si$_x$)N$_y$ thin solid films have been studied by analytical electron microscopy, X-ray diffraction, scanning tunneling microscopy, X-ray photoelectron spectroscopy, elastic recoil detection analysis, and nanoindentation. As-deposited films form cubic solid solutions with Si substituting for Ti up to x = 0.09. Si segregation in films with higher Si content, up to x = 0.20, results in a feather-like microstructure consisting of cubic TiN:Si nanocrystallite bundles with low-angle grain boundaries and a very high dislocation density of 10^{14} cm^{-2} (corresponding to a cold-worked alloy). Correspondingly, N content in the films increases almost linearly with Si content from $y = 1.00$ for $x = 0$ to $y = 1.13$ for $x = 0.20$. Upon annealing at 1000 °C, films with Si contents between $x = 0.04$ and 0.20 develop a metastable crystalline SiN_z ($1.0 \leq z \leq 1.33$) tissue phase, which is semicoherent to TiN. These films exhibit retained hardness between 31-42 GPa and are compositionally stable. Thus, superhard TiN-SiN_z nanocomposites without amorphous silicon nitride phase can be produced by arc-evaporation and subsequent annealing. At 1100-1200 °C, the films soften due to amorphization of the SiN_z tissue phase, followed by recrystallization of the TiN grains, and Si and N diffusion out of the film. Ab-initio calculations performed in parallel to these experiments reveal that c-Si_3N_4 can be stabilized with $D0_{22}$ or $L1_2$ ordered Si vacancies in a ZnS-like structure, in agreement with previous experimental results published by us,[1-3] while phonon calculations show that stoichiometric c-SiN is dynamically unstable in the NaCl and ZnS structures.[4,5]

[1] Hans Söderberg, Jon Molina-Aldareguia, Lars Hultman, and Magnus Odén, J. Appl. Phys. 97 (2005) 114327.

[2] Lars Hultman, Javier Bareño, Axel Flink, Hans Söderberg, Karin Larsson, Vania Petrova, Magnus Odén, J. E. Greene, and Ivan Petrov, Phys. Rev. B75 (2007) 155437.

[3] Hans Söderberg, Axel Flink, Jens Birch, Per O.Å. Persson, Manfred Beckers, Lars Hultman, and Magnus Odén, J. Materials Research 22 (2007) 3255.

[4] Axel Flink, PhD Thesis "Growth and Characterization of Ti-Si-N Thin Film" Linköping Studies in Science and Technology, Dissertation No. 1190, Linköping, Sweden (2008). www.ep.liu.se.

[5] B. Alling, E. I. Isaev, A. Flink, L. Hultman, I. A. Abrikosov, submitted.

11:40am **SE-WeM12 Phase Stabilization in CrN by Addition of Si and O**, *L. Castaldi*, EMPA, Switzerland, *D. Kurapov, A. Reiter*, OC Oerlikon Balzers AG, Switzerland, *V. Shklover*, ETH Zurich, Switzerland, ***J. Patscheider***, EMPA, Switzerland

The influences of adding silicon and oxygen during deposition of CrN by reactive cathodic arc evaporation on composition, structure, hardness and thermal stability were investigated. Both Cr-N-X phase ternary systems, where X denotes O or Si, exhibit a strong influence of X on hardness and thermal stability. Addition of these two elements leads to a decrease of the grain size of the cubic Cr-N-X phase, at the composition of optimum performance, down to a third or fourth of that of undoped CrN. XRD investigations suggest at least a partial substitution of N by O accompanied by the formation of an amorphous phase at higher O content, thereby forming a nanocomposite structure. The hardness of Cr-N-O coatings increases with increasing the oxygen content up to a value of 28 GPa, while fully oxidized Cr_2O_3 films showed lower hardness values around 12 GPa. The addition of Si resulted in a maximum hardness of Cr-N-Si of about 25 GPa. Cr-N-X coatings showed both an onset of oxidation which was promoted by about 200°C as compared to that of CrN. The underlying mechanisms, as evidenced by the performed measurements, will be discussed.

Energy Science and Technology Focus Topic
Room: 203 - Session EN+AS+TF+VT+NC-WeA

Energy: Tools and Approaches
Moderator: T.A. Dobbins, Louisiana Tech University and Grambling State University

1:40pm **EN+AS+TF+VT+NC-WeA1 Continuous, In-Line Processing of CdS/CdTe Devices**, ***W.S. Sampath***, Colorado State University, *R.A. Enzenroth, K.L. Barth,* AVA Solar Inc., *V. Manivannan,* Colorado State University, *K. Barricklow, P. Noronha*, AVA Solar Inc. **INVITED**

A continuous, in-line process suitable for high throughput manufacturing of CdS/CdTe photovoltaic devices has been demonstrated. Utilizing this process, devices with efficiencies of 13% has been fabricated with a low iron soda lime glass (3”x3”) with ant-reflection coatings. The process has been extended to large area devices (16” x16” substrate size). After $CdCl_2$ treatment, devices showed V_{oc} > 700 mV and J_{sc} > 20 mA/cm^2. This performance is similar to the performance of small area devices which showed good stability. Also we have employed many methods including Spectroscopic Ellipsometry (SE) as a non-destructive tool to characterize CdS/CdTe heterojunction specifically studying the effects of processing on the optical properties of the thin-film layers.

2:20pm **EN+AS+TF+VT+NC-WeA3 Molecular Dynamics and Experimental Investigations of Reversible Absorption of H_2, CH_4, and CO_2 in Calixarenes**, ***J.L. Daschbach***, *P.K. Thallapally, B.P. McGrail, L.X. Dang*, Pacific Northwest National Laboratory

Molecular solids based on calix[4]arenes have been shown to exhibit reversible absorption of small gas molecules, and remain stable, at temperatures above 400 K. As such, they are interesting as prototypical molecular systems for storing guests like hydrogen and methane, and potentially selectively trapping carbon dioxide in hydrocarbon based systems. We have conducted high-pressure and temperature gas absorption experiments with low density p-tert-butylcalix[4]arene (TBC4) in which calixarenes are slightly offset to form a skewed capsule with an estimated free volume of 235 Å^3. Hydrogen and methane absorption near 300 K were 1.0 and 2.2 wt% respectively. Carbon dioxide is absorbed at a 1:1 loading per TBC4 molecule at 3 atm. In recent work we have shown that the high density form of TBC4 will absorb CO_2 at 3 atm, undergoing a phase transformation in the process, and it can be reversibly cycled between these states using moderate combinations of temperature and pressure. Somewhat surprisingly, we have found that TBC4 can be loaded with up to two CO_2 per TBC4 molecule. We have used empirical molecular simulation techniques to study the dynamics of CO_2 and CH_4 in TBC4. The rattling motion of the absorbed small molecules have been characterized using velocity autocorrelation. The coupling to the host lattice is probed by temperature dependent calculations. The effects of increased loading are studied up to the 2:1 loading of CO_2, and clearly show differences in the host-guest coupling for molecules outside the cavities relative to the cage entrapped molecules. The free energy of absorption of CH_4 and CO_2 is studied under range of conditions by thermodynamic integration. These data support the experimental observations that these molecules can be reversibly absorbed at moderate pressures and temperatures.

2:40pm **EN+AS+TF+VT+NC-WeA4 Sustainable Energy and the Role of Advanced Electron Microscopy**, ***D.J. Stokes***, *B. Freitag, D.H.W. Hubert*, FEI Company, The Netherlands

Advanced electron microscopy, using the latest aberration-corrected and monochromated (scanning) transmission electron microscopes (S/TEM) is helping to bring new scientific and technological insights that are advancing progress in areas such as health, energy and the environment. Specifically, with global energy resources under increasing pressure, great efforts are being made to develop new nanomaterials that will lead to renewable energy sources and increased efficiency, to sustain energy supplies into the long term future whilst helping to preserve and protect the Earth’s environment. To get there, we are being taken to atomic realms such that, to tailor new nanomaterials for specific functions, it is essential to precisely understand, accurately control and truly visualize structure-property relations at an unprecedented level. The atomic structure of nanomaterials and the energy needed for their function can be optimized by the fundamental understanding of catalytic behavior of nanoparticles and by a better understanding of the physical properties on the atomic level of systems such as solar cells, fuel cells and light sources (LEDs). This requires advanced tools that allow us to see down to the individual atoms and sense their chemical environment. It means having the ability to perform experiments in situ, to follow specific chemical reactions and physical processes, and there is a need to be able to do this in multi-dimensions, both spatial and temporal. We discuss and demonstrate the role of advanced electron microscopy in answering some of the most challenging and fundamental scientific questions in the field of catalysis, ranging from electron tomographic 3D reconstruction of the crystal facets of catalyst nanoparticles and aberration-corrected imaging correlated with density functional theory for elucidating precise atomic positions, to in situ studies of catalytic reactions for visualization of otherwise unseen intermediate nanostructures. These examples relate the nanostructures investigated to the property manifested by that particular structure, enabling us to gain new information about catalytic function.

3:00pm **EN+AS+TF+VT+NC-WeA5 Investigation of Low Temperature-Annealed TiO_2 Electrodes Prepared by Sol-Gel Technique for the Fabrication of Dye-Sensitized Solar Cells**, *M.F. Hossain, S. Biswas, M. Shahjahan, A. Majumder,* ***T. Takahashi***, University of Toyama, Japan

Dye sensitized solar cells (DSCs) are considered as a low cost alternative to conventional p-n junction solar cell devices. The high light-to-energy conversion efficiencies achieved with dye sensitized solar cells (DSCs) may be attributed to the nanoporous TiO_2 electrode. Among the various techniques for the preparation of TiO_2 photo-electrode, the relatively simple sol gel method is the most widely used because of its ability to obtain films with tailored properties on large, curved substrates, and also it is a low temperature process. Crystallinity is one of the key factors behind the photovoltaic performances of TiO_2; therefore achievement of better crystallinity at relatively low temperature is an important issue. In our present study, the titanium dioxide porous films were deposited on SnO_2:F coated glass by sol–gel technique; where, an alcoholic solution of tetra-buthylorthotitane was hydrolysed in a water/alcohol/acetic acid mixture. These films were transparent and crack free. For this investigation; annealing temperature and number of coating layers were varied. All the films were annealed at different annealing temperatures, ranging from 350 to 500°C. Sufficiently good crystalline samples were obtained by annealing at 350°C. The X-ray diffraction patterns of all TiO_2 films confirmed the anatase structure. The surface morphology of the films has been observed by atomic force microscope and field emission scanning electron microscope. The morphology of TiO_2 thin films strongly depends on annealing temperatures and number of coatings. Incident photon-to-current conversion efficiency is calculated for all the solar cells with different TiO_2 thin films to evaluate the economic viability of this technique. It has been observed that the photoelectric conversion efficiency of DSCs increases with the optimization of annealing temperature as well as with the increase of the numbers of layers.

Advanced Surface Engineering
Room: 204 - Session SE+NC-WeA

Hard and Nanocomposite Coatings: Synthesis, Structure, and Properties II
Moderator: J. Patscheider, EMPA, Switzerland

1:40pm **SE+NC-WeA1 Structural Development and Mechanical Properties of TiN-Ni Nanocomposite Coatings**, ***J.P. Riviere***, University of Poitiers, France, *A. Akbari,* Sahand University of Technology, Iran, *C. Templier*, University of Poitiers, France **INVITED**

Superhard nanocomposite coatings represent an important class of new materials with enhanced mechanical properties. The synthesis of these coatings has been principally obtained by both techniques: plasma-assisted chemical vapour deposition or reactive magnetron sputtering. It appears that dual ion beam assisted deposition could be also an effective tool for tailoring the structure and properties of nanocomposite coatings because it permits independent control of the process variables such as particle nature, energy, flux. A particular important effect of the bombardment of a growing film with energetic ions is the enhanced adatom mobility which plays an important role in the renucleation of nanograins and on the formation of the percolation network of the intergranular phase We have investigated the formation of hard nanocomposite coatings with improved toughness consisting of TiN nanograins embedded in a soft metallic intergranular phase of Ni using reactive ion beam assisted deposition. A composite Ti-Ni target was sputtered with 1.2 keV Ar^+ ions and the growing films were simultaneously bombarded with a mixture of 50 eV Ar^++N2$^+$+N^+ ions. The chemical composition was deduced from RBS analysis and a N/Ti ratio of ~

0.85 independent of the Ni content was determined. Phases, grain size, and texture of the coatings were investigated by XRD and HRTEM. In the composition range 0-22,5 at% Ni, δ-TiN is the only crystalline phase and Ni appears as an X Ray amorphous phase. The hardness increases up to a maximum of 41 Gpa at 6 at.% Ni which corresponds to a TiN crystallite size of ~ 8 nm and a Ni intergranular phase thickness of roughly 1 monolayer. Stress analysis was performed by XRD using the crystallite group method (CGM) developed for textured materials and coatings. It is shown that the hardness enhancement in TiN-Ni nanocomposite coatings is not correlated with residual stresses, but rather with the intrinsic nanostructure. An important improvement in wear resistance is observed however the highest wear resistance is obtained for the coatings exhibiting the highest toughness and not the highest hardness. These results show the beneficial influence of the ductile metallic amorphous intergranular phase on the mechanical behaviour of nanocomposite coatings.

2:20pm **SE+NC-WeA3 Processing and Characterization of Polymer-Ceramic Nanolaminate Thin Films**, ***A.R. Waite***, Air Force Research Labs/UTC, Inc./University of Dayton, *J.O. Enlow*, Air Force Research Labs/UES, Inc., *C. Muratore*, Air Force Research Labs/UTC, Inc., *J.G. Jones*, Air Force Research Labs, *H. Jiang*, Air Force Research Labs/Materials Science & Technology Applications, LLC, *T.J. Bunning*, *A.A. Voevodin*, Air Force Research Labs

Polymer-ceramic nanolaminate thin films were synthesized by coupling chemical and physical vapor deposition processes. Highly cross-linked fluoropolymer layers were deposited by room temperature plasma enhanced physical vapor deposition from octafluorocyclobutane (OFCB) precursor gas. Gas flow rates, substrate position and rf power were examined to produce a dense polymer coating with a minimum refractive index of 1.38. Magnetron sputtering processes were investigated for deposition of amorphous TiO_2 with a high refractive index. Stoichiometric TiO_2 with a refractive index >2.3 was produced via reactive sputtering and sputtering of a titania target in pure Ar, however, reactive sputtering in an oxygen atmosphere resulted in decomposition of the polymer film. Multiple polymer-ceramic film architectures were investigated, including a quarter wave stack notch filter consisting of alternating TiO_2 and fluoropolymer layers (3 and 2 layers, respectively). Analysis of nanoindentation results was used to compare the fracture toughness and other mechanical properties of multilayered and monolithic films. The combination of optical and mechanical properties for different nanolaminate architectures revealed that the coupling of polymer-ceramic thin film materials has potential for the development of useful electro-optical devices with remarkable toughness and flexibility compared to the current state of the art.

2:40pm **SE+NC-WeA4 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 because of 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 deposited onto metal substrates, lower thermal expansion coefficients of ceramic coatings 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. Since the coating matrix is identical to that of the substrate, this should result 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_2 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.

3:00pm **SE+NC-WeA5 Influence of Nb on Structure, Properties, and Phase Stability of Ti-Al-N Hard Coatings**, ***P.H. Mayrhofer***, *R. Rachbauer*, Montanuniversität Leoben, Austria, *L. Hultman*, Linköping University, Sweden

Metastable $Ti_{1-x}Al_xN$ thin films synthesized by plasma-assisted vapour deposition crystallize in the industrially preferred cubic NaCl (c) structure with AlN mole fractions (x) ≤ 0.7. We reveal, via X-ray diffraction (XRD) and transmission electron microscopy (TEM), that the addition of niobium to c-$Ti_{1-x}Al_xN$ has only a minor influence on the structure and morphology of as deposited coatings. By a combination of differential scanning calorimetry, XRD, and TEM investigations we can conclude that the onset temperature for decomposition of the formed metastable phases increases with increasing Nb content. After annealing at 1450 °C the coating decomposed into c-$Ti_{1-y}Nb_yN$ and h-AlN phases. This decomposition process is initiated via spinodally formed cubic Ti-rich and Al-rich domains. As these domains influence plastic deformation during the nanoindentation experiments an increased hardness is observed after annealing at temperatures in the range 800—1000 °C. At higher temperatures c-AlN transforms to h-AlN. Due to the reduced mechanical properties of h-AlN compared to c-AlN this transformation is accompanied by a hardness reduction. The experimentally observed results are corroborated by a combination of ab intio and continuum-mechanical calculations.

4:00pm **SE+NC-WeA8 Development of MoN-Ag-Based Nanocomposite Films for Severe Tribological Applications**, ***A. Erdemir***, *O.L. Eryilmaz*, Argonne National Laboratory, *M. Urgen*, *V. Ezirmik*, *K. Kazmanli*, Istanbul Technical University, Turkey

Using the principles of a crystal-chemical model, we designed and produced novel nanocomposite coatings that are made of hard MoNx and soft Ag phases. Because of the very high ionic potentials of the complex sulfides and phosphates that they form during lubricated sliding tests in formulated engine oils, these nanocomposite coatings are able to drastically reduce friction and at the same time increase resistance to wear and scuffing under severe boundary lubricated sliding regimes. In this paper, we will concentrate on the fundamental tribological mechanisms that control the sliding friction and wear behaviors of these nanocomposite coatings. The major implications of this study is that using such a fundamental approach one can design and manufacture coatings that are very compatible with lubricants and hence suitable for a wide range of rolling, rotating and sliding bearing applications in engines and other lubricated mechanical systems.

4:20pm **SE+NC-WeA9 Process Variables Effect of PVD Nitride Hard Coatings Deposited on Chromium-Based Tool Steel Substrates**, ***A. Neira***, North Carolina State University, *F. Sequeda*, *A. Ruden*, Universidad del Valle, Colombia, *J.M. Gonzales*, Universidad Nacional, Colombia

Process variables parameters as substrate temperature, bias voltage and N2/Ar ratio were studied during the deposition of IV, V and VI group materials in the form of nitrides, (TiAlVN, ZrN and CrN). Those coatings were deposited on chromium-based steels, like AISI H-13 and AISI-4140 commonly used for high mechanical performance even after long exposure at high working temperatures and AISI D-3 designed for high resistance to wear or to abrasion and for resistance to heavy pressure. This work was done using available coating production techniques like Plasma Assisted Physical Vapor Deposition (PAPVD) and DC-Reactive Magnetron Sputtering and physical properties resulting from modifying the process parameters like crystal structure, film texture, and mechanical properties like strain micro deformation, hardness, wear resistance friction coefficient and adhesion of the coating to the substrate were addressed in this study and conducted through film characterization techniques such as X-Ray Diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscope (SEM), micro and nanoindentation, wear and adhesion test. An special attention was given to the deposition of TiAlVN due to the differences on bonding types between components Al and V considered as “film stabilizers” increasing the film hardness and promoting the Magneli phase formation type (VxO3X-1), offering a reduction in the friction coefficient for auto lubrication phenomena, increasing its use for tribological coating applications.

4:40pm **SE+NC-WeA10 Water Adsorption on Phosphorous-Carbide Thin Films**, ***E. Broitman***, Carnegie Mellon University, *A. Furlan*, *G.K. Gueorguiev*, Linköping University, Sweden, *Zs. Czigány*, Research Institute for Technical Physics and Materials Science, Hungary, *A.J. Gellman*, Carnegie Mellon University, *S. Stafström*, *L. Hultman*, Linköping University, Sweden

Amorphous phosphorous-carbide films have been considered as a new tribological coating material with unique electrical properties. However, the coatings cannot be practically used until now because CP_x films rapidly oxidize/hydrolyze and delaminate when in contact with air. Recently we demonstrated that CP_x thin solid films with a fullerene-like structure can be deposited by magnetron sputtering. Thus, the introduction of P atoms in the graphene structure induces the formation of bent and interlinked grapheme planes.[1,2] In this work we compare the uptake of water of amorphous phosphorous-carbide (a-CP_x) films, with fullerene-like phosphorous-carbide (FL-CP_x) and amorphous carbon (a-C) films. Films with thickness in the range 10-300 nm were deposited on quartz crystal substrates by reactive DC magnetron sputtering. The film microstructure was characterized by X-ray photoelectron spectroscopy, and transmission electron microscopy and diffraction. A quartz crystal microbalance placed in a vacuum chamber as described in[3] was used to measure their water adsorption. Measurements indicate that the amount of adsorbed water is highest for the pure a-C films and that the FL-CP_x films adsorbed less water than a-CP_x. To provide additional insight into the atomic structure of defects in the FL-CP_x, a-CP_x and a-C compounds, we performed first-principles calculations within the framework of Density Functional Theory. Emphasis was put on the energy cost for formation of vacancy defects and dangling bonds in relaxed systems.[4] Cohesive energy comparison reveals that the energy cost formation for dangling bonds in different configurations is considerable higher in FL-CP_x than for the amorphous films. These simulations thus confirm the experimental results that dangling bonds are less likely in FL-CP_x than in a-CP_x and a-C films.

[1] A. Furlan, G.K. Gueorguiev, Zs. Czigány, H. Högberg, S. Stafström, and L. Hultman, Phys. Stat. Solidi Rapid Research Letters (2008) in press

[2] G.K. Gueorguiev, A. Furlan, H. Högberg, S. Stafström, and, L Hultman, Chem. Phys. Lett. 426 (2006) 374

[3] E. Broitman, VV. Pushkarev, A.J. Gellman, J. Neidhardt, A. Furlan, and L. Hultman, Thin Solid Films 515 (2006) 979

[4] E. Broitman, G. K. Gueorguiev, A. Furlan, N. T. Son, A.J. Gellman, S. Stafstrom, and L. Hultman, ICMCTF, San Diego, CA (May 2008).

5:00pm **SE+NC-WeA11 Structure-Property Relationships of Galvanic Nickel-NanoDiamond Composite Coatings**, *D.L. Schulz, **R.A. Sailer***, North Dakota State University, *G.E. McGuire, O. Shenderova*, International Technology Center

Galvanic nickel coatings have been in use for decades and have many desirable properties including corrosion resistance and relative ease of application. Recently, work has been performed to enhance the tribological properties of nickel-based coatings by incorporation of diamond nanoparticles as a wear-resistant component of this functional coating.[1] In this previous study, detonation nanodiamonds (DNDs) produced from a mixture of carbon-containing explosives were used. The DNDs were then employed as a hard filler in nickel electroplated films giving Ni-DND composite coatings. It was found that the presence of the DNDs significantly affected the properties of the coatings in an intriguing fashion. Toward that end, Ni-DND coatings exhibited improved microhardness and wear resistance when compared to Ni-only control coatings but the latter showed better erosion resistance.[1] These observations warrant a better understanding of the structure of the Ni-DND coatings and the effect on various mechanical properties. The work presented in this paper relates to an investigation of the structure/tribological properties of Ni-DND composite coatings. Characterization data to be discussed includes wear rates, hardness profiles and composite structure as measured by pin-on-disk, nanoindentation and high resolution SEM test methods.

[1] I. Petrov, P. Detkov, A. Drovosekov, M.S. Ivanov, T. Tyler, O. Shenderova, N.P. Voznecova, Y.P. Toporova, D. Schulz, Diamond & Related Materials 15 (2006) 2035–2038.

5:20pm **SE+NC-WeA12 Deposition of Various Nitride and Oxiceramic Coatings by an Industrial-Scale LAFAD Process**, ***V. Gorokhovsky**, C. Bowman, D. VanVorous, J. Wallace*, Arcomac Surface Engineering, LLC

Nearly defect-free nitride and oxiceramic coatings were deposited by the unidirectional dual large area filtered arc deposition (LAFAD) process. One LAFAD dual arc vapor plasma source was used in both gas ionization and coating deposition modes with and without vertical magnetic rastering of the plasma flow. Substrates made of different metal alloys, as well as carbide and ceramics were installed at different vertical positions on the 0.5 m diameter turntable of the industrial scale batch coating system which was rotated at 12 rpm to assess coating thickness uniformity. Targets of the same or different compositions were installed on the dual cathodic arc sources of the LAFAD plasma source to deposit a variety of coating compositions by mixing the metal vapor and reactive gaseous components in a magnetized strongly ionized plasma flow. The maximum deposition rate typically ranged from 1.5um/hr for TiCr/TiCrN to 2.5 um/hr for Ti/TiN multilayer and AlN single layer coatings, and reached up to 6 um/hr for AlCrO based oxi-ceramic coatings. The vertical coating thickness uniformity was +/-15% inside of the 150mm area without vertical rastering. Vertical rastering increased the uniform coating deposition area up to 250 mm. The coating thickness distribution was well-correlated with the output ion current distribution as measured by a multi-sectional ion collector probe. Coatings were characterized for thickness, surface profile, adhesion, hardness and elemental composition. Estimates of electrical resistivity indicated good dielectric properties for most of the AlCrO based oxi-ceramic coatings. The multi-elemental LAFAD plasma flow consisting of fully ionized metal vapor with reactive gas ionization rate in excess of 50% was found especially suitable for deposition of nanocomposite, nanostructured coatings. Potential applications of this highly productive coating deposition process are discussed.

Advanced Surface Engineering
Room: 204 - Session SE+TF+NC-ThM

Glancing Angle Deposition (GLAD) I
Moderator: T. Karabacak, University of Arkansas at Little Rock

8:00am **SE+TF+NC-ThM1 Sculptured Thin Films: Something Old, Something New, Something Borrowed, Something Blue**, ***A. Lakhtakia***, Pennsylvania State University **INVITED**

Sculptured thin films (STFs) are assemblies of parallel shaped columns with nanoscale features.[1] The demonstrated optical and biological functionalities of STFs suggest their classification as nanoengineered metamaterials. Deliberate engineering of the shape of columns was accomplished about 35 years before the formal conceptualization of STFs as optical materials in the early 1990s. Thereafter, the language of liquid crystals was borrowed to describe their optical constitutive properties. The design of columnar morphology for STF-based devices to engineer the optical polarization state became well-established about five years ago. The research front for optical applications of STFs now comprises electrically controllable optical filters, light sources of specific polarization states, and plasmonics. High-quality optical performance may necessitate post-deposition processes that result in blue-shifting of spectral features. In contrast, high precision in morphology appears unnecessary for using STFs as platforms for cell cultures.

[1] A. Lakhtakia and R. Messier, Sculptured Thin Films (SPIE Press, 2005).

8:40am **SE+TF+NC-ThM3 Randomness and Roughening in Glancing Angle Deposition**, ***K. Robbie***, *T. Brown*, Queen's University, Canada, *S. Asgharizadeh, M. Sutton*, McGill University, Canada

The unique highly-porous nanostructures created with Glancing Angle Deposition are a direct result of the randomness inherent to the condensation of atomic or molecular vapors. This randomness arises through quantum indeterminism in the atom-by-atom evaporation of the source material. At one extreme of film growth conditions, when adatom diffusion is high, the influence of vapor-substrate geometry is minimized and the resulting films are typically dense with isotropic structure and properties - in essence this is the regime of molecular beam epitaxy. When adatom mobility is reduced (e.g. through reduced temperature or the introduction of a reactive gas) geometrical effects become increasingly important and a balance develops between roughening due to the random arrival of atoms and smoothing due to the reduced, but still finite, adatom diffusion. Films grown under these conditions with normal-incidence vapor can be quite dense, yet the film surface will always roughen due to the random arrival of the vapor atoms, eventually resulting in a cauliflower-like fractal morphology. The unique nanostructures of GLAD are created when geometrical shadowing is used to amplify randomness-induced roughening - requiring the vapor to arrive at an angle larger than approximately 70 degrees from the substrate normal. We present here the first experimental observation, through x-ray reflectivity (XRR) measurements of thin silicon films, of the transition to the glancing angle growth regime. We find that film porosity increases as a function of thickness in the GLAD regime, whereas it decreases with thickness under the same growth conditions yet with nearer-normal vapor incidence. Silicon films deposited at room temperature onto rapidly rotating substrates exhibit linearly increasing density as a function of thickness when deposited at vapor incidence angles of less than 70 degrees, and linearly decreasing density (increasing porosity) when deposited at incidence angles above 70 degrees. We also show that significant 'filling-in' can occur during glancing-angle growth, where vapor deposits some distance below the growing film surface. These XRR measurements provide valuable new insight into the glancing angle deposition growth process, and will help to refine film nanostructure simulation and design models.

9:00am **SE+TF+NC-ThM4 Scaling of Nanorods during Glancing Angle Deposition: Effect of Surface Diffusion**, ***S. Mukherjee***, *D. Gall*, Rensselaer Polytechnic Institute

Ta, Al, and Cr nanorods, 65–430 nm wide and 440 nm tall, were grown by glancing angle sputter deposition onto continuously rotated Si(001) substrates from a deposition angle of 84º at substrate temperatures T_s = 300–1125 K. Surface diffusion is negligible at low homologous temperatures $T_s/T_m < 0.08$ (T_m: melting point) and for systems with a high activation energy for surface diffusion E_m. This leads to a chaotic growth process where the surface morphological evolution is controlled by long-range shadowing interactions and the rod width w (= 58 nm) at a constant height h (= 400 nm) is material independent. However, at higher growth temperatures, w increases with T_s and scales with T_s/T_m for all investigated metals as well as for data from the literature. This is attributed to an increase in the average island size on the growth surface which results in additional shadowing interactions and a chaotic divergence in the microstructure. Applying mean-field nucleation theory and non-linear dynamics within the kinetically limited growth regime yields a Lyapunov exponent λ of 0.033 for the divergence from the zero-temperature morphology and an effective E_m that scales with the melting point according to $E_m = 2.46kT_m$. The data also suggests a transition from a 2D to a 3D island growth mechanism as T_s increases from below to above a critical temperature $T_c = 0.24T_m$. The growth exponent p decreases monotonously from 0.5 to 0.31 as T_s increases from 300 K to T_c, in agreement with Meakin and Krug's model and Mullins-Herring model for 2+1 dimensional moving interfaces. However, p exhibits a discontinuity at Tc and becomes anomalous ($p > 0.5$) for $T_s > T_c$.

9:20am **SE+TF+NC-ThM5 Glancing Angle Deposition on Rotating Patterned Substrates: Experiment and Simulation**, ***C. Patzig***, Leibniz-Institute of Surface Modification Leipzig, Germany, *T. Karabacak*, University of Arkansas at Little Rock, *B. Fuhrmann*, Martin-Luther-University Halle, Germany, *B. Rauschenbach*, Leibniz-Institute of Surface Modification Leipzig, Germany

When glancing angle deposition is combined with a continuous substrate rotation, the growth of nanostructures with various shapes such as vertical posts, spirals and screws is possible. The shape is controllable with the ratio $\rho = r/\omega$ of the deposition rate r to the rotational speed ω. Besides the control of ρ, other deposition parameters such as the deposition angle β between particle flux and substrate normal, or the substrate temperature can be used to alter morphology and density of the grown sculptured thin films. Additionally, the use of a patterned substrate as an array of artificial seeds for the incoming deposition flux can lead to the growth of periodically arranged nanostructures. Here, nano sphere lithography was used to structure Si(100) substrates with Au dots in both hexagonally close packed and honeycomb arrangement as templates for the subsequent glancing angle deposition that was done by ion beam sputter deposition of a Si target. The influence of ρ, β, and the height of the Au seeds h on the morphology of the Si nanostructures for the case of the honeycomb pattern is discussed and compared with Monte Carlo simulations of glancing angle deposited sculptured thin films on templated substrates. It is found that in both experiment and simulation, depending on ρ either periodically arranged spiral-like or vertical column-like structures are grown, whereas changing β from 0° to a glancing 85° shifts the film morphology from dense with honeycomb-like arranged caps over partially grown together nanocolumns with hexagonally arranged pores in-between to separated nanostructures that replicate the templates honeycomb arrangement. Additionally, it was found both experimentally and in simulations that glancing angle sputter deposition on rapidly rotating substrates causes nanocolumns with triangular cross section on honeycomb templates and with circular cross sections on hexagonally close packed templates, showing that not only the inter-seed-distances, but also the symmetry of the template pattern influences the form of the growing nanostructures.

9:40am **SE+TF+NC-ThM6 Fabrication of Inclined Nano-Rough Columns by Combined Glancing Angle Deposition (GLAD) and Colloidal Lithography for Biological Applications**, ***A. Dolatshahi-Pirouz***, *M. Foss, D. Sutherland, J. Chevallier, F. Besenbacher*, University of Aarhus, Denmark

Recently there has been an increasing focus on methods to produce surfaces with a varying topography on the nanometer length scale for applications in e.g. biotechnology, photonics, and catalysis, since the nanoscale surface topography is known to influence the performance in these areas. Here, colloidal lithography is combined with glancing angle deposition (GLAD) to generate well-separated platinum nano-rough columns with a brush like appearance. The columns were fabricated by physical vapor deposition (PVD) with an e-gun evaporator onto surfaces pre-coated with polystyrene particles with a diameter at 137 nm by colloidal lithography at different deposition angles between the substrate and incoming flux (θ = 35, 10 and 5) as well as different depositions times. The effect of θ and deposition time t on the morphological characteristics of the nano-columns was investigated by utilizing scanning electron microscopy (SEM) and subsequently analyzing the images in order to determine the height, width and inclination angle of the nano-rough columns. From the SEM images we observe that the morphology of the nano-rough columns depend on the angle of incidence and as the deposition angle approaches grazing incidence sharp brush like columnar protrusions are grown on the colloidal particles, while more smoothly shaped surface features are grown at higher deposition angles. Moreover, by changing the incidence angle of the incoming flux, well-separated nano-rough columns can be synthesized with an angle of inclination ranging from 26 to 90 degrees. As the deposition time increases the height and width of the nano-rough columns follows a power law and increases accordingly. The power law exponents for the height and width increment as function of the deposition time both depends on the angle of incidence decreasing from 1.06 ± 0.04 to 0.81 ± 0.16 and 0.71 ± 0.07 to 0.19 ± 0.01, respectively, as the deposition angle decreases from 35 to 5 degrees. The change in the power law exponents indicates that the kinetics of the growth of the nano-rough columns is influenced by surface diffusion and shadowing effects. Moreover, from the power law exponents we were able to tailor inclined nano-rough columns with the same height and an inclination angle ranging from 90 to 26 degrees. The nano-rough surfaces are currently being used in cell experiments which indicate that inclined nano-rough columns can be used to guide the cellular behavior on a surface.

10:40am **SE+TF+NC-ThM9 Growth of Al Nanowhiskers on the Patterned Substrate by Glancing Angle Deposition at High Temperature**, ***M. Suzuki***, *R. Kita, K. Hamachi, K. Nakajima, K. Kimura*, Kyoto University, Japan

Recently, we have found that peculiar metal (Al, Fe, Ag, Au etc.) nanowhiskers grow when metal is deposited at a glancing angle on a high-temperature substrate (HT-GLAD). The key factors for producing nanowhiskers are a glancing deposition angle larger than 80° and a temperature higher than almost half of the melting point of the metal. Since the growth of the nanowhiskers may be concerned with the general crystal growth mechanisms, an understanding of the growth mechanisms will provide a novel technique to fabricate nanostructures. Further, if the growth of nanowhiskers is controlled, metal nanowhiskers will become important components for nanoelectromechanical devices because of their mechanical compliance, high electric and thermal conductance, catalysis, plasmonic properties, magnetism, etc. In order to understand the effect of the detailed geometric deposition condition on the growth of nanowiskers, we have demonstrated HT-GLAD of Al on a heated substrate with trench patterns. Al was deposited on a surface-oxidized Si(110) substrate using an electron beam (EB) evaporation apparatus specially designed for HT-GLAD. Six groups of trenches with a nominal width of 1, 3, 5, 10, 15, and 20 μm, respectively, and a depth of 1.7 μm were prepatterned along the direction. The substrate temperature during the deposition was maintained constant at a temperature of 390 °C. By choosing an appropriate substrate attitude during the deposition, the deposition angle on the sidewalls of the trenches was kept constant at 85°, while that on the surface was varied between 55° and 87°. The amount of Al deposited on the sidewalls was 30 nm in average thickness for all samples. The number of nanowhiskers growing on the sidewalls significantly increased with deposition angle on the surface. This suggests that Al atoms deposited in front of the growing nanowhiskers play an important role in the growth of nanowhiskers. The directive migration and/or reflective scattering are possible candidates for the transport process of the deposited atoms.

11:00am **SE+TF+NC-ThM10 Characteristic Length Scale of Nanorods**, ***H. Huang***, RPI

Glancing angle deposition has led to numerous exotic structures of nanorods. It is natural to ask: what makes nanorods nano. Following the discovery of three-dimensional Ehrlich-Schwoebel barrier, we have discovered a new length scale that dictates the formation of crystalline nanorods. This presentation starts with the physics origin of such length scale, and continues with atomistic simulations demonstrating the variation of the length scale and validation experiments, and ends with design of nanosynthesis based on the knowledge of this new length scale & its experimental validation. It is interesting to note that this length scale is the very reason that nanorods synthesis is possible, even though nanorods had been realized long time ago (and it was patented a decade ago).

11:20am **SE+TF+NC-ThM11 Crystalline Organic Nanocolumn Arrays**, ***J. Zhang***, *I. Salzmann, P. Schaefer, J.P. Rabe, N. Koch*, Humboldt University Berlin, Germany

Nanocolumn arrays based on organic semiconductor materials have significant potential for realizing various devices, such as sensors, field emitters, and nanoelectronic devices, on large-area flexible substrates at room temperature. In our work, crystalline nanocolumnar arrays of two widely studied organic semiconductors, i.e., Fullerene (C_{60}) and pentacene were fabricated by glancing angle deposition (GLAD), and characterized by scanning electron microscopy and X-ray diffraction. For both materials, column diameters of typically 100 nm are found on the transparent conductive oxide ITO at the rotation speed of 3 rpm (rounds per minute), essentially independent of column height (up to 360 nm for pentacene). However, on Si-oxide only C_{60} formed nanocolumns, while pentacene exhibited a morphology resembling that obtained by regular normal incidence deposition. The difference is attributed to the different molecular surface diffusion lengths on the substrate. Furthermore, the morphology of nanocolumns on ITO grown by GLAD is studied for molecular materials forming amorphous and crystalline solids. Amorphous tris(8-hydroxyquinoline)aluminum nanocolumn arrays were obtained at sample rotation speeds varying from 0.3 rpm to 30 rpm. For crystalline pentacene, a nanocolumn array formed at a rotation speed of 3 rpm, while a wide distribution of column heights and shapes was formed at rotation speeds of 0.3 rpm and 30 rpm. The incoming molecular flux and molecular diffusion length on column surface, both determined by rotation speed, were found to govern the resulting morphology of crystalline pentacene nanocolumns on ITO.

11:40am **SE+TF+NC-ThM12 Competitive Growth Mechanisms of Aluminum Nitride Thin Films Deposited by Off-Normal Reactive Magnetron Sputtering**, ***D. Deniz***, University of New Hampshire, *T. Karabacak*, University of Arkansas at Little Rock, *J.M.E. Harper*, University of New Hampshire

We have recently shown that AlN (0002) (c-axis) is tilted abruptly towards the deposition direction as N2 concentration is increased in N2/Ar sputtering gas mixtures. Here we present a Monte Carlo simulation model to describe the phenomenon of sudden c-axis AlN tilt. The model is based on the assumption that AlN islands with their c-axis parallel to substrate normal and AlN islands with tilted c-axis coexist at the initial stages of the growth and they can provide the adatoms with different surface mobilities. It is believed that the adatom mobilities are quenched when N2 concentration reaches a certain amount in the reactive sputtering of AlN. Our model further assumes that adatom mobility differences on different islands result in a growth rate difference of the islands. At the initial stages of the growth, AlN islands with tilted c-axis grow taller due to the lower adatom mobility on these islands. As they grow taller they win the competition and stop the further growth of AlN islands with their c-axis parallel to substrate normal due to shadowing effect. Monte Carlo simulations revealed that the shadowing effect combined with different adatom mobilities promotes the sudden c-axis tilt in AlN thin films.

Tribology Focus Topic
Room: 205 - Session TR+SE+TF-ThM

Advances in Surface Engineering for Friction and Wear Control
Moderator: K.J. Wahl, U.S. Naval Research Laboratory

8:00am **TR+SE+TF-ThM1 Evaluation of Ti-In-N Films for Tribological Applications**, ***J.E. Krzanowski***, *M. Nowicki*, University of New Hampshire

Titanium nitride and indium have both found applications as tribological coatings. While TiN is used primarily for its high hardness and wear resistance, indium can be used as a solid lubricant layer. In this study, we have examined the concept of using co-deposited TiN-In films for tribological applications. Ti-In-N films have been deposited by RF co-sputtering of Ti and In in a nitrogen/argon atmosphere. By varying the power to the Ti and In sources, the In/Ti ratio in the film was varied. Films were deposited at DC substrate bias levels of -50V and -150V. In both cases, as the In/Ti power ratio was increased, the indium content increased, but in a highly non-linear manner. At lower power ratios, the films had a cubic TiN structure, but as the power ratio increased, there was an abrupt transition to a hexagonal structure. Near the transition point, the films could also be amorphous, depending on film thickness, and thicker films were more likely to be crystalline. Below the transition point, the film composition depended strongly on substrate bias, and films deposited at -150V bias exhibited significantly reduced indium contents. Tribolgical tests were conducted using a pin-on-disk test with an alumina counterface. Most films showed shorter wear lives compared to TiN alone. The friction coefficients were found to depend on the In content in the films, and it was also found that heating films for short times in the range of 100-250C reduced friction coefficients.

8:20am **TR+SE+TF-ThM2 Nanostructured Sulfur Doped CHx-TiB2 Coatings for Improved Mechnical and Friction Performance**, ***B. Zhao***, *Y.W. Chung*, Northwestern University

Hydrogenated amorphous carbon films are known to attain ultra-low friction performance only in dry environments. Our work demonstrated that sulfur doping of hydrogenated carbon films results in ultra-low friction performance in both dry and humid environments. However, these films have a hardness of 7 - 10 GPa and an elastic modulus around 80 GPa, which are too low for some high stress applications. Formation of nanostructured coatings is known to improve hardness. With the aim to produce hard, low-friction coatings, we synthesized nanolayered and nanocomposite films of sulfur-doped hydrogenated carbon and titanium diboride using dual-target magnetron sputtering. Titanium diboride deposited by this method had a hardness >30 GPa. This paper will discuss the film structure and how such structure correlates with its tribological and mechanical properties.

8:40am **TR+SE+TF-ThM3 Latest Developments on the Family of C-alloyed TMD Self-lubricating Coatings**, ***A. Cavaleiro***, SEG-CEMUC - University of Coimbra, Portugal, *T. Polcar*, CTU Prague, Czech Republik, *M. Evaristo*, SEG-CEMUC - University of Coimbra, Portugal **INVITED**

Due to their layered structure and weak inter-layer bonding, transition metal dichalcogenides (TMD) exhibit very interesting physical and tribological properties. Among different TMD families (TmS2, TmSe2 and TmTe2, with Tm = Mo, W, Nb) MoS2 and WS2 have been the most intensively studied in last decades. They are now currently used either as oil additives or as thin self-lubricating coatings. The industrial applicability of these coatings is still very limited owing to their two main drawbacks: (1) the loss of the tribological performance in humidity-containing environments and, (2) the low load bearing capacity. Several solutions have been proposed to overcome these problems as, for example, alloying TMD coatings with other elements or compounds, such as C, Ti, Pb, and TiN. The concept of coatings based on TMDs alloyed with carbon was introduced in the 90´s and was based on the expected synergy between the excellent frictional behavior of TMD in vacuum/dry air and the tribological performance of C-based materials. Improved frictional performance of the W-S-C coatings could be achieved when the coatings were tested by environmental cycling from dry to humid air (FC - friction coefficient from 0.02 to 0.15). Successive changes in the sliding mechanisms based on the modification of the contact layers were assigned as responsible for this behaviour. The TMD+C solution was adopted by the authors for their research by studying its extension to other TMD-C systems. The aim of this talk was to present the latest developments achieved within TMD-C magnetron sputtering deposited coatings concerning di-selenides (Mo-Se-C and W-Se-C). Lower friction coefficient was achieved in comparison to previous deposited W-S-C coatings, particularly in humid air. FC was possible to be kept lower than 0.05 in all testing conditions. Tests were performed with contact stress as high as 1.5 GPa without destruction of the coating. The frictional and wear mechanisms under different operating conditions were studied by nanoscale analysis of the wear tracks. The tribological performance, whatever the testing conditions, was attributed to the formation of a thin tribolayer consisting exclusively of TMD platelets with the (002) plans oriented parallel to the sliding motion. C is removed from the contact area during the re-orientaion process, only playing a secondary role by increasing the coatings density, avoiding surface oxidation and improving the loading bearing capacity.

9:20am **TR+SE+TF-ThM5 Reduction in Friction and Micropitting by Coatings and Lubricants Containing Inorganic Fullerenes**, ***S.J. Bull***, *A. Oila*, Newcastle University, UK

Improvement in component performance by reduction in friction and wear has been the focus of considerable research over the last forty years. As products become more highly engineered and component size is reduced the significance of friction and wear is increased, particularly in terms of improvements in energy efficiency, and the need to develop materials with improved triboloigcal performance becomes critical. Nanostructured materials are one way whereby this might be achieved. Recent work has focussed on the development and assessment of nanomaterials and composites for triboloigcal performance. In particular, the use of inorganic fullerene-like materials in the form of coatings and nanoparticles (and as the reinforcement for nanocomposites) has shown a lot of promise for tribological applications. This talk will highlight the use of inorganic fullerene nanoparticles as additives for lubricating oils or coatings to achieve a significant increase in the operational life of rolling/sliding components such as gears.

9:40am **TR+SE+TF-ThM6 Tribology of Carbon Films in Hydrogen and Deuterium Gas Environments**, *A. Erdemir*, ***O.L. Eryilmaz***, Argonne National Laboratory

Recent systematic studies in our laboratory have shown that certain diamond-like carbon (DLC) films are able to achieve superlow friction and wear when tested in hydrogen-containing test environments. In the presence of deuterium, we were also able to achieve very low friction and wear on these films. In this study, we used a combination of controlled-environment atmospheric pressure and vacuum tribometers to further verify the critical effects of hydrogen and deuterium on friction and wear of such films; then we used imaging SIMS and XPS methods to ascertain the near surface chemistry of their sliding surfaces. The combined results of tribological tests and surface analytical studies revealed that there exist a close correlation between the chemical nature of sliding DLC surfaces and their friction and wear behaviour. Specifically, we found that in the presence of both hydrogen and deuterium, the sliding contact areas of carbon films were covered by a hydrogen and deuterium film (only a few Å thick). The wear rates and friction coefficients are much higher if tests were run in dry nitrogen or vacuum than in hydrogen and deuterium. Overall, we show that superlow friction behaviour of certain DLC films is largely controlled by gas-surface interactions.

10:40am **TR+SE+TF-ThM9 Tribomaterials for Spacecraft: Testing & Surface Chemistry**, ***J.R. Lince***, The Aerospace Corporation **INVITED**

The spacecraft environment is challenging for tribocoatings and lubricants used in devices in satellites and launch vehicles. Areas of concern include vibration during launch, thermal cycling on orbit, and the need to work effectively for missions up to twenty years in duration without lubricant replenishment. Especially challenging is the need for tribomaterials to withstand the vacuum of space during lengthy missions. Spacecraft tribomaterials must exhibit low vapor pressures, since evaporation of lubricants can result in loss from and premature failure of devices, as well as contamination of sensitive spacecraft components. A relatively small set of liquid lubricants meet the vapor pressure requirement – while also meeting performance requirements for current spacecraft applications – including synthetic hydrocarbons and perfluorinated polyalkylethers. Soft solid lubricants such as molybdenum disulfide (MoS_2) and polytetrafluoroethylene (PTFE) have been used traditionally. More recently, hard low friction coatings such as hydrogenated diamond-like carbon have shown promise for operation in vacuum with existing spacecraft lubricants, or even unlubricated operation in vacuum. These solid- and liquid-based tribomaterials show performance in vacuum that differs with that in air, nitrogen, or even with small partial pressures of oxygen and water. This is especially important for spacecraft hardware, because it is often prohibitive to test them in a space-like environment, including vacuum, before launch. As such, differences between non-vacuum and vacuum testing need to be understood in order to predict how lubricated devices will perform in space. This talk will focus on a series of recent studies done at The Aerospace Corporation that elucidate the effects of vacuum and other environments on the tribological performance of several important spacecraft tribomaterials. The emphasis will be on how varying environments affect the surface chemistry of the materials.

11:20am **TR+SE+TF-ThM11 Nano-Smooth Diamond Coatings on Various Alloys for Ultralow Friction in the Presence of OH-Containing Lubricants**, ***T. Gries***, CNRS - ICARE, France, *C. Matta, M.I. De Barros Bouchet, B. Vacher*, Ecole Centrale de Lyon, France, *S. de Persis*, ICARE - CNRS, France, *L. Vandenbulcke*, CNRS, France

Titanium alloys and titanium-coated alloys are important materials for aerospace, mechanical, chemical and biomedical applications; however their applications could be extended by improving their tribological behaviour. This can be done by using diamond-based coatings which are outstanding materials for changing their surface properties. We have shown that nano-smooth fine-grained diamond coatings could be deposited on these alloys at moderate temperature, equal to or lower than 600°C, from CH_4-CO_2 species. They are in fact duplex coatings with an external diamond film, a titanium carbide sub-layer and a diffusion solid-solution. These coatings exhibit particularly strong adherence with the substrates as shown by various mechanical tests and very high induced stresses without peeling off. They are first described in terms of sp^2-hybridized carbon contents relatively to the sp^3-carbon ones, a parameter which influences the structure and the intrinsic diamond properties (surface roughness in the 15-35 nm range, micro-hardness, Young's modulus and residual stresses). The whole is correlated to the plasma enhanced CVD process through the formation of different concentrations of the gaseous precursors in the plasma which include both radicals and stable species as revealed by molecular beam mass spectrometry and corroborated by kinetic calculations in the C-H-O plasmas. These coatings are studied by micro-Raman spectroscopy and their structure is revealed by TEM studies. A sp^2-C enriched layer is especially evidenced at their extreme surface by Energy-Filtered TEM on transverse cross-sections, a layer which is important for tribochemical reactions. While the friction coefficient is high under ultra high vacuum, ultra low friction is obtained in saline corrosive solution. Ultra low friction with no wear is also obtained with gas phase lubrication by glycerol under boundary lubrication regime, in conditions which permit a better identification of the friction mechanism from advanced surface characterizations. These studies allow concluding that lubrication of these diamond coatings by OH-containing molecules can permit new or improved applications in various fields. Some examples of ultra low friction and low wear are provided when nano-smooth diamond coatings or alumina are sliding on nano-smooth diamond in corrosive saline solution or in the presence of glycerol lubricant, a model of environmentally friendly molecules.

11:40am **TR+SE+TF-ThM12 Tribology of Nanocrystalline Diamond Coatings**, ***N.D. Theodore***, North Carolina State University, *K.J. Wahl*, Naval Research Laboratory

The tribological behavior of several nanocrystalline diamond (NCD) coatings was compared to correlate compositional, structural, and chemical bonding differences to their friction performance. The diamond coatings were confirmed by X-ray diffraction (XRD) to be nanocrystalline with crystallite sizes ranging from to 4 to 60 nm. These diamond coatings could be differentiated from each other by their visible wavelength Raman absorption bands. Some coatings had a single strong peak at 1332 cm^{-1} typical of crystalline diamond bonding; others also had broad peaks at 1340 cm^{-1} and 1580 cm^{-1} characteristic of the D and G peaks in sp^2 hybridized carbon; and still others had additional peaks at 1135 cm^{-1} and 1470 cm^{-1}, which are commonly attributed to polyacetylene bonding. Reciprocating sliding tests using diamond counterfaces in controlled humidity environments resulted in low friction values for all coatings, between 0.02 and 0.09. The coatings exhibiting lower friction values possessed lower mean surface roughnesses, as measured using an atomic force microscope (AFM), smaller crystallite sizes, and increased amounts of non-sp^3 carbon content. Transmission Fourier transform infrared (FTIR) microscopy was used to examine the bonding chemistry in the coatings and wear tracks. The role of diamond coating microstructure, surface roughness, and bonding chemistry to the tribological behavior of NCD will be presented.

Advanced Surface Engineering
Room: 204 - Session SE+TF+NC-ThA

Glancing Angle Deposition (GLAD) II
Moderator: D. Gall, Rensselaer Polytechnic Institute

2:00pm **SE+TF+NC-ThA1 Glancing Angle Deposition at the Nano-Bio Interface**, ***Y. Zhao***, University of Georgia **INVITED**

Glancing angle deposition (GLAD) technique is a physical vapor deposition method to design three-dimensional nanostructures by programming the vapor incident angle and substrate azimuthal rotation. This method offers large area growth of aligned nanorod arrays with additional capability of self-alignment. There is almost no limitation on materials that can be fabricated into desired nanostructures. With recent advance in a multilayer deposition procedure, one can design complex and multifunctional heterogeneous nanostructures. In addition, with a co-deposition system of two or more sources, novel nanocomposites or doped nanostructure arrays can be produced, which results in nanostructures with different morphology. Here, I will highlight our recent progress in multi-component nanorod array fabrication and their potential biological applications. We find that aligned silver nanorod array substrates can be used as a high sensitive virus and bacteria sensor base on surface enhanced Raman spectroscopy (SERS) principle. This SERS based sensor can be used to detect the molecular fingerprints of several important human respiratory viruses including respiratory syncytial virus, rhinovirus, adenovirus, human immunodeficiency virus, influenza virus, and bacteria, with high sensitivity and selectivity, and to discriminate between different virus/bacterium strains. Using a unique multilayer deposition configuration, catalytically driven nanomotors have been fabricated and demonstrated, which can directly convert chemical energy into mechanical energy. This device holds a great potential to mimic smart biological systems via hybrid organic-inorganic nanostructures.

This work was supported by NSF, NIH, and ARL.

2:40pm **SE+TF+NC-ThA3 Growth and Characterization of Magnesium, Magnesium Alloy, and Doped TiO$_x$ Sculptured Thin Films (STFs)**, ***S.M. Pursel***, *M.W. Horn, B.A. Shaw*, The Pennsylvania State University

Bioabsorbable materials such as magnesium, which is essential for cellular function, have recently been studied for use in heart stents, bone plates and screws, and dental and orthopedic implants. However, the use of vapor deposition to form non-equilibrium magnesium alloys has had little if any commercial interest even though certain properties of these alloys, namely corrosion resistance, can be improved. Engineering of surface morphology using dip coatings and etching has been used in biomedical materials to enhance certain application specific surface properties. Sculptured thin film (STF) technology potentially provides a path to merge the advantages of non-equilibrium alloy formation and engineering nanoscale surface morphology. We present here our results utilizing a vapor co-deposition scheme to improve nucleation and corrosion properties of magnesium alloys. By utilizing co-deposition with materials such as titanium, yttrium, zirconium, and others the growth mode of magnesium can be modified and the solid solution limit can be surpassed leading to an improvement in corrosion resistance. Characterization of the growth of magnesium alloy thin films has been done utilizing various alloying elements, substrate temperatures, post-deposition treatments, and substrate positions (to deposit STFs). The results point towards a growth mode controlled by crystallization effects that are not common in higher melting temperature materials. The results of the study are presented in terms of x-ray diffraction data, microscopy analysis of growth evolution, and corrosion testing. We will also present results that extend our work on TiO$_x$ chiral STFs utilizing the circular Bragg phenomenon (CBP) for sensor applications. The CBP is observed in the circularly polarized transmission spectrums of chiral STFs as a stop band for co-handed light. The location and shape of this stop band is dependant on the material properties among other factors. Using an impurity material from a second source may allow added sensitivity for sensor applications while maintaining STF morphology and function.

3:00pm **SE+TF+NC-ThA4 Performance and Response Time of Nanostructured Relative Humidity Sensors**, ***M.T. Taschuk***, *J.J. Steele, M.J. Brett*, University of Alberta, Canada

Applications requiring relative humidity (RH) measurement will require differing sensitivity, range of humidity operation, and response times. These properties are determined by the properties of the sensing medium: material, porosity, surface area, pore size distribution and morphology. We have been investigating the use of glancing angle deposition (GLAD) for the fabrication of RH sensors with interdigitated electrode (IDE) substrates.[1,2] While GLAD offers some significant advantages for RH sensors, there remain a number of open questions regarding the underlying physics of GLAD RH sensor performance and response time. The response of our devices depend on the extremely large low frequency dielectric constant of water adsorbed to metal oxides, which can results in a three order of magnitude change in capacitance as RH is increased from 0 to 100%. We have recently employed an electromagnetic model with simple dielectric mixing laws to compare our device performance with literature values for dielectric constants[2]. Further work is ongoing to include structural effects in the dielectric mixing laws to improve accuracy. Response time varies with the size and nature of pores in our sensors, which in turn relies on column properties such as diameter and surface roughness. Experimental values for response time of the GLAD RH sensors have been reported, but a neither a model nor thorough study of response time as a function of deposition angle and film thickness has been presented. Constructing a model for our devices requires an understanding of the diffusivity of GLAD films, the interaction between water vapour and TiO2, and the electromagnetic behaviour of IDE devices. In this paper we characterize the performance and response time of GLAD RH sensors as a function of film thickness and deposition angle. The microstructure column radius as a function of film thickness and deposition angle is investigated. A 1D numerical model describing response time of our devices is developed, which includes diffusion, adsorption and IDE physics. The modeling results are compared with our experimental data, and demonstrates that response time of our sensors is dominated by adsorption.

[1] J.J. Steele, G.A. Fitzpatrick, and M.J. Brett. IEEE Sensors Journal, Vol. 7:955 – 956, 2007.

[2] J.J. Steele, M.T. Taschuk, and M.J. Brett. IEEE Sensors Journal, (In Press), 2008.

3:20pm **SE+TF+NC-ThA5 Patterned Ag Nanorod Arrays as SERS Substrates by Template Mediated Oblique Angle Deposition**, ***Y. Liu***, *Z. Zhang, Y. Zhao*, University of Georgia

Surface enhanced Raman scattering (SERS) is widely used in the analytical, biomedical, clinical, environmental, and security applications. The practical application of a SERS-based sensor requires an efficiency SERS substrate which can not only provide a high enhancement factor, but also be uniform, stable and reproducible. In this work, a highly ordered, uniform and periodic patterned Ag nanorod arrays as SERS substrates are fabricated by combining electron beam lithography (EBL) and oblique angle deposition (OAD) techniques. Two dimensional nano Au post arrays with different separations are fabricated by EBL. There are only very weak SERS signal can be detected after the Au post arrays are treated by a 1 μL 10^{-4} M BPE (trans-1,2-bis (4-pyridyl) ethene) droplet. However, after a layer of ~ 400 nm Ag nanorods are deposited on those BPE treated Au post array, strong SERS signals have been obtained. Furthermore, the SERS intensities become more than 8 times stronger, after the Ag arrays are further treated by a droplet of 1μL 10^{-5} M BPE. These results demonstrate that most SERS signals could come from the molecules adsorbed on the side surfaces of the Ag nanorods, rather than the ends. The SERS signal is also strongly dependent on the separation of the Au posts. A numerical calculation on the electric field enhancement has been carried out to confirm this result.

4:00pm **SE+TF+NC-ThA7 Quantification of Porosity and Deposition Rate of Nano-Porous Films Grown by Oblique Angle Deposition**, ***D.J. Poxson***, *F.W. Mont, M.F. Schubert, J.K. Kim, E.F. Schubert*, Rensselaer Polytechnic Institute

We propose analytic formulas accurately predicting the refractive index and film thickness of obliquely deposited thin films for a given incident angle. Recently, it was shown that accurate control of the refractive index of physical-vapor deposited thin film materials can be achieved through the use of oblique-angle deposition. Refractive index tunability and low refractive index (low-n) films are highly desirable for a variety of optical applications. For example, broadband antireflection coatings, omni-directional reflectors, distributed Bragg reflectors, optical micro-resonators, light-emitting diodes, photovoltaic solar cells, and optical interconnects. While the qualitative tenets of oblique-angle deposition were demonstrated over a century ago, no quantitative formulas for the porosity and deposition rate have been described in the literature. In this work, we propose a model relating the porosity and deposition rate of a material to its vapor flux incidence angle for oblique-angle deposition. Our model is based upon geometrical arguments, employs a single fitting parameter, and takes into account surface diffusion. We have measured the refractive index and thickness for SiO$_2$ and indium tin oxide (ITO) nano-porous films deposited over a wide range of deposition angles ($0° < \theta < 90°$). The porosity of a material is determined from the measured refractive index. Comparison of experimental SiO$_2$ and ITO porosity values and deposition rates with theory reveals excellent agreement. The theoretical model allows for the predictive control of refractive index, porosity, and deposition rate for all deposition angles, potentially a very useful tool in the development of high quality low-n optical coatings. Furthermore, given the set of basic assumptions used, we expect these formulas to be valid for a wide range of materials.

4:20pm **SE+TF+NC-ThA8 Sculptured Thin Films from Aluminum**, ***E.B. Schubert***, *T. Hofmann, D. Schmidt, M.M. Schubert*, University of Nebraska-Lincoln

Three-dimensional (3D) structure design of chiral materials on the nanoscale is a current demand in modern material science and engineering and various intriguing applications are foreseen for example in the fields of optics, electromechanics or electromagnetic. Glancing angle deposition is a method which allows for "bottom-up" fabrication of 3D shaped and tailored chiral nanostructures arranged in sculptured thin films (STF). We will present an investigation of the growth of STF's from aluminum on highly p-type doped silicon substrates by using either ion beam sputtering or electron beam evaporation. Various growth schemes have been used to obtain films with different nanostructure shapes such as posts, plates, screws or spirals. The films have been characterized regarding their optical and electrical properties by means of 4x4 Mueller-Matrix ellipsometry, IR spectroscopic ellipsometry and electrical measurements. Whereas Mueller-Matrix Ellipsometry reveals an optical response which can be related to the symmetry of the three-dimensional nanostructures,[1] the IR data give hint to electron or lattice absorptions. We found that the IR optical response depends on the shape of the nanostructures. STF's from aluminum plates for example show a strongly metallic behavior, whereas films containing Al spirals show multiple resonances, with a periodic spectral distance of 7.2 THz between neighboring absorption features. The IR optical data for the Al nanocoils are discussed in terms of coupled inductance and capacitance pairs, where the inductance is formed from the coil itself and the depletion layer capacitance is created on the footprint of the metallic Al coil with the highly p-type doped Si substrate. A Drude-like background term, which accounts for free carriers in the aluminum nanospirals was also used during sample regression. It is found, that resistivity and free mean path of the electron depends of the shape of the Aluminum nanostructures as well. This behavior is verified by electrical measurements under dc conditions.

[1] D. Schmidt, E. Schubert, and M. Schubert, phys. stat. sol. (a) 205, 748 (2008).

4:40pm **SE+TF+NC-ThA9 Mueller Matrix Ellipsometry Studies of the Optical Properties and Structure of Serial Bi-Deposited Titanium Oxide Sculptured Thin Films**, *N.J. Podraza, S.M. Pursel*, The Pennsylvania State University, *R.W. Collins*, University of Toledo, ***M.W. Horn***, The Pennsylvania State University

In this work, titanium oxide (TiO_2) chiral sculptured thin films (STFs) are fabricated using serial bi-deposition (SBD) electron beam evaporation and studied using Mueller matrix ellipsometry (MME). Chiral STFs are of interest for a wide range of applications in optoelectronic devices such as photovoltaics, microelectronic devices, microcavities, biological sensors, and bioabsorption devices. These films can be described as assemblies of upright, parallel, helical columns. Their helicoidal morphology, being periodic, engenders the circular Bragg phenomenon: circularly polarized light couples to the helices present in the film, if the handedness of the light and the STF coincide, resulting in enhanced reflectance in the Bragg regime spectral range. TiO_2 STFs fabricated using SBD are of particular interest for fundamental studies due to its high bulk index of refraction and films prepared using this technique can be fabricated to exhibit Bragg resonances in the visible spectral range at wavelengths ~450-650 nm. Although normal incidence transmission and reflection measurements can demonstrate this behavior, it is often impossible to discern the various optical and structural properties of optically anisotropic materials like STFs. MME, however, allows us to extract each of the principal indices of refraction (n_x, n_y, n_z) as well as the microstructural parameters such as film thickness and the initial polar and in-plane orientation of the helices. The complete Mueller matrices for SBD TiO_2 STFs are measured using a dual-rotating compensator spectroscopic ellipsometer over a spectral range from 250-825 nm in transmission mode at normal incidence ($\Theta_i = 0^0$) and non-normal incidence ($5 \le \Theta_i \le 55^0$). The normal incidence measurements provide the principal indices of refraction and the microstructure, while the non-normal incidence measurements allow us to monitor the blue-shift in the Bragg resonance with increasing angle of incidence. The fundamental understanding gained from MME is expected to provide assistance in further engineering and optimizing these types of materials for specific applications requiring control of the Bragg resonance feature.

5:00pm **SE+TF+NC-ThA10 Low Hydrogen Desorption Temperature of Hydrided Pd Coated Novel Mg Nanoblades**, ***F. Tang***, *T. Parker, H.-F. Li, G.-C. Wang, T.-M. Lu*, Rensselaer Polytechnic Institute

We grew Mg nanoblades standing nearly vertically on the substrates by oblique angle vapor deposition. The thickness of the nanoblades along the vapor incident direction ranges from ~15 nm to ~30 nm at a vapor incident angle ~75^o, while the width perpendicular to the incident vapor direction is as wide as a few hundred nm.[1] These novel nanoblade structures have several advantages over the bulk materials for hydrogen storage: such as a large surface-area-to-mass ratio of ~60 m^2/g and ultrathin thickness (~22 nm), which will significantly enhance the kinetics of hydrogen absorption/desorption. The spacing between the nanoblades can also accommodate the large volume change ($Mg \leftrightarrow MgH_2$) during hydrogenation/de-hydrogenation processes. We have studied hydrogenation/de-hydrogenation properties of ultrathin Mg nanoblades coated with Pd as a catalyst, using in situ temperature desorption spectrum (TDS), ex situ scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The Pd coated Mg nanoblades were hydrogenated at a pressure of 1 bar with substrate held at ~333 K for ~15 hours. The de-hydrogenation property of the hydrided Pd/Mg/Pd nanostructure was characterized in situ by TDS, which showed that the hydrided nanostructure has a low hydrogen desorption temperature at ~365 K. Through a combinational microstructure by TEM and TDS analyses of hydrided nanoblades as well as hydrided nanoblades covered with additional Mg layers, we found that the effect of Pd catalyst on reducing the hydrogen desorption temperature is significantly stronger than the conventionally proposed grain size and strain effects. The ex situ SEM images showed that the hydrided Pd/Mg/Pd and hydrided Pd/Mg (one sided Pd coating) nanoblades became highly curved. Various shapes such as circular, helical or spiral have been formed in the hydrided Pd/Mg nanoblade films. The formation of these curly structures could be related to the strain induced by the partial decomposition of MgH_2 after the sample was exposed to air. The understanding of hydrogenation/de-hydrogenation properties of Pd coated Mg nanoblades could help us in designing promising nanoscale metal hydrides for hydrogen storage with low desorption temperatures. FT was supported by the NSF award 0506738 and TP was supported by the DOE (education) GAANN P200A030054.

[1] F. Tang, T. Parker, H.-F. Li, G.-C. Wang, and T.-M. Lu, J. of Nanosci. and Nanotechnol. 7, 3239 (2007).

5:20pm **SE+TF+NC-ThA11 Improving Stiffness of Silicon Chevrons by 1.2 MeV Ar^{+8} Ion Irradiation**, ***R. Nagar***, Indian Institute of Technology Delhi, *C. Patzig, B. Rauschenbach*, Leibniz-Institute of Surface Modification Leipzig, Germany, *P. Kumar, D. Kanjilal*, Inter-University Accelerator Centre, India, *B.R. Mehta, J.P. Singh*, Indian Institute of Technology Delhi

Five-armed silicon chevrons were grown by oblique angle ion beam sputter deposition on Si(111) substrates pre-patterned with 260 nm diameter silica spheres and 500 nm diameter polystyrene spheres. The patterning spheres self-assemble in hexagonal network, act as nucleation sites, and control the dimensions as well as the distance between the growing chevrons. The chevron arms are about 500 nm long, 350 nm wide and 200 nm thick with odd numbered arms making an angle of about 45° and even numbered arms an angle of about 55° from the vertical. In order to tailor the mechanical strength of the chevron coatings, the samples were irradiated with 1.2 MeV Ar^{+8} ions at liquid nitrogen temperature at different fluences of 10^{15}, 10^{16} and 10^{17} ions/cm^2. The range of Ar ions in the amorphous Si matrix as determined by the simulation code SRIM is about 1.1 μm. Therefore, the Ar ions traverse the complete length of the chevrons before getting implanted in the Si(111) substrate. The spring constant of the chevrons was determined by force-distance spectroscopy using an atomic force microscope. Results show that the spring constant of the irradiated Si chevrons grown on 260 nm diameter silica spheres increases from 480 N/m for pristine to 1320 N/m for a fluence of 10^{16} ions/cm^2. For chevrons grown on 500 nm diameter polystyrene spheres, an increase from 370 N/m for pristine to 1325 N/m for fluence of 10^{17} ions/cm^2 is observed. Thus, irradiated chevrons are stiffer as compared to pristine ones. Finite element analysis of chevrons provides an insight into the dynamics of the resulting deformations when the chevrons are loaded. The modeling establishes that for these odd-armed chevrons a vertically downward load results in a torque about the base of the chevrons. The load produces a significantly larger lateral stress/displacement relative to the vertical, thus making them more robust to the loading force. Investigations by micro-Raman and glancing angle X-ray diffraction suggest that the Ar irradiation fosters a transformation from amorphous to poly-crystalline Si. The improved mechanical strength of the chevrons indicates that ion irradiated chevron coatings are capable of withstanding higher loads as compared to pristine coatings without getting delaminated.

Advanced Surface Engineering
Room: Hall D - Session SE-ThP

Advanced Surface Engineering Poster Session

SE-ThP1 Investigation of Polarization Conversion Effect in Obliquely Deposited SiOx and As_2S_3 Films, ***M.V. Sopinskyy**, I.Z. Indutnyy, V.I. Mynko, P.E. Shepeliavyi*, V Lashkaryov Institute of Semiconductor Physics, NASU, Ukraine

Polarization conversion effect have been studied to find out anisotropy in the obliquely deposited SiOx and As2S3 films. The films were obtained by thermal evaporation and oblique deposition of SiO and As2S3 onto polished Si and silica substrates. During deposition the substrates were oriented at the angles β between the normal to the substrate surface and the direction to the evaporator. The polarization conversion is an interesting phenomenon which causes the fraction of p(s)-polarized light incident on an anisotropic thin film be reflected as s(p)-polarized light.[1] The optical anisotropy of the obliquely deposited SiOx and As2S3 films was detected using the data on the polarization conversion of the electric vector caused by the passage of polarized light through the film. For this purpose the light beam with the electric vector linearly polarized in the direction perpendicular to the plane of incidence (the s-polarized light beam) was projected on the samples and the ellipsometer table was rotated around the normal to the sample surface (rotation angle α = 0°-360°). The angular rotation of analyzer (θ) was measured by means of the ellipsometer with a sensitivity of 0.02°. Normally deposited SiOx and As2S3 films don't show any in-plane anisotropy. For As2S3 films deposited at β=75° and SiOx films deposited at β=60° there are observed θ(α) dependencies with the period of 180° (symmetrical, or assymetrical). In this case, principal axes of high-frequency dielectric constant tensor εik for those films are mutual perpendicular, and two of them lie in the plane parallel to film substrate (one is parallel, and another perpendicular to the direction of the projection of the vapor-beam's direction on the substrate surface). The third principal axis of εik is perpendicular to the substrate surface or is slightly inclined to the perpendicular. For SiOx films deposited at β=75° θ(α)-dependencies have 360°period value. In this case the third principal axis of εik is inclined toward the substrate surface. It directly shows that obliquely inclined columns are formed in such films. Thus, investigation of polarization conversion effect is simple, nondestructive and useful method to distinguish the type of in-plane and out-of-plane structural anisotropy of obliquely deposited films.

[1] R. M. A. Azzam and N. M. Bashara, (1986). Ellipsometry and Polarized Light (Amsterdam: North-Holland).

SE-ThP2 Influence of Oblique Incidence on the Properties of Ion Beam Sputtered Chromium and SmCo Films, *B. Ramamoorthy,* Indian Institute of Science*, A. Raju,* Honeywell Technology Solutions Lab, ***S. Mohan***, Indian Institute of Science

Ion Beam Sputter Deposition (IBSD) technique with its unique characteristics like lower operating pressure, well collimated mono energetic beam, independent control over the energy and flux is considered superior over the conventional sputtering techniques in processing thin films with tailored properties. In addition to the above features, the energy of the sputtered species is also relatively higher in IBSD. The spatial and angular distribution of the sputtered species here, also could be controlled by controlling the incident angle of ions over the target. This ability to fine control the energy of the sputtered species has been well utlized in depositing high density optical films. This energy imparting kinetics also forms the basis for the commonly used ion assisted deposition. Though the energy advantages have been well utilized, the angular distribution has not been explored much. In this work, we explore the advantages of angular distribution of the sputtered species, in modifying the properties of Cr and SmCo films. In the IBSD system used in the present study , ions were incident over the targets at an angle of 45^o degrees and substrates were placed at angles 10^o, 20^o and 30^o measured from the target normal. The substrates were heated to 600^o C. Chromium and SmCo films were deposited sequentially without breaking the vaccum. The deposited films were studied for their composition, structure and their magnetic properties. The structural studies indicate different structural orientations with different substrate position. Self shadowing of the condensed atoms, higher mobility on the plane of the substrate during oblique incidence have been found to be responsible for the structural variations which otherwise would not have been possible with other process parameter combinations. The change in the structure has also been found to alter the magnetic properties of the films. The films deposited at normal incidence show a coercivity of 4kOe whereas the films deposited at an angle of 30^o show a coercivity of 6kOe. The increase in the coercivity has been attributed to the preferential orientation of SmCo films caused due to the oblique incidence. The results obtained will be discussed in detail from the context of oblique deposition.

SE-ThP3 Characterizations of Polarization-Discriminatory Inverters Fabricated by Glancing Angle Deposition, ***Y.J. Park**, K.M.A. Sobahan, C.K. Hwangbo*, Inha University, Republic of Korea

Glancing angle deposition (GLAD) is a thin-film fabrication technique with controlled microstructures and provides advantages over conventional evaporation techniques. Based on physical vapor deposition, it employs an oblique-angle-deposition and substrate motion to allow nanometer-scale control of the structure in engineered thin-film materials. The films deposited in this technique show the optical anisotropy originating from the microstructures and the porosity of the films increase due to shadow effects. These controls can be utilized to engineer thin films for specific applications such as three-dimensional photonic crystals, gradient index optical filters, broadband antireflection coatings, and linear polarizer, etc. In this study, we investigate the optical and structural properties of linear and circular polarization-discriminatory inverters. Circular polarization-discriminatory handedness inverter is realized as a combination of half-wave plate and Bragg reflector and that of linear polarization inverter is realized as a combination of quarter-wave plate, Bragg reflector and quarter-wave plate. The zigzag microstructures of the quarter-wave plates as well as the half-wave plates and the helical structure of the Bragg reflector are fabricated by electron beam evaporation using GLAD technique and Ti@O@sub 2 material is used in this purpose. The physical thicknesses of the half and quarter-wave plates are calculated using their anisotropy. The polarization-discriminatory inverters show that the incident linear and circular polarized light becomes opposite linear and circular polarized lights with Bragg effect at output. The structural and surface morphology of this device are also investigated using scanning electron microscope (SEM).

SE-ThP4 Influence of Substrate Temperature on Reactive-sputtered Tin-nitride Thin Films Prepared by Glancing Angle Deposition, ***H. Tsuda**, H. Takeuchi, Y. Inoue, O. Takai*, Nagoya University, Japan

1. Introduction Properties of tin-nitrogen compounds have not been recognized in detail. Tin-nitride was reported to exhibit a spinel structure (Sn_3N_4) at low temperature, while tin-nitride films deposited at high temperature showed a zinc blende (SnN) structure. As one of the properties of tin nitride, we found that amorphous tin-nitride (a-SnN) films prepared by reactive ion plating show an erectrochromic (EC) phenomenon, which is a reversible color change of materials induced by applying a burst of electrical charge. We have reported that the EC phenomenon occurs due to the change of surface adsorption at indium nitride film, so that the color-change efficiency is strongly influenced by surface area. Moreover, it is influenced by crystallinity. Therefore, both the expansion of surface area and the improvement of crystallinity are important. In this study, we aim to investigate the properties of reactive-sputtered tin-nitride thin film prepared by glancing angle deposition (GLAD). 2. Experimental procedure The tin-nitride films were prepared by using a conventional rf magnetron sputtering system. After evacuation of a deposition chamber under 1×10^{-3} Pa, high-purity N_2 gas was introduced into the chamber up to 1 Pa. Then rf power (13.56MHz, 75W) was applied to a metallic tin target of 4N purity. The angle of a substrate holder against the sputtered tin flux was set at 0° and 85°. In-plane rotation condition of the substrate holder was controlled by a motor. We used both Si (100) single crystal wafers and glass plates as substrates. The substrate temperature was controlled by a halogen spot heater. Crystallinity and microstructure of the films was characterized by an X-ray diffractometer (XRD) and a scanning electron microscope (SEM). 3. Results In the case of non-heating substrates, we confirmed that both the samples deposited at 0° (sample A) and at 85° (sample B) have the spinel (Sn_3N_4) crystal phase. The cross-sectional surfaces of the sample A showed a dense columnar structure. EC characterization revealed that the sample A shows no EC phenomenon. On the other hand, the microstructure of the sample B is quite similar to the microvillus structure of small intestine, which consists of isolated nanocolumns. The sample B showed small EC phenomenon, which may due to the surface area much expanded than that of the sample A.

SE-ThP5 Electrochromic Response of InN Thin Films with Microstructures Controlled by Glancing-angle Deposition, ***H. Ishikawa**, H. Takeuchi, Y. Inoue, O. Takai*, Nagoya University, Japan

1. Introduction Electrochromic (EC) materials change their colors reversibly by applying a burst of electrical charge. Indium nitride (InN) thin films also show EC phenomenon by applying electric potential in a solution. The mechanism of the EC phenomenon in InN is quite unique. We have found that the EC of InN is induced by alternation of surface adsorbates, which

means that InN is suitable for high-response EC devices. We have improved the EC properties of InN films by introducing a microvillus-like isolated nanocolumnar structure prepared by glancing-angle deposition (GLAD) in order to expand the effective surface area. However, the microvillus-like structure includes so deep gaps that the EC response property is degraded. In this study, we deposit InN films which have large effective surface area with low-height columnar structure, and their EC response property is investigated. 2. Experimental procedure InN films were deposited on ITO-coated glass plates by using a reactive ion plating system. After evacuation of a deposition chamber, pure N_2 gas was fed into the chamber at a constant gas flow of 19.0 sccm. The total pressure was controlled from 1.0 to 7.0 Pa. In order to activate N_2 plasma, a 13.56 MHz RF power of 150 W was applied to a RF antenna in the chamber. The crucible for In was resistively-heated to evaporate In metal shots (6N) in the N_2 plasma. The substrate holder was rotated during deposition at the angle of 0° or 85° with respect to the vapor fluxes. The crystallinity of the deposited films was investigated by using an X-ray diffractometer (XRD). We investigated the EC properties of the films by using both a UV-Vis spectrophotometer and an EC response measuring unit which consist of a laser diode (650 nm) and a Si photodiode. 3. Results From the XRD profiles, we confirmed that any film deposited in this study has a wurtzite crystal structure. The films deposited without GLAD technique at the total pressure of 1.0 Pa (sample A) and 2.0 Pa (sample B) have a vertical columnar structure with the columnar radius and porosity dependent on the pressure. The EC response of the sample B is faster than that of the sample A. The film deposited with GLAD configuration at the substrate angle of 85° (sample C) has much higher porosity than the samples A and B. Therefore the EC amplitude of the sample C is improved, while the EC response of the sample C was almost same as that of the sample A.

SE-ThP6 Hard Transparent Conducting Nb-doped Titania Films by Reactive Co-Sputtering, ***K.H. Hung***, *H.C. Hsing, W.C. Hsu, M.S. Wong*, National Dong Hwa University, Taiwan

The outstanding properties of titania have made them useful for many applications including photocatalysis, gas sensors, dielectric thin-film capacitors and solar cells. However, researchers have not paid much attention to their transport properties and mechanical behaviors. We have produced a series of niobium-doped titania films by reactive co-sputtering titanium and niobium targets and by subsequent annealing the films in a hydrogen environment. The composition of the films was modulated by changing the niobium target power; consequently, niobium content of the films changed from 0 to 4.2 atomic percent. The characterization studies show that the annealed films are polycrystalline with anatase phase without accompanying other crystalline oxide phases. The results also demonstrate that the films possess high visible-light transparency as well as enhanced hardness and conductivity. For instance, the doped titania film of 2.8 at% Nb deposited at a substrate temperature of 350 °C and annealed at 600°C exhibits an average transmittance of 70% in visible light region and a high hardness up to 11.4 GPa. Moreover, the Hall measurements of the film reveal n-type semiconducting behavior for this film with a reduced resistivity of 9.2E-4 ohm-cm, a carrier density of 6.61E21 cm^{-3} and a mobility of 1.0 $cm^2v^{-1}s^{-1}$.

SE-ThP7 Effect of Water Pulsed Plasma on Electrode Surface, ***N. Apetroaei***, *N. Saito, O. Takai*, Nagoya University, Japan

The aim of this paper is to contribute to a better understanding of the mechanisms, which conducted to the electrode surface modifications using the water plasma, and to correlate these experimental results with the results which we obtained from diagnosis of the plasma. The water pulsed plasma is non-equilibrium highly collisional plasma produced at rather high pressure by high voltage pulse applied to a special system of electrodes. Different electrode materials, shapes and configuration have pronounced effect on liquid discharge. In our case were used to form the electrodes, wire and rod of copper, tungsten, tantalum, molybdenum, nickel and stainless steel (SUS) with different diameter from 1mm up to 3mm for tip to tip electrode configuration and sheet of Cu and SUS for plan to plan and tip to plan electrode configuration. The high voltage power supply (4 kV) generates bipolar pulses in the range of 2 – 10μs and frequency in the range of 1 - 30 kHz. Modification of surface properties of a metallic electrode has been analyzed by contact angle measurement, scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS). Water plasma changes the electrode surface structure. There are few things which conduct to these changes. One is strong local heating and formation of hot spots at the electrode surface. Temperatures above the boiling point of the electrode material can de necessary depending on the work function of the metal. Another is discharge physical sputtering caused by the collision of energetic electrons or other heavy particles with electrode surface. Another is the chemical reaction between water plasma and electrode surface. Water plasma generates very active species such as: chemical aggressive atoms and radicals, charged particles-electron and ions, excited atoms and molecules. After solution plasma we observed that the proprieties (surface tension, adhesion work, roughness, oxidization) of electrode surface have changed, comparing to a new one unused to water plasma. Surface wettability is improved from contact angle measurements and SEM images show an increase of surface roughness.

SE-ThP8 A Comparative Study on the Mechanical Properties and Thermal Stability of Cr-Zr-N and CrSi-Zr-N Coatings Synthesized by Closed Field Unbalanced Magnetron Sputtering, ***G.S. Kim***, *Y.S. Kim, S.M. Kim, S.Y. Lee, B.Y. Lee*, Korea Aerospace University

Recently, the synthesis of Cr-Zr-N coatings by adding an heterogeneous atom, Zr into CrN film was successfully made using a closed field unbalanced magnetron sputtering and these Cr-Zr-N coatings are reported to have not only much improved mechanical properties, but also a very low surface roughness with increasing Zr content. Especially, the average friction coefficient against Al_2O_3 counterpart ball of the $Cr_{1-x}Zr_xN$ (X=0.34) coating was measured to be approximately 0.17 at room temperature and this value is approximately 3.5 times lower than that of CrN film (approximately 0.6). However, investigations on the high temperature characteristics of the Cr-Zr-N coatings revealed their mechanical properties are severely deteriorated at 500 ℃ due to the surface oxidation and the decrease of hardness by means of the residual stress relaxation. In this work, to improve the high temperature mechanical properties of the Cr-Zr-N films, the CrSi-Zr-N coatings were synthesized from CrSi(Si=10 and 20 at.%) and Zr targets by a closed field unbalanced magnetron sputtering and their chemical composition, crystal structure, morphology and mechanical properties were characterized by glow discharge optical emission spectroscopy (GDOES), X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM) and nanoindenter. Also, the thermal stability of the CrSi-Zr-N coatings was evaluated by annealing the thin films at temperatures between 300 and 900 ℃ for 30min in air. The experimental results showed the CrSi-Zr-N coatings exhibit higher thermal stability and mechanical properties compared to those of Cr-Zr-N coating with increasing Si content. Detailed experimental results included wear test at 500 ℃ will be presented.

SE-ThP9 A Comparative Study on the Thermal Stability of CrN, CrSiN and CrSiN/AlN Multilayer Coatings, ***S.M. Kim***, *G.S. Kim, S.Y. Lee, B.Y. Lee*, Korea Aerospace University

In this work, CrN, CrSiN and CrSiN/AlN multilayer coatings were synthesized from Cr, Al and CrSi (Si= 10 at. %) targets using a closed-field unbalanced magnetron sputtering system (CFUBMS). The coatings have been characterized by glow discharge optical emission spectroscopy (GDOES), X-ray diffractometry (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and nano-indentation. The maximum hardness of CrSiN/AlN multilayer coating with the bilayer period (@lamda@) of 3 nm was approximately 32 GPa, whereas CrN and CrSiN coatings exhibited the maximum hardness of 22 and 27 GPa, respectively. Thermal stability of CrN, CrSiN and CrSiN/AlN multilayer coatings was investigated with annealing treatment for 30 min in air in the temperature range of 600 to 800 °C. The XRD patterns showed that CrN and CrSiN coatings were severely oxidized at 700 °C. However, in the case of CrSiN/AlN multilayer coating, no detectable oxides were observed even at 800 °C. After annealing at 800 °C, the hardness of the CrSiN/AlN multilayer coating exhibited approximately as high as 29 GPa compared to the CrN and CrSiN coatings, which showed only 8 and 18 GPa, respectively. These results revealed that the thermal stability of the CrSiN/AlN multilayer coatings were much superior to that of the CrN and CrSiN coatings at elevated temperatures because the AlN films in the CrSiN/AlN multilayer coatings retard the oxygen diffusion into the coatings. The detailed experimental results will be presented.

SE-ThP10 Investigation of Photocatalytic Activity of TiO_2/WO_3 Bilayered Thin Films with Various Amounts of Exposed WO_3 Surface, *S. Biswas, M.F. Hossain, M. Shahjahan,* ***K. Takahashi****, T. Takahashi*, University of Toyama, Japan, *A. Fujishima*, Kanagawa Academy of Science and Technology, Japan

TiO_2 is the most widely used photocatalyst for effective decomposition of organic compounds in air and water. However, its technological application is limited by the need for an ultraviolet (UV) excitation source. One of the most promising methods to extend the light-absorbing property of TiO_2 and to enhance its photocatalytic efficiency is to couple TiO_2 with narrow-bandgap semiconductors, which act as a sensitizer. Tungsten oxide (WO_3) with band-gap 2.8 eV, is a promising candidate to be used as under-layer for TiO_2 photocatalysts. However, WO_3 should have some amount of uncovered surface so that it can act as a reducing agent. In this study, WO_3 films were deposited on glass substrates, using facing target dc reactive sputtering technique and the upper TiO_2 thin films were also deposited with the same technique using different masks to leave various amounts of WO_3-exposed surfaces: 0%, 30% and 80%. The crystallographic properties, surface structures and optical properties of WO$_3$ films were investigated in detail. The X-ray diffraction patterns show triclinic and anatase crystal structure for the WO$_3$ films and TiO$_2$ films, respectively. The optical and surface morphological properties of both WO$_3$ and TiO$_2$ layers have been studied using UV-visible spectrometer, field emission scanning electron microscope (FESEM) and atomic force microscope (AFM). The photocatalytic activity was measured by the rate of photodecomposition of methanol in UV and visible light irradiation, evaluated by Fourier transform infrared spectrometer (FTIR). The results show that with the variation of WO$_3$ exposed area, photocatalytic activity of WO$_3$/ TiO$_2$ system varies significantly. It is revealed that, with the increase of WO$_3$-exposed surface photocatalytic activity increases initially, but it decreases with the further increase. The result has been tried to be explained on the basis of methanol-photodecomposition mechanism and the amount of relative exposed surface of WO$_3$ and TiO$_2$.

SE-ThP11 Structural, Optical and Photocatalytic Study of Spray Pyrolysis-Deposited ZnO: Al Thin Films

M. Shahjahan, University of Toyama, Japan, *K.R. Khan,* Rajshahi University, Bangladesh, *M.F. Hossain, S. Biswas,* University of Toyama, Japan, *T. Takahashi*, Toyama University, Japan

ZnO is a semiconductor with unique properties such as transparency in the visible and high infrared reflectivity, acoustic characteristics, high electrochemical stability and excellent electronic properties. ZnO has received much attention because of its promising applications of optoelectronic nano-devices, piezoelectric nano-generators, dye-sensitized solar cells, bio-devices and photocatalysts for degradation and complete elimination of environmental pollutants. Porous ZnO films with large surface area have great applications in photovoltaic and photocatalytic devices. Moreover Al-doped ZnO (ZnO:Al) shows lower band gap. In the present study an effort has been made to fabricate ZnO:Al on glass substrate using low-cost spray pyrolysis method with higher surface area. Structural, optical, electrical and surface morphological studies of the fabricated films have been performed. Photocatalytical activity of the fabricated films has been studied. The crystal structure of annealed samples was investigated by X-ray diffraction (XRD). XRD patterns show crystalline nature of the spray deposited ZnO and Al-doped ZnO thin films with three main peaks, (100), (002) and (101) planes. ZnO crystal has wurtzite structure and the calculated lattice constants a and c are 3.242 Å and 5.209 Å respectively and the grain sizes are in the range of 16.75 to 52.19 nm. The surface morphology of the films was observed by a scanning electron microscope. It has been observed that the film surfaces are varied with the deposition conditions and doping concentrations. The spectral absorption coefficient of the ZnO and ZnO:Al films was determined using the spectral data of transmittance and reflectance in the UV-visible wavelength range. The direct and gap energies for ZnO and ZnO:Al were determined and the values obtained are 3.2 eV and 2.88 eV, respectively. Photocatalytic activity of ZnO:Al thin films have been evaluated with various pollutant under UV-visible irradiation.

SE-ThP12 Strain-Rate Sensitivity of Nanocrystalline Nanolaminates

H.S.T. Ahmed, *A.F. Jankowski*, Texas Tech University

The strain-rate sensitivity of strength is one of the key parameters to understand the deformation mode of nanocrystalline materials. It is widely reported that many nanocrystalline materials strength harden with increasing strain rate. Often, an increasing strain rate exponent is observed as the grain size decreases from the micro- to the nano- scale. This trend suggests that the mode of mechanical deformation is transitioning from within the grains to becoming a grain boundary effect. For nanocrystalline nanolaminates, another dimensional feature becomes significant. The layer pair spacing must now be accounted for in addition to the grain size. This additional nanoscale feature can become especially important when its size decreases below that associated with conventional dislocation-based strengthening mechanisms. We now investigate the hardness of transition metal nanolaminates for which both grain size and laminate dimensions are less than 10 nm. New data is acquired through the technique of nanoscratch testing. We report an increasing rate sensitivity of strength, as measured by the plastic flow associated with hardness, when dimensional features are further reduced to below 10 nm.

SE-ThP13 Effect of Deposition Temperature on Microvillus-structured InGaN Films Deposited by Glancing-angle Reactive Evaporation

H. Takaba, ***H. Takeuchi***, *Y. Inoue, O. Takai*, Nagoya University, Japan

1. Introduction Electrochromic (EC) materials have a unique property of reversible color change with a burst of electrical charge. Much attention has been paid to the EC materials for application to “smart windows”, which control electrically the light and heat through the windows. We have investigated the EC properties of indium nitride (InN). The EC of InN is based on so-called Burstein-Moss shift induced by alternation of surface adsorbates. We have improved the EC properties of InN both by doping Ga to shift the color-change wavelength region and by introducing a biomimetic structural design in nano order to increase the EC amplitude. In this study, we deposit microvillus-structured InGaN films at some substrate temperatures and investigate the effect of deposition temperature on crystallinity, biomimetic structure and EC properties. 2. Experimental procedure The Ga-doped indium nitride (In$_{1-x}$Ga$_x$N, $0 \leq x \leq 1$) films were deposited in a vacuum evaporation system assisted with an active nitrogen source. Indium and gallium were deposited simultaneously from respective crucibles through a downstream of the nitrogen plasma generated from the active nitrogen source at the conditions of the nitrogen pressure of 0.04 Pa and the RF power of 300 W. The substrate holder was rotated at the speed of 10 rpm with the angle against the metal fluxes at 85° in order to synthesize the biomimetic microvillus-like nanostructures, and heated by lamp heater from behind. Crystallinity, microstructure and EC properties of the In$_{1-x}$Ga$_x$N films were characterized by XRD, FE-SEM and UV-VIS spectrophotometry, respectively. 3. Result From XRD analysis, we confirmed that the In@1-x@Ga@x@N films prepared at high substrate temperature had higher crystallinity than at non-heated temperature. EC measurements showed that the EC amplitude of InGaN increased with the crystallinity improvement at high Ga composition. However, at low Ga composition, that of prepared at 150°C was larger than at 200°C because the effective surface area decreased due to microstructure evolution.

SE-ThP14 Surface of Pb1-xSnxTe Films by Pulsed Laser Deposition

M. González-Alcudia, CICATA-IPN, México, *M. Meléndez-Lira*, CINVESTAV-IPN, México, *O. Calzadilla-Amaya,* Universidad Habana, Cuba, ***M. Zapata-Torres***, CICATA-IPN, México

The interest in pulsed deposition was tirggered by the observation that PLD is superior to thermal deposition in inducing layer by layer growth of heteroepitaxial metal films. We present the design of a pulsed laser deposition modified system (PLD-M) which is suitable for materials engineering work. Various concepts in growth structure of Pb1-xSnxTe films for PLD-M have been pursued to optimize its performance. A macroscopic description of growth insatabilitiesn of Pb1-xSnxTe films is usually presented in the framework of only 2D nucleation, determined by the supersaturation, limited interlayer mass transport results in nucleation on top of 2D islands before completion of a film layer. Extensive measurements (AFM, XRD and SEM) were carried out to test the micro structural characteristics of the Pb1-xSnxTe films. In the case of PLD-M, a typical value for the deposition rate within one pulse is of the order of 10 mm/s and the radius of droplets formed during single pulse irradiation is the r KH ≈ 0.05 μm. These new approaches offer new possibilities for further development of the field in close connection with surface science and materials science.

SE-ThP15 Enhancement of Hydrophilicity and Photo Catalytic Activities of Nanocrystalline TiO$_2$ Thin Film Doped with Tungsten

R.R. Pandey, K.K. Saini, National Physical Laboratory, India, ***M. Dhayal***, University of Washington, *C. Chander Kant, S.C. Jain*, National Physical Laboratory, India

In this study tungsten ion doped nanocrystalline TiO2 thin films has been fabricated using dip-coating technique on glass substrates. Surface structure and chemistry of the films was characterized using X-ray diffraction, transmission / scanning electron microscopy, UV-visible spectroscopy, X-ray photoelectron spectroscopy and FTIR. The tungsten ions doping in the film have significant influence on the morphology and surface chemistry. These nanocrystalline films have shown improved activity on the oxidation of organic pollutants possibly due to enhanced surface area with more active site in presence of tungsten.

SE-ThP16 High Power Pulse Plasma Generator for Material Processing

R. Chistyakov, Zond Inc., ***B. Abraham***, Zpulser LLC

High Power pulse Plasma Generator for Material Processing. Roman Chistyakov1,2, Bassam Abraham1,2 Zond, Inc1/Zpulser2, LLC, 137A/137 B High Street, Mansfield, MA 02048, A new high power pulse plasma generator was developed. This plasma generator can generate negative arbitrary voltage pulse shapes in the range 200 – 1500 microsecond in wide range of output power. By applying these pulses to the sputtering magnetron arbitrary pulse power magnetron discharge can be produce. The typical arbitrary voltage pulse shape for magnetron sputtering consists from two stages. The first stage is a low power discharge and the second stage is a high power discharge. The presence of two power stages in one pulse reduces the probability to have arc and increases ionization of sputtered material. High power pulse plasma generator is a switching power supply. User friendly software enables full control of the switching device. This plasma generator was successfully used for different sputtering applications including reactive and non reactive processes. The principals of building arbitrary voltage pulse shapes will be discussed. The examples of different voltage pulse shapes for different sputtering conditions will be presented.

Advanced Surface Engineering
Room: 204 - Session SE+PS-FrM

Pulsed Plasmas in Surface Engineering
Moderator: A. Erdemir, Argonne National Laboratory

8:20am **SE+PS-FrM1 On the Plasma Parameters in the High Power Impulse Magnetron Sputtering Discharge (HiPIMS)**, ***J.T. Gudmundsson***, University of Iceland **INVITED**

The development of ionized physical vapor deposition (IPVD) was mainly driven by the formation of metal and nitride thin films into deep, narrow trenches and vias that are essential in modern microelectronics. More recently, the control of the ion energy and direction of the deposition species has proved to be an important physical tool in the growth process of new materials and new structures. Over the past few years, various ionized sputtering techniques have appeared that show a high degree of ionization of the sputtered atoms, in the range 50 - 90 %. This is often achieved by the application of a secondary discharge to a magnetron sputtering discharge, either inductively coupled plasma source (ICP-MS) or a microwave amplified magnetron sputtering[1]. High power impulse magnetron sputtering (HiPIMS) is a more recent sputtering technique that utilizes ionized physical vapor deposition (IPVD)[1],[2]. High density plasma is created by applying a high power pulse to a planar magnetron discharge. Measurements of the temporal and spatial behavior of the plasma parameters indicate peak electron density of the order of 10^{19} m^{-3}, that expands from the target with a fixed velocity that depends on the gas pressure[3]. The high electron density results in a high degree of ionization of the deposition material. Fractional ionization of the sputtered material has been measured to be over 90 %[2]. The ions are controllable with respect to energy and direction as they arrive to the growth surface. The spatial and temporal variation of the plasma parameters, electron density, electron energy, plasma potential and ion energy, in a HiPIMS discharge are reviewed. The plasma physics of the HiPIMS will be discussed as well as some of applications of the HiPIMS technique.

[1] U. Helmersson, M. Latteman, J. Bohlmark, A. P. Ehiasarian, and J. T. Gudmundsson, Ionized Physical Vapor Deposition (IPVD): A Review of Technology and Applications, Thin Solid Films 513 (2006) 1-24

[2] U. Helmersson, M. Lattemann, J. Alami, J. Bohlmark, A.P. Ehiasarian, and J.T. Gudmundsson, Proceedings of the 48th Annual Technical Conference of the Society of Vacuum Coaters, April 23-28, 2005, Denver, CO, USA, p.458

[3] J.T. Gudmundsson, J. Alami, and U. Helmersson, Spatial and temporal behavior of the plasma parameters in a pulsed magnetron discharge, Surf. Coat. Technol. 161 (2002) 249 .

9:00am **SE+PS-FrM3 Deposition of Metal Oxide Coatings using Reactive High Power Impulse Magnetron Sputtering**, ***E. Wallin***, *M. Aiempanakit,* Linköping University, Sweden, *T.I. Selinder, E. Coronel,* Sandvik Tooling, Sweden, *U. Helmersson*, Linköping University, Sweden

Metal oxides have been deposited using reactive high power impulse magnetron sputtering (HiPIMS) of metal targets in Ar/O_2 gas mixtures. The use of HiPIMS has in previous studies of deposition of alumina been shown to drastically influence the process characteristics compared to conventional reactive sputtering [Wallin and Helmersson, Thin Solid Films, in press]. Under suitable conditions, oxide formation on the target was found to be suppressed, and the hysteresis effect commonly observed as the gas flow is varied during conventional sputtering was reduced, or even completely eliminated, using HiPIMS. In the present work, these investigations are extended to a wider range of process parameters as well as to other material systems, including CeO_2, in order to better understand the reactive process. Based on this, reasons for the altered process characteristics will be discussed. Moreover, film properties of alumina deposited by this type of process have been investigated. α-alumina was found to form readily on both cemented carbide and Mo substrates at a temperature as low as 650 °C. α phase growth was retained over the studied range of substrate bias voltages (from floating potential to -100 V), while growth at lower temperatures resulted in the formation of γ-alumina at 575 °C and x-ray amorphous films at 500 °C or lower. The film microstructure was studied using electron microscopy techniques, revealing a plate-like structure of the α-alumina films with wider grains and a denser structure for higher bias values. Reasons for the phase composition and microstructure observed with different process parameters will be discussed together with possible pathways for further reduction of the α-alumina growth temperature and improvements of the microstructure.

9:20am **SE+PS-FrM4 A Mass/Energy Analysis of the Plasma during Modulated Pulse Power Sputtering**, ***W.D. Sproul***, Reactive Sputtering, Inc., *J. Lin, J.J. Moore, M. Hasheminiasari,* Colorado School of Mines, *R. Chistyakov, B. Abraham*, Zond, Inc./Zpulser, LLC

During modulated pulse power (MPP) sputtering, there are multiple steps within the overall pulse. Usually there are 3 steps, but there can be many more if needed. The first step is the application of a high voltage to the cathode that ignites a weakly ionized sputtering plasma. This weakly ionized plasma is allowed to stabilize in step 2, and then the voltage to the cathode is increase to transition the plasma into a strongly ionized plasma in step 3. This strongly ionized plasma is characterized by a significant increase in the current to the cathode accompanied with a moderate voltage increase. The overall power to the cathode is thus also greatly increased. At the substrate when a bias is used, there is also an increase in the substrate ion current density during step 3, and this ion current density increases as a function of the peak power. The deposition rate for the Cr films is a function of the peak power on the target, but there is a pronounced increase in the deposition rate when the peak power exceeds approximately 100 kW. In this study, a mass/energy analyzer was used to characterize the species in the plasma during the different steps of MPP sputtering of Cr films. Cr plus one ions were readily detected by the mass/energy analyzer in step 3 of the pulse, but it was more difficult to detect multiply charged Cr ions due to the location of the analyzer with respect to plasma and the target. It is possible that multiply ionized Cr ions are not detected due to charge exchange collisions in the plasma. The changes in the species in the plasma will be correlated with observed changes in the structure and properties of the Cr films deposited under different peak power conditions.

9:40am **SE+PS-FrM5 Process, Structure and Properties of Chromium and Chromium Nitride Coatings Synthesized using Modulated Pulse Power (MPP) Sputtering**, *J. Lin, Z. Wu,* Colorado School of Mines, *W.D. Sproul,* Reactive Sputtering, Inc., *B. Mishra,* ***J.J. Moore***, *M. Hasheminiasari,* Colorado School of Mines, *R. Chistyakov, B. Abraham*, Zond, Inc./Zpulser, LLC

Modulated pulse power (MPP) sputtering is a variation of high power pulse magnetron sputtering that overcomes the rate loss issue and achieves the enhanced plasma ionization through modulation of the pulse shape, intensity, and duration. In the current studies, Cr and CrN coatings were synthesized using MPP under different pulse durations and different combinations of the voltage rise and fall times, which were found to exhibit strong influence on the deposition parameters. It was found that the target power, voltage, current, and ion current density were increased with an increase in the long pulse durations and the voltage rise time. For Cr coating depositions, the MPP exhibits higher deposition rates than in the dc conditions when the average power is about 10-12 W/cm^2. A high deposition rate of 230 nm/min for the Cr coating deposition can be achieved with optimized pulsing parameters. The structure of the Cr and CrN coatings were characterized using x-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The mechanical and tribological properties were measured by performing depth-sensing nanoindentation tests, micro-scratch tests and a ball-on-disc wear test in ambient atmosphere. It was found that the microstructure of the coatings changed from large columnar grains to dense and fine nano grains with an increase in the power and ion current densities on the target. A high hardness of 18 GPa has been achieved in Cr coatings deposited with an average power density of 21 W/cm^2 and an ion current density of 1.2 A/cm^2 on the target with a floating substrate bias.

10:00am **SE+PS-FrM6 Deposition Rate of High-Power-Pulse Magnetron Sputtering Processes**, ***J. Emmerlich***, *S. Mráz, S. Konstantinidis,* RWTH Aachen University, Germany, *R. Snyders,* University of Mons, Belgium, *J.M. Schneider*, RWTH Aachen University, Germany **INVITED**

In high power pulsed magnetron sputtering (HPPMS), a large power density is applied giving rise to a high degree of ionization. From an application point of view, the major drawback of this technology is the considerably lower metal deposition rate as compared to DC magnetron sputtering. Using transport-of-ions-in-matter simulations (TRIM), it is shown that the apparently low deposition rate can be understood based on the non-linear energy dependence of the sputtering yields. The simulations are consistent with deposition-rate measurements on Cu films as well as with published deposition rate data for Ti [Konstantinidis et al., J. Appl. Phys. 99, 013307 (2006)]. TRIM simulations in combination with deposition rate experiments as a function of pulse width using Cu, W, and Ti as target materials reveal predominantly self-sputtering during Cu depositions. For W as well as Ti discharges, Ar contributes significantly more to sputtering, which may be explained by the low metal-self-sputtering yield. HPPMS deposition rates during reactive sputtering are reported to be comparable or even larger compared to DC magnetron sputtering rates [Wallin and Helmersson, Thin Solid Films in press]. Target erosion rate measurements for an HPPMS discharge exhibit two orders of magnitude larger erosion rates compared to DC magnetron sputtering.

10:40am **SE+PS-FrM8 Effects on Thin Film Growth Due to Anomalous Transport in High Power Impulse Magnetron Sputtering**, ***D. Lundin***, *P. Larsson, E. Wallin,* Linköping University, Sweden, *M. Lattemann,* TU Darmstadt and Forschungszentrum Karlsruhe GmbH, Germany, *N. Brenning,* Royal Institute of Technology, Sweden, *U. Helmersson*, Linköping University, Sweden

In this study, the effect of a previously reported anomalous transport[1] on thin film growth in high power impulse magnetron sputtering (HiPIMS) has been investigated for the case of a planar circular magnetron. It was found that a large fraction of ions are transported radially outwards in the vicinity of the cathode, across the magnetic field lines, leading to enhanced deposition rates directly at the side of the cathode (on a substrate oriented perpendicular to the target surface). An important consequence of this type of mass transport parallel to the target surface is that the fraction of sputtered material reaching a substrate placed directly in front of the target is substantially lower in HiPIMS compared to conventional direct current magnetron sputtering (dcMS). This would help to explain the lower deposition rates generally observed for HiPIMS compared to dcMS. Moreover, time-averaged mass spectrometry measurements of the energy distribution of the cross-field transported ions were carried out. The measured distributions show a direction-dependent high-energy tail, which can be explained by an increase in the azimuthal force on the ions, exerting a volume force on the ions tangentially outwards from the circular race track region. These results are in agreement with predictions as well as recent modeling results of the anomalous transport mechanism.

[1] D. Lundin, U. Helmersson, S. Kirkpatrick, S. Rohde, and N. Brenning, Plasma Sources Sci. Technol. 17, 025007 (2008).

11:00am **SE+PS-FrM9 High Power Impulse Magnetron Sputtering of Ti-Si-C Multifunctional Thin Films**, ***M. Samuelsson***, Linköping University, Sweden, *H. Högberg, H. Ljungcrantz,* Impact Coatings, Sweden, *U. Helmersson*, Linköping University, Sweden

Nanocomposite Ti-Si-C thin films grown by dc-magnetron sputtering (dcMS) are interesting for many applications, such as in electrical contacts. This is due to a property envelope including low contact resistance, ductility and hardness that can be combined. Other areas of applications are also suggested, which call for increased possibility to design the material for specific needs. A promising deposition technique is high power impulse magnetron sputtering (HiPIMS), which offers a high degree of ionization of the sputtered material not found in conventional dc-magnetron sputtering. Growth from ions instead of neutrals is likely to further increase the possibility of designing the film microstructure and thereby the properties. In this study we have investigated sputtering from a Ti_3SiC_2 target by HiPIMS and compared the technique with dcMS. The techniques have been compared for different process pressures and substrate bias voltages using a pilot plant deposition system under production like conditions. The results show that the obtained HiPIMS growth rate was approximately 13% of that of dcMS for comparable average powers. Further studies employing SEM, TEM, XRD measurements, surface resistivity and film adhesion will be presented.

11:20am **SE+PS-FrM10 Modulated Pulse Power Deposition of Aluminum Oxide Nanometer Scale Multilayer Films**, ***R. Chistyakov***, Zond Inc., *B. Abraham,* Zpulser LLC, *W.D. Sproul,* Reactive Sputtering, Inc., *J.J. Moore, J. Lin*, Colorado School of Mines

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. Different levels of applied voltage in the same voltage pulse will generate different power levels for the magnetron discharge. Usually each pulse shape has a weakly ionized plasma (low power magnetron discharge) step that was generated first, and then the second stage that has a strongly ionized plasma (high power magnetron discharge) by applying a voltage increase to the cathode. These arbitrary voltage pulse shapes can be used within a given deposition run to form multilayer film structure. Therefore every layer can be sputtered with a different voltage pulse shape. In this study, two different voltage pulse shapes were selected. The first pulse had a shorter duration that the second pulse, but by varying the repetition rate the same average power could be delivered during the sputtering of each layer. The peak power applied to the plasma was greater during the second pulse, which meant that a greater amount of energy was applied to the process during the peak power phase of the second pulse. The difference in the applied energy between the two MPP pulse shapes was used during the reactive sputter deposit of aluminum oxide films . This two-pulse approach did produce a nanometer scale layering of the aluminum oxide coatings, which was observed in a scanning electron microscope. The thickness and structure of each nanometer scale layer was controlled by varying the output voltage pulse shape of the MPP plasma generator and deposition time. The layering of the aluminum oxide affected not only the structure of the films, but it also affected the mechanical properties of the films. The film structure, orientation, and mechanical properties were analyzed and measured, and the results of the film property measurements will be presented.

11:40am **SE+PS-FrM11 The Specification and Optimization of HIPIMS Power Supply Parameters**, *D. Ochs,* Huettinger Electronics GmbH, Germany, *P. Ozimek,* Huettinger Electronics Sp. z.o.o., Poland, ***A.G. Spencer***, Alacritas Consultancy Ltd., UK

HIPIMS is a rapidly emerging technique for surface modification. It is well know the improvements in surface properties that can be acheived (in particular in mechanical properties). What is less well known is how to specify and operate the HIPIMS power supply. There are many aspects of the HIPIMS power supply that need to be specified at time of purchase, and adjusted for process optimization (average power, pulse power, pulse frequency, pulse length). Usually HIPIMS users are upgrading from a sputtering or evaporation process. These new HIPIMS parameters are therefore unfamiliar. This paper details the effects of each of these parameters, gives examples, and guidance on specifying a HIPIMS power supply.

Authors Index

Bold page numbers indicate the presenter