

# Wednesday Morning, November 15, 2006

## Advanced Surface Engineering Room 2007 - Session SE-WeM

### Glancing Angle Deposition

Moderator: D. Gall, Rensselaer Polytechnic Institute

8:00am **SE-WeM1 New Developments in Glancing Angle Deposition, M.J. Brett**, University of Alberta, Canada

The Glancing Angle Deposition (GLAD) process has been the subject of considerable study over the last 10 years, and significant improvements in the quality of and control over film nanostructure have been demonstrated. This presentation will report two of the recent developments that have extended the range of materials deposited and have provided new architectures with promising applications. First, using GLAD in conjunction with an advanced substrate motion algorithm called PhiSweep, we have been able to tune the column diameter of vertical post microstructures from the typical 200nm width to values as small as 20nm, demonstrated in both Si and Ti films. This control is enabled by a periodic sweep of the substrate about the desired orientation, in a manner that defeats the tendency of a growing column to broaden. An application of such films to microfluidics will be demonstrated. Second, we have recently used e-beam evaporation and the GLAD process for deposition of organic tris-(8-hydroxyquinoline) aluminum (Alq3) with chiral and post nanostructures. The films produced show helices arranged in a near periodic self organized array over the substrate, and also display a remarkable structural uniformity. Alq3 is commonly used as an organic luminescent material, thus characterization of the luminescent and optical properties will be reported.

8:20am **SE-WeM2 Effects of Shadowing on Microstructure Evolution during Oblique Angle Deposition, T.-M. Lu**, Rensselaer Polytechnic Institute

INVITED

The study of thin film surface morphology and microstructure is still one of the most intriguing and challenging research areas in thin film science and technology. The geometrical structure and crystal orientation of the thin film growth front formed by the physical vapor deposition technique are controlled by many factors including: surface diffusion, sticking coefficient, and shadowing. Instabilities of growth can occur if the shadowing is more dominant compared to other surface effects and can lead to many diverse physically self-assembled 3D quasi-periodic nanostructures. In this talk I will discuss the fundamental nucleation and growth mechanisms of isolated islands resultant from the shadowing effect in an oblique angle deposition configuration (which becomes a glancing angle deposition when the angle between the incident flux and the surface normal is close to 90°). We explain the formation of the quasi-periodic nature of the islands, which transform into a columnar structure, by a shadowing length  $\lambda_{sh}$  concept that is similar to the surface diffusion length in conventional thin film growth. We show that the change in the spatial frequency of the periodicity is a result of the elimination of shorter columns due to the shadowing effect during growth. Another interesting aspect is the dramatic change of crystal orientation of the islands during growth. Typically, the initial islands with random crystal orientations are transformed into a fiber texture structure with a tilt angle (with respect to the surface normal) which is correlated to the angle of the incident deposition flux. Vertices of columns having the highest growth velocity normal to the substrate receive the maximum flux and would dominate the film growth. Most intriguingly, the columns often develop a well defined azimuthal orientation even when the substrate is amorphous. The shadowing effect combined with the geometrical effect is proposed to explain these phenomena.

9:00am **SE-WeM4 Super Poisson Growth through Glancing Incidence Deposition, H. Wormeester, F.L.W. Rabbering, T. Warnaar, B Poelsema**, MESA+ Institute for Nanotechnology, Netherlands

Short - and long range attractive forces between a substrate and an incoming atom result in a morphology dependent heterogeneous flux. Already at submonolayer coverage, this flux heterogeneity leads to shape anisotropy of Cu-ad-structures on Cu(001). With increasing coverage the anisotropy becomes progressively larger and above 20 ML strongly rectangular mounds have formed. The anisotropy has been revealed by high resolution electron diffraction. For Co on Cu(001) also the formation of a strongly uniaxial magnetic axis was observed. The evolution of the morphology as a result of the steering effect, the change in trajectory of incoming atoms as a result of attractive forces has been modeled within a KMC scheme that takes into account many of the diffusion processes

known to occur on the Cu(001) surface. Simulations show that pure geometric shadowing does not lead to the reproduction of most of the experimentally observed anisotropy features. However, the incorporation of the steering effect does allow to reproduce many of the experimental details. The focus of the flux near ascending steps results in a strong increase of the roughness of the grown layer. For normal incidence, the roughness increases finally with an exponent  $\beta=0.5$ , i.e. a Poisson distributed roughness, while initially even growth oscillations are observed. Above a polar angle of incidence of 60°, the roughness increase is much larger and exponents up to  $\beta=2$  are found, i.e. super Poisson roughness. Both the asymmetry and the strong roughness increase bear potential for technological applications.

9:20am **SE-WeM5 Formation of Al Nanowires by High Temperature Glancing Angle Deposition, M. Suzuki, K. Nagai, K. Nakajima, K. Kimura**, Kyoto University, Japan; **T. Okano, K. Sasakawa**, KOBELCO Research Institute, Inc., Japan

It is well known that the physical origins of the columnar structure in obliquely deposited thin films are the self-shadowing effects and the limited mobility of the deposited atoms. In order to keep the mobility at low value, the substrate temperature was kept as low as possible in most works on the morphology control by oblique deposition. Recently, some peculiar properties for the crystallographic orientation<sup>1</sup> and the compositional distribution<sup>2</sup> in the obliquely deposited thin films have been reported. These works suggest that the novel/metastable phases can be expected to grow by controlling the mobility of obliquely deposited adatoms. However, it is not easy to predict the growth mode for the high temperature oblique deposition, since conventional crystal-growth theories treat only the case in which the atoms are supplied homogeneously. In this work, we investigated experimentally the growth of obliquely deposited Al films on a high temperature substrate. Al was deposited onto a Si or glass substrate held at a temperature of RT-400 °C at a deposition angle  $\alpha=58-85^\circ$ . Average thickness of deposited Al was 72-78 nm for all samples. The ordinary oblique columnar structures, which were observed in the films deposited at RT, completely disappeared for the samples deposited at 400 °C and the rugged granular structures were formed. In addition to the grains, we found nanowires of 30-300 nm in diameter and  $> 0.5 \mu\text{m}$  in length for the samples deposited at  $\alpha > 73^\circ$ . TEM observations clarified that these nanowires were single crystalline aluminum. The number and the size of nanowires increased with increasing  $\alpha$ . This indicates that the shadowing effect plays an important role even at the high temperature region, where the mobility of adatoms becomes high. <sup>1</sup>T. Karabacak et al., Appl. Phys. Lett., 83 (2003) 3096. <sup>2</sup>S. Jomori et al., Mater. Res. Soc. Symp. Proc., 849 (2005) 127.

9:40am **SE-WeM6 Ta Nanocolumns Grown by Glancing Angle Deposition: Effect of Surface Diffusion on Column Branching, Merging, and Growth Competition, C. Zhou, D. Gall**, Rensselaer Polytechnic Institute

Periodic arrays of Ta nanocolumns were grown by glancing angle sputter deposition onto patterned substrates at growth temperatures  $T_{sub}$  ranging from 200 to 900 °C. The substrates were patterned using colloidal self-assembly of 260-nm-diameter SiO<sub>2</sub> nanospheres that form a close-packed monolayer. At low growth temperatures,  $T_{sub} \leq 500$  °C, the 200-nm-wide and 500-nm-tall Ta columns replicate the hexagonal arrangement of the initial pattern. However, the arrays randomize with increasing  $T_{sub}$  and completely degrade at  $T_{sub} = 900$  °C, due to strong inter-pillar competition caused by the increasing adatom diffusion length with increasing  $T_{sub}$ . The competitive growth mode results in a decrease in the pillar separation and pillar number density, an increase in the average pillar width, the accelerated growth of some pillars at the cost of others which die out, and an increased probability for the merging of neighboring pillars. In addition, kinetic roughening at pillar tops leads to the branching of some pillars. The fraction of branched pillars decreases with increasing  $T_{sub}$ , due to an increased lateral diffusion length, from 30% at 200 °C to 4% at 700 °C. The branching at high  $T_{sub} \geq 500$  °C occurs during the nucleation stage where multiple nuclei on a single SiO<sub>2</sub> sphere develop into subpillars during a competitive growth mode which, in turn, leads to intercolumnar competition and the extinction of some nanopillars.

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10:40am **SE-WeM9 Onset of Nanocolumn Formation in Extreme Self-Shadowing Conditions**, *A. Amassian*, Cornell University; *K. Kaminska*, National Research Council, Canada; *M. Suzuki*, Kyoto University, Japan; *L. Martinu*, Ecole Polytechnique de Montreal, Canada; *K. Robbie*, Queens University, Canada

We have investigated the early stages of growth of glancing angle deposited (GLAD) amorphous silicon (a-Si) films onto room-temperature c-Si (001) substrates. Using a combination of in situ spectroscopic ellipsometry and ex situ atomic force microscopy (AFM), we have found that following nucleation, the normal incidence ( $\theta = 0^\circ$  from substrate normal) deposit coalesces into a continuous and smooth film in the thickness ( $t$ ) range between  $1 < t < 5$  nm, whereas the GLAD deposit ( $\theta = 87^\circ$  from substrate normal) does not coalesce, instead becoming increasingly porous for  $t > 1$  nm. Atomic force microscope scans of GLAD deposits detected a significant roughening behaviour in this thickness range, and revealed large disc-like island formations with spacing in the range of  $\sim 45 \pm 10$  nm. The difference in sub-nanometer growth behaviours of normal incidence and GLAD deposits are attributable to the presence of extreme atomic self-shadowing in the latter case, which significantly alters the nucleation and growth patterns of the first monolayers of a-Si with respect to normal incidence depositions. The disc-like formations form the seeds to nanocolumns observed during subsequent growth, a conclusion which is also supported by 3D Monte-Carlo simulations.

11:20am **SE-WeM11 Nanospring Pressure Sensors and Branched Nanorods grown by Glancing Angle Deposition**, *S.V. Kesapragada*, *D. Gall*, Rensselaer Polytechnic Institute

Periodic arrays of Cr zigzag nanosprings and nanorods, 15-55 nm and 40-80 nm wide respectively, and Y-shaped Cu nanopillars were grown on patterned substrates by Glancing Angle Deposition (GLAD) in pure Ar discharges at 1 mTorr. Cr nanospring and nanorod arrays exhibit a reversible change in resistivity upon loading and unloading, by 50% for nanosprings and 5% for nanorods, indicating their potential as pressure sensors. The resistivity drop is due to a compression of nanosprings (by a measured 19% for an applied external force of  $10^{-10}$  N per spring), which causes them to physically touch their neighbors, providing a path for electric current to flow between nanosprings. We demonstrate a novel process for the formation of Y-shaped nanorods by exploiting the combination of atomic shadowing effects during GLAD and the spontaneous stacking fault formation in fcc metals. oriented Cu nanorods self-organize into branched Y-structures due to stacking fault formation on two oppositely tilted 111-facets, followed by a growth suppression at the developing grain boundary. @FootnoteText@ @footnote 1@ S.V. Kesapragada, P. Victor, O. Nalamasu, and D. Gall, "Nanospring Pressure Sensors by Glancing Angle Deposition" Nano Lett. 6 [4] 854 (2006)@footnote 2@ J. Wang, H. Huang, S.V. Kesapragada, and D. Gall, "Growth of Y-shaped Nanorods by Physical Vapor Deposition" Nano Lett. 5 [12] 2505 (2005).

11:40am **SE-WeM12 Optical Behaviour of Sculptured Thin Films**, *E.B. Schubert*, *F. Frost*, Leibniz-Institut für Oberflächenmodifizierung e.V., Germany; *J. Rivory*, Pierre et Marie Curie Universit@aa e@, France; *M. Schubert*, University of Nebraska-Lincoln; *B. Rauschenbach*, Leibniz-Institut für Oberflächenmodifizierung e.V., Germany

Glancing angle ion beam assisted deposition in combination with a computer controlled substrate rotation is a sophisticated method for the growth of sculptured thin film consisting of three-dimensional building blocks with customized geometries. Glancing angle deposition uses a very oblique angle-of-incidence particle flow that produces a highly porous thin films structure. The building block geometry within the sculptured thin films can be tailored by utilizing an additional azimuthal substrate rotation or a continuous substrate tilt yielding for instance to chevron-, screw- or post-like nanostructures. Sculptured thin films are grown from different materials such as aluminium, silicon dioxide or silicon. The growth is studied with respect to the particle flux angle-of-incidence, substrate temperature, substrate surface and substrate movement. Physical properties of sculptured thin films are mainly influenced by the nature of their three-dimensional building block components. This phenomenon will be discussed exemplarily on structure related optical properties with special emphasize on the demonstration of chirality in sculptured thin films by experimental and theoretical investigation of three-dimensional Mueller Matrix elements. Additionally, concepts for sub-wavelength antireflection coatings and optical nanogratings obtained from self-organized sculptured thin film growth will be demonstrated.

12:00pm **SE-WeM13 Circular Bragg Reflectors Formed by Glancing Angle Deposition of Helically-Structured Thin Films**, *A.C. van Popta*, *J.C. Sit*, *M.J. Brett*, University of Alberta, Canada

The glancing angle deposition (GLAD) process is capable of generating thin films with anisotropic physical properties that can be manipulated to produce unique materials and devices. For instance, substrate rotation can be used to shape the columnar morphology of a GLAD film into helical structures that exhibit circular Bragg effects similar to cholesteric liquid crystals. At extremely oblique deposition angles, the high porosity of a helically-structured thin film can be used to create electrically-addressable hybrid optical materials by embedding liquid crystals within the pores of the thin film matrix, while less oblique deposition angles result in helical films that exhibit stronger circular Bragg reflections due to diminished scattering and enhanced form birefringence. By replacing the continuous rotation of the local optical axis in a helical GLAD film with discrete incremental rotations, it is possible to form polygonal helix structures that exhibit both left-handed and right-handed circular reflection bands, and introducing a twist defect or spacing layer defect will lead to the formation of narrow bandpass filters. This work will highlight experimental results involving helically-structured inorganic thin films produced by GLAD, including novel deposition schemes to control the form birefringence of a GLAD film, post-processing steps for enhancing optical anisotropies in GLAD films, and methods for depositing improved chiral filter designs.

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## Advanced Surface Engineering Room 2007 - Session SE1-WeA

### Glancing Angle Deposition

**Moderator:** M.J. Brett, University of Alberta Edmonton

2:00pm **SE1-WeA1 Atomic Chaos and Emergent Phenomena in Glancing Deposition**, *K. Robbie, T. Brown, C. Elliott, C. Buzea*, Queen's University, Canada

**INVITED**

The atomic-scale porosity created in thin films by glancing angle deposition is the result of chaotic atomic competition. A so-called growth instability arises when atomic vapor arriving at glancing incidence condenses under conditions where the behavior of each atom strongly affects the condensation behavior of subsequent atoms - a sensitivity to initial conditions, or chaos - creating oriented dendritic structures that can be engineered on the scale of nanometers by varying the deposition geometry. The chaotic nature of this growth results in fractal morphologies, with scale-invariant self-similarity and power-law scaling in observable parameters such as the 'column' diameter. While the stochastic arrival of atoms clearly plays a role in the chaotic dynamics of this system, it appears that atomic-scale condensation dynamics also contribute - and perhaps constitute a form of quantum chaos. Examining the morphologies of films deposited at glancing incidence reveals a rich set of structures not well described by simple ballistic aggregation models. Particularly interesting are morphological rare-events that occur in some materials, and include self-organized pyramidal structures in several noble metals. These structures may be described as emergent phenomena, and suggest that there are quantum contributions to this chaotic condensation process. Experimental studies of this film growth process will be presented, including measurements of growth exponents and observations of material-dependent variation in film morphology. Existing theories of ballistic aggregation will be reviewed, followed by several proposals of directions that might be pursued to explain the formation mechanisms of the observed emergent phenomena. Finally, the potential of geometrically-controlled atomic self-assembly for technological applications will be presented.

2:40pm **SE1-WeA3 Fabrication and Characterization of Square Spiral Photonic Crystals Made by Glancing Angle Deposition**, *M.A. Summers, M.O. Jensen, M.J. Brett*, University of Alberta, Canada

The square spiral architecture is a promising candidate for photonic band gap (PBG) materials due to its ease of fabrication. The silicon square spiral structure is predicted to yield an optimum PBG width of 15% relative to the gap center frequency and can be fabricated using the glancing angle deposition (GLAD) technique. The GLAD fabrication process uses controlled substrate motion and highly oblique deposition to engineer precise architectures on the nanometer size scale. These nanostructures are grown with lateral and longitudinal periodicity using a pre-patterned substrate consisting of a tetragonal array of relief structures that can be fabricated using a number of lithographic techniques. Photolithography offers the possibility of large-scale manufacturability, while techniques such as laser direct-write lithography and electron-beam lithography provide the significant advantage of easy parameter modification and defect inclusion since no master is required. The GLAD process enables the scaling down of photonic crystal dimensions throughout the near infra-red wavelength region. Additionally, the versatility of the GLAD process enables the fabrication of a 3D-2D-3D photonic crystal hetero-structure, providing a foundation for potential use in optical networking applications. We report the structural and optical characterization of various silicon square-spiral photonic crystal structures fabricated using the GLAD technique.

3:00pm **SE1-WeA4 Structurally-chiral Films Fabricated for DUV Wavelengths by Serial Bi-Deposition**, *L. De Silva, I. Hodgkinson*, University of Otago, New Zealand

We report serial bi-deposition (SBD) of structurally-chiral films for deep ultraviolet (DUV) wavelengths. Scanning electron micrographs confirm that the films have a twisted-columnar nanostructure similar to a double-start screw. Observation of circular Bragg resonances in reflection and transmission at around 230 nm indicates a dielectric pitch of 65 nm, an average refractive index of 1.75 and local in-plane linear birefringence of 0.05. Possible applications of DUV chiral media include novel thin film polarizing devices for use in the DUV spectral region where the range of available devices is severely constrained by material properties.

3:20pm **SE1-WeA5 Nanoporous Thin Films for Optical Interference Coatings**, *M.M. Hawkeye, M.J. Brett*, University of Alberta, Canada

Thin films with periodically varying refractive indices display photonic bandgap effects and are commonly used as optical interference filters for a variety of applications. Glancing angle deposition (GLAD) offers a straightforward method for depositing thin films with controlled nanoscale porosity gradients, allowing fabrication of inhomogeneous optical coatings. Thin films of titanium dioxide with sinusoidal refractive index profiles were deposited by reactive e-beam evaporation and their applicability as optical filters was investigated. We found that a wide range of filter characteristics may be achieved using the GLAD process to control the film porosity. By introducing intentional defects in the sinusoidal index profile, narrow bandpass optical filters are realized. Through modification of the defect parameters, the optical properties of the narrow bandpass may be controlled. Tunability of the filter characteristics such as spectral location, bandwidth, and polarization dependence is demonstrated through simulation and experimental results. Apodization of the refractive index profile to reduce the interference sidelobes characteristic of these optical filters is also discussed. The presented work shows the precision of the GLAD technique for fabricating optical interference filters for applications in the visible spectrum.

## Advanced Surface Engineering Room 2007a - Session SE2-WeA

### Pulsed Plasmas in Surface Engineering

**Moderator:** M.J. Brett, University of Alberta Edmonton

3:40pm **SE2-WeA6 In-Situ Ellipsometric Studies of HPPMS Deposited Chromium Thin Films**, *S.L. Rohde, J. Li, S.R. Kirkpatrick*, University of Nebraska-Lincoln

Chromium thin films have been deposited using high power pulsed magnetron sputtering (HPPMS). In order to study the sputter etch conditions used to clean surfaces prior to depositions of hard coatings, the films were deposited for 30 minutes with a base pressure of 3mtorr and a large DC substrate bias of -1000V. The substrate bias was run in both the on (-1000V) and off condition and an unbalanced magnetic coil current was run at both 0 and 5 A to observe their effect on the process. The deposition process was monitored at the substrate using a 44 wavelength ellipsometer. Deposition rates varied between 0.5 and 1 Angstroms/second as measured by ellipsometry and confirmed with profilometry. Ellipsometric data indicates initial island growth followed by layer growth. Ellipsometry also indicates increasing roughness during the deposition at about 1 Angstroms/minute. Lower roughness rates and slower deposition rates resulted with magnetic coil assisted depositions.

4:00pm **SE2-WeA7 Plasma Spectroscopy of Carbon Nanotubes**, *J.G. Jones, C. Muratore, A.R. Waite, A.A. Voevodin*, AFRL/MLBT

Carbon nanotubes (CNTs) have unique properties of thermal and electrical conductance, as well as structural properties. Samples of vertically aligned CNTs on silicon substrates were plasma treated in different background gas environments including argon/hydrogen, and argon/nitrogen for the purposes of functionalization. A high power pulsed plasma treatment was used to modify CNT surface by attaching N and H atoms. In situ spectroscopy was used to detect atomic and molecular excitation for each of the background gas environments including mixtures of argon/hydrogen, pure hydrogen, pure nitrogen and argon/nitrogen. The result demonstrated the presence of both atomic and ionized species at the vicinity of the CNT sample surfaces. In situ X-ray photoelectron spectroscopy (XPS) was performed on the treated samples to determine the chemical bonding structures, both before and after treatment. The analyses shows formation of both C-N and C-H bonds for CNT surfaces. Correlations of the plasma characteristics and chemistry and bonding of the modified CNT surfaces is discussed for different environments pulsed plasma process settings.

4:20pm **SE2-WeA8 Pulsed RF PECVD of a-SiN@sub x@:H Alloys: Film Properties, Growth Mechanism and Applications**, *R. Vernhes, O. Zabeida, J.E. Klemberg-Sapieha, L. Martinu*, Ecole Polytechnique of Montreal, Canada

In PECVD of thin films, control of plasma chemistry and plasma-surface interaction during the growth are critical for the tailoring of film composition and microstructure. In this context, pulsing the plasma provides additional parameters (frequency, duty cycle) to control the deposition process, while decreasing the thermal load on the substrate. In

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this work, we present the pulsed PECVD of a-SiN<sub>x</sub>:H alloys, the films' properties being varied simply by adjusting the duty cycle of the RF power, while keeping the N<sub>2</sub>/SiH<sub>4</sub> gas mixture constant. Spectroscopic ellipsometry analysis in the UV-VIS-NIR and FIR ranges, atomic force microscopy, and elastic recoil detection reveal strong variations of optical properties (1.88 ≤ n ≤ 2.75, 10<sup>-4</sup> ≤ k ≤ 5 × 10<sup>-2</sup> at 550 nm), microstructural characteristics (1.3 nm ≤ surface roughness ≤ 8.3 nm), and chemical composition (0.3 ≤ x ≤ 1.3) of the coatings as a function of duty cycle. This behavior is interpreted in terms of radical concentration changes in the gas phase and variations of the average ion bombardment energy at the film surface, leading to modifications of the growth mechanism. Using this process, we fabricated two types of a-SiN<sub>x</sub>:H-based thin film devices, namely (i) a high-quality Fabry-Perot optical filter deposited on plastic substrate without monitoring, and (ii) a superlattice structure displaying a photoluminescence signal four times higher than the reference single layer. These two examples of applications point out the main advantages of this pulsed RF PECVD process, in particular low deposition temperature, reproducibility, versatility and ease of use.

4:40pm SE2-WeA9 **The Role of Oxygen Impurities in Anisotropic Etching of Crystalline Silicon by Atomic Hydrogen, and in the Deposition of Single-Phase Nanocrystalline Silicon**, S. Veprek, Technical University Munich, Germany; Ch.L. Wang, Consultant; M.G.J. Veprek-Heijman, Technical University Munich, Germany

Nanocrystalline silicon, nc-Si (and germanium) was originally prepared by means of chemical transport in hydrogen plasma, which combines the etching of silicon in the charge zone with the formation of monosilane as the main product, Si(s) + 4H → SiH<sub>4</sub>, and the decomposition reaction SiH<sub>4</sub> → nc-Si + 2H<sub>2</sub> in the deposition zone.<sup>1-4</sup> The etching rate is highest at a temperature of about 60-80 °C and it strongly decreases to essentially zero above 350 °C.<sup>2</sup> After a sufficiently long dwell time, partial chemical equilibrium with monosilane concentration of about 0.3 - 0.5 mol.% is established in glow discharge hydrogen plasma at a temperature of 40 - 80 °C, regardless if monosilane, or solid silicon and hydrogen are used as reactants.<sup>4</sup> In the present paper we shall show, that minor oxygen impurities of about 5 - 10 at. ppm (atomic parts per million) strongly decrease the reaction rate, and above 50 - 60 ppm of oxygen this reaction cannot occur. The etching by atomic hydrogen is isotropic below about 5 ppm of oxygen impurities, whereas controllable addition of a few 10 ppm of oxygen in combination with negative bias to the crystalline silicon results in highly anisotropic etching with thin oxide acting as side-wall passivation. Oxygen impurities also hinder the formation of single-phase nc-Si and cause occurrence of a significant fraction of a-Si in the deposited films. Oxygen impurities of about > 0.5 at. % in the hydrogen plasma can completely hinder nc-Si to form. In a pure hydrogen glow discharge plasma, single-phase nc-Si without any detectable a-Si tissue can be deposited under conditions close to the partial chemical equilibrium.<sup>1</sup> S. Veprek and V. Marecek, Solid-State Electronics 11(1968)683. <sup>2</sup> S. Veprek and A. P. Webb, Chem. Phys. Lett. 62(1979)173. <sup>3</sup> Z. Iqbal, A. P. Webb and S. Veprek, Appl. Phys. Lett. 36(1980)163. <sup>4</sup> J. J. Wagner and S. Veprek, Plasma Chem. Plasma Process. 2(1982)95.

## Advanced Surface Engineering Room 2007 - Session SE1-ThM

### Pulsed Plasmas in Surface Engineering

**Moderator:** J.M. Schneider, RWTH Aachen, Germany

8:00am **SE1-ThM1 Pulsed Metal Plasmas**, A. Anders, Lawrence Berkeley National Laboratory **INVITED**

A review is presented on pulsed metal plasmas used for surface engineering and thin film deposition. Pulsed laser ablation, pulsed (filtered) arc plasmas, and high power (im)pulse sputtering are the main approaches to producing pulsed metal plasmas. Each of them has a set of distinct properties. By partially or fully ionizing the metal (and background gas, if applicable) one can extend the possibilities of widely used physical vapor deposition (PVD) methods. The knowledge gained in the fields of plasma-assisted and ion-beam-assisted deposition (IBAD) can be applied: pulsed metal plasmas can be used for self-ion-assisted deposition. Effects of energetic condensation include interface mixing, densification, buildup of compressive stress, thermal spike annealing and stress reduction, and texturing for selected materials. This work was supported the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

8:40am **SE1-ThM3 Optimization of Adhesion Promoting Substrate Pre-Treatment using Metal Ions of a High Power Impulse Magnetron Discharge**, M. Lattemann, U. Helmersson, Linköping University, Sweden

A high power impulse magnetron sputtering (HIPIMS) plasma consists of a high amount of single- and double-ionized metal species identified by mass spectrometry. The resulting high metal ion-to-neutral flux on the substrate can be used for sufficient substrate surface cleaning and modification by applying a negative substrate bias  $U_{\text{sub b}} = 0 - 1200$  V, enhancing the adhesion of industrial-relevant coatings. The HIPIMS pre-treatment was carried out in an inert gas atmosphere at a low pressure of  $p_{\text{Ar}} = 1$  mTorr to minimize the inert gas incorporation. The subsequently grown metal nitride coating (CrN, TiN, TiAlN) was deposited in an  $\text{Ar}/\text{N}_2$  atmosphere using conventional dc magnetron sputtering. The microstructure and constitution of the interfacial region for different process parameters (substrate bias  $U_{\text{sub b}} = 0 - 1200$  V, substrate temperature  $T_{\text{sub s}} = RT - 450^\circ\text{C}$ ) was investigated employing Transmission Electron Microscopy (TEM) and Analytical Scanning Transmission Electron Microscopy (A-STEM), respectively. The critical load of failure values were determined in scratch tests (CSEM Revetest). The influence of the process parameters on the constitution and microstructure of the interfacial region after the pretreatment and its effect on the coating adhesion will be discussed.

9:00am **SE1-ThM4 Modulated Pulsed Power Generator for High Density Magnetron Discharges**, R. Chistyakov, Zond, Inc.; B. Abraham, Zpulser; W.D. Sproul, Reactive Sputtering Consulting, LLC; J.J. Moore, Colorado School of Mines

A unique high power pulsed magnetron plasma generator has been developed to generate high density plasmas for sputtering applications with typical pulse durations in the range of 0.5-5 msec. By creating a combination of weakly-ionized and strongly-ionized plasmas by modulating the cathode voltage within a single pulse, highly ionized plasmas have been produced. Films of aluminum, copper, titanium, aluminum oxide, and titanium nitride have been deposited. The film structure and orientation are a function of the pulse shape and duration and the degree of ionization. Optical emission measurements show that there is a very high degree of ionization of the sputtered species, and this high degree of ionization promotes the formation of the reactive films. For the aluminum oxide films deposited with an average power of 4.5 kW with a target to substrate distance of 23 cm, the deposition rate was 12 microns per hour. Possible applications for this new high power pulsed sputter deposition technology will be discussed.

9:20am **SE1-ThM5 Surface Wettability of Stainless Steel Treated using  $\text{C}/\text{H}_2$  Plasma using Plasma-based Ion Implantation**, T. Tanaka, R. Wang, T. Takagi, Hiroshima Institute of Technology, Japan

Plasma-based ion implantation (PBI) with negative voltage pulses to the test specimen has been applied to the surface treatment process as a technique suitable for three-dimensional work pieces. Also, the surface property of stainless steel for semiconductor process using corrosive gases is important. The surface of stainless steel was treated in  $\text{C}/\text{H}_2$  gas using Plasma base ion implantation (5  $\mu\text{sec}$  pulse width,

300 pulses/s, -10 kV). The contact angle of a water-droplet on each specimen surface was measured by using a digital microscope and the contact angle was obtained. The contact angle of specimens without  $\text{C}/\text{H}_2$  plasma treatment was about 90 degree, while that of specimens with  $\text{C}/\text{H}_2$  plasma treatment was about 64 degree. It found that the surface wettability of stainless steel largely enhanced by the  $\text{C}/\text{H}_2$  plasma treatment using plasma-based ion implantation.

## Advanced Surface Engineering Room 2007a - Session SE2-ThM

### Hard and Nanocomposite Coatings: Synthesis, Structure, and Properties

**Moderator:** J.M. Schneider, RWTH Aachen, Germany

9:40am **SE2-ThM6 Surface Engineering for Improved Resistance to Contact Damage**, S. Suresh, M. Dao, MIT **INVITED**

The tribological resistance of materials and surfaces during monotonic and repeated contact with other objects depends on a wide variety of complex interactions among material microstructure/properties, contact geometry, loading conditions, initial surface roughness, surrounding environment and lubricants. This presentation will provide a broad overview of our recent work on strategies to enhance the contact-damage resistance of surfaces. For this purpose, depth sensing, instrumented, continuous contact measurements are obtained over multiple length scales, from nm to macro-scale, using nanoindentation, quantitative frictional sliding measurements, cyclic normal indentation, repeated frictional sliding, as well as fretting fatigue. For material properties, a broad spectrum of microstructural conditions spanning nanocrystalline materials to commercial alloys are studied experimentally. These experimental studies are also accompanied by detailed, multi-scale computational modeling. In addition, strategies for improved in tribological properties by the introduction of controlled gradients in elastic and plastic properties, either through reinforcements or through grain size gradations, are explored. The presentation will conclude a summary of key advances in the area of instrumented contact mechanics and in the engineering of surfaces for improved contact-damage resistance.

10:20am **SE2-ThM8 Cr-B-N Coatings Deposited by Cathodic Arc Evaporation**, K. Polychronopoulou, J. Neidhardt, B. Sartory, R. Kaindl, R. Tessardi, Christian Doppler Laboratory for Advanced Hard Coatings; C. Rehbolz, University of Cyprus; M. O Sullivan, Plansee SE; A.E. Reiter, Balzers AG; C. Mitterer, Christian Doppler Laboratory for Advanced Hard Coatings

Transition metal boron nitride (Me-B-N) coatings receive increasing attention for their excellent combination of mechanical, chemical and tribological properties. Thus, this study presents nanocomposite Cr-B-N coatings deposited onto various substrates by high-rate reactive cathodic arc evaporation from Cr/B (80/20 at%) targets at  $500^\circ\text{C}$  using a commercial Balzers RCS system. The total pressure ( $\text{Ar}/\text{N}_2$ ) was kept constant at 2 Pa, while the  $\text{N}_2$  fraction was varied between 0 and 1. The coating composition and microstructure and mechanical as well as tribological properties were determined. X-ray diffraction studies revealed that Cr-B-N coatings deposited in a range of  $\text{N}_2$  fractions from 1/8 - 1 contain randomly orientated CrN crystallites. No crystalline BN or  $\text{Cr}_2\text{N}$  phases were identified, whereas after vacuum annealing at  $700^\circ\text{C}$  during stress-temperature measurements peaks attributable to the  $\text{Cr}_2\text{N}$  phase emerged. The as-deposited coatings are with 2-3 GPa in a compressive stress state for higher  $\text{N}_2$  fractions, while the hardness and elastic modulus values range from 18 to 23 GPa and 21.0 to 24.0 GPa, respectively. During ball-on-disc tests, these coatings revealed a coefficient of friction decreasing from 0.8 to 0.4; values between 0.5-0.6 were observed at an elevated testing temperature of  $500^\circ\text{C}$ . Raman investigations after tribological experiments revealed mainly chromium oxide suggesting a predominantly oxidative wear mechanism.

10:40am **SE2-ThM9 Growth and Characterization of Diamond/CNT Nanocomposites using Hot-Filament Assisted Chemical Vapor Deposition**, N. Shankar, N.G. Glumac, M.-F. Yu, S.P. Vanka, University of Illinois Urbana-Champaign

Superhard materials are characterized by a bulk hardness of 40 GPa or more. However this extreme hardness is often offset by their inherent brittleness. In wear application where hard materials are typically used, it may be necessary to improve the toughness of the hard coatings for improved reliability, performance and durability. Reinforcing these hard

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materials with a tough second phase would possibly produce hard and tough composites which have the potential to outperform conventional hard coatings. We have developed a superhard-supertough composite from diamond and carbon nanotubes (CNT) by Hot Filament assisted Chemical Vapor Deposition (HFCVD). The growth was achieved by initially pre-dispersing commercially available multiwalled CNT onto a Si(100) surface and then subsequently growing diamond over this layer. The diamond/CNT composites were characterized using SEM, TEM, and Raman Spectroscopy. It was found that at 1% CH<sub>4</sub> in H<sub>2</sub> (a typical condition for diamond growth using HFCVD) most of the CNT are destroyed by the harsh growth conditions. A parametric study of growth phase-space revealed a selective window between 2-5% of CH<sub>4</sub> in H<sub>2</sub> wherein the CNT are not destroyed and the resulting diamond film still retained a high percentage of its sp<sup>3</sup> structure. The TEM analyses showed that nanometer sized diamond particles nucleate on the surface of the CNT and grow radially outward. Based on the detailed characterization of the composites, a growth mechanism for diamond onto the CNT has been proposed. To the best of our knowledge, this is the first time that a successful composite of diamond and multiwalled CNT has been produced with direct bonding between the diamond and CNT resulting in good load transfer at the interface between the matrix and reinforcement.

## Advanced Surface Engineering Room 2007 - Session SE-ThA

### Hard and Nanocomposite Coatings: Synthesis, Structure, and Properties

**Moderator:** A. Anders, Lawrence Berkeley National Laboratory

**2:00pm SE-ThA1 Characterization of Inorganic Nanomaterial Composite Coatings,** J.J. Hu, J. Steffens, J.S. Zabinski, J.H. Sanders, A.A. Voevodin, Air Force Research Laboratory

Inorganic nanomaterials including metals, oxides, carbides and sulfides etc. are mostly larger-scale synthesized and commercially available in powder/colloid states. Therefore, for some special applications such as surface protection and lubrication, there is a strong request to make or incorporate the inorganic nanomaterials into coatings. High density and uniformity of the nanomaterial distribution in coatings are desired for pursuing the extraordinary properties of precursor nanomaterials. In this study, the coatings containing nanomaterials were deposited using laser ablation from frozen liquid targets, where the original liquid material was loaded with nano-tubes and nanosized particles. This laser ablation source was operated in a high vacuum chamber and was assisted with magnetron sputtering of metals and ceramics to adhere and encapsulate nanomaterials into a composite coatings. The chemistry and microstructure of the coatings were characterized using X-ray diffraction (XRD), X-ray energy dispersive spectrometry, scanning electron microscopy (SEM), focused ion beam (FIB) and transmission electron microscopy (TEM). Some advantages of the laser ablation technology from frozen liquid targets for insertion nanomaterials into coatings include: (1) good coating uniformity and smooth surface topography; (2) enhanced coating adhesion to substrates; and (3) being free of solvent molecules and contamination-free. Nanomaterial composite coating benefits for wear protection will be discussed.

**2:20pm SE-ThA2 Microstructure and Surface Properties of Ti-Si-C Nanocomposite Thin Films Deposited by dc Magnetron Sputtering,** P. Eklund, J. Emmerlich, J. Frodelius, C. Virojanadara, L.I. Johansson, Linköping University, Sweden; O. Wilhelmsson, U. Jansson, Uppsala University, Sweden; H. Hogberg, L. Hultman, Linköping University, Sweden

Nanocomposites from the Ti-Si-C system are of growing interest as a multifunctional coating material in electrical and tribological applications. We have previously demonstrated beneficial electrical contact properties and a ductile deformation behavior for Ti-Si-C nanocomposite thin films deposited by magnetron sputtering from a Ti@sub 3@SiC@sub 2@ compound target@footnote 1@ at substrate temperature below 300 °C.@footnote 2@ Here, we report on detailed characterization of the microstructure and surface conditions of Ti-Si-C nanocomposites. As evidenced by XRD, TEM, and XPS, the Ti-Si-C films consist of TiC nanocrystallites (<20 nm), embedded in a matrix of amorphous SiC with presence of graphitic carbon. The nc-TiC/a-SiC/g-C nanocomposite exhibited nanoindentation hardness and elastic-modulus values of 20 GPa and 290 GPa, respectively. The ductility of the material can be attributed to rotation and gliding of nc-TiC grains in the matrix. Furthermore, photoemission studies of as-deposited films on Si substrates show a native oxide thickness of 3-4 nm. The thermal stability of the coating was investigated by annealing in vacuum. Upon heating to 1000 °C, the oxide layer is removed and large amounts of free surface carbon appear, as well as surface silicon. This can be interpreted as C and Si segregation during the annealing. @FootnoteText@ @footnote 1@Maxthal, courtesy of Kanthal AB@footnote 2@P. Eklund et al. J. Vac. Sci. Technol. B 23(6) 2486 (2005).

**2:40pm SE-ThA3 Characterisation of Nanocomposite Alumina-Zirconia Thin Solid Films Deposited by Reactive Dual RF Magnetron Sputtering,** D.H. Trinh, Linköping University, Sweden; M. Collin, I. Reineck, Sandvik Tooling AB, Sweden; S.S. Nonnenmann, J.E. Spanier, Drexel University; L. Hultman, H. Högberg, Linköping University, Sweden

Alumina-zirconia composites are of interest for a wide range of applications. These include wear resistant coatings, requiring a combination of high hardness, thermal and chemical stability, and more advanced high-k dielectric thin films for microelectronics, which require the inherent insulating properties of both phases. A deeper understanding of the microstructure is required to fully harness the potential of the mixed oxide system and, in particular, nanocomposites within the aforementioned system. This is complicated, however, by the spontaneous phase separation process into binary oxides and the variety of possible

stable and metastable phases that form within each respective binary system. In this study dual RF reactive magnetron sputtering has been utilised to deposit pure and mixed oxide films at a substrate temperature of 450°C on substrates such as Si (100) and WC-Co. High-resolution electron microscopy revealed that the films are nanocomposite in nature with grain sizes <50nm and that phase separation between alumina and zirconia occurs. The phase composition of the films was studied by x-ray diffraction. Complementary electron energy loss spectroscopy (EELS) and Raman scattering spectroscopy were performed for more in depth studies of the atomic arrangement and bonding. The pure zirconia films feature the monoclinic zirconia phase, while the pure alumina films consist of @gamma@-alumina phase. The composite films are nanocrystalline and are comprised of a mixture of phases that included the metastable zirconia phases, @gamma@-alumina, and some amorphous phase. The mechanical properties of the films were characterised by nanoindentation.

**3:00pm SE-ThA4 Tailoring the Nanostructure and Surface Properties of Nanocrystalline Diamond Thin Films on Micro-End Mills for Micro-manufacturing Applications,** A.V. Sumant, P. Heaney, F. Pfefferkorn, R.W. Carpick, University of Wisconsin-Madison

The growing interest in high-precision machining to fabricate miniaturized parts with meso-scale machine tool systems (mMTs) for medical devices, and optical components requires high-performance micro-end mills with diameters ranging from 10 to 500 microns. This technology complements standard silicon-based microfabrication processes by its ability to directly produce true 3D structures with high accuracy, low cost, and short cycle time from metals. Presently, tungsten carbide (WC) with cobalt binder is widely used as a standard cutting tool material. However, these tools suffer from a limited operational life and have difficulty in machining adhesive metals such as aluminum and copper. Nanocrystalline diamond (NCD) thin films are an attractive possibility for coating these tools, because of its high hardness and the low friction and wear rate of its surface. We have developed a new approach using CH<sub>4</sub>/H<sub>2</sub>/Ar growth chemistry to grow a conformal, sub-micron thick coating of NCD on tungsten carbide micro-end mills using Hot Filament Chemical Vapor Deposition (HF-CVD). The percentage of Ar in the gas phase is varied to simultaneously optimize the grain size and the high sp<sup>3</sup> content. The characterization of the sp<sup>3</sup> content of the NCD coatings is performed using Raman and near edge x-ray absorption (NEXAFS) spectroscopy. The performance of the uncoated and NCD-coated tools have been evaluated by performing dry slot milling experiments on aluminum. The initial test results show a substantial dependence of the performance of the tool on the sp<sup>3</sup> content of the film. Dramatic improvement in the tool integrity, extremely low wear, no observable adhesion of aluminum, and a significant reduction in the cutting forces (~ 50%) with improved surface finish are observed for NCD films with high sp<sup>3</sup> content. This translates into a micro-machining process with minimal environmental impact, and offers great promise for micro and meso-scale manufacturing applications.

**3:20pm SE-ThA5 Growth Study of TiN- and TiCxNy-based Superhard Nanocomposite,** E. Bousser, Ecole Polytechnique, Canada; P. Jedrzejowski, Plasmionique; A. Amassian, L. Martinu, J.E. Klemberg-Sapieha, Ecole Polytechnique, Canada

Recent advances in the area of aerospace, automobile and biomedical industries, in microsystems and manufacturing of specialized industrial componentry stimulate the development of new functional coating materials and surface engineering processes that provide an ever increasing mechanical and tribological performance. In the present work, we investigate in situ and in real-time the growth of superhard ternary nanocomposite nc-TiN/a-Si<sub>3</sub>N<sub>4</sub> and quaternary nc-TiCxNy/a-SiCN. These materials were synthesized by plasma enhanced chemical vapor deposition (PECVD) from TiCl<sub>4</sub>/CH<sub>4</sub>/SiH<sub>4</sub>/N<sub>2</sub> gas mixtures at substrate temperature of 500°C. Using nondestructive, noncontact spectroscopic ellipsometry and appropriate ellipsometric models, we determine the variation of optical constants, film resistivity, and electron scattering time and mean free path as a function of thickness and particle size. We will show how real-time in situ measurements allow one to evaluate the evolution of the electrical properties that can be described on the basis of existing models (Thompson, Fuchs-Sondheimer, Mayadas-Shatzkes), and related to electron scattering due to phonons, point and line defects (grain boundaries), and surface effects. The films' electrical characteristics derived from optical measurements were confirmed by direct four-point evaluations, and interpreted in terms of the evolution of their microstructure and chemical composition. This approach then became the basis for a generalized microstructural model that takes into account the microstructural features including grain size, inter-grain spacing and

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interfaces, that are closely related to the film hardness (>50 GPa), and the highest reported H3/E2 ~ 1.8 GPa parameter characterizing resistance to plastic deformation obtained for such nanocomposite films. High resolution TEM micrographs of the evolution of the nanostructures are also presented in support of the structural model.

**3:40pm SE-ThA6 Preparation and Characterization of Reactively Sputtered Al@sub x@CoCrCuFeNi Oxide Films, T.K. Chen, M.S. Wong, National Dong Hwa University, Taiwan, ROC**

Multicomponent Al@sub x@CoCrCuFeNi (x=0.5, 1 and 2) metallic and oxide thin films were prepared by reactive sputtering using single alloy target in a mixture of argon and oxygen gases with various oxygen/argon flow ratio. The dependence of the oxygen to argon ratio, such as the evolution of films structure and properties was investigated in this study. At low oxygen flow rate, the oxygen atoms seemed to be incorporated into the metallic films as solute atoms. At higher oxygen to argon fraction, new crystalline oxide phases, matching the XRD patterns of spinel-structured AB@sub 2@O@sub 4@ like NiCr@sub 2@O@sub 4@ were detected. The films resistivity increased from hundreds of micron ohm-cm for metallic films to nearly 1000 ohm-cm for oxide films grown at high oxygen/argon ratio. UV-Vis absorption spectra of the oxide films revealed a narrow transmission band that only light with wavelength between 650 nm to 850 nm was allowed to pass. These oxide films exhibited unexpected high hardness, compared with their metal and metal nitride counterparts, to a value of 20 GPa.

**4:00pm SE-ThA7 Magnetron Sputtered Nanolaminate Coatings for Debonding of Segmented Structures, J.D. Demaree, J.K. Hirvonen, US Army Research Laboratory; M.P. Blickley, The Pennsylvania State University; N.A. Soroka, United States Military Academy; P.G. Dehmer, M.A. Minnicino, US Army Research Laboratory**

Reactive coatings consisting of repeated bilayers of aluminum and nickel/vanadium capable of self-propagating reactions were deposited onto carbon composite and steel coupons using magnetron sputtering. Such sacrificial coatings, when embedded in an adhesive joint, can provide reliable on-demand debonding of segmented structures when ignited. Adhesion of the metallic nanocomposite coating to carbon composite substrates was enhanced by in-vacuum plasma treatments. The energy required to initiate the self-propagating intermetallic reaction and the propagation velocity of that reaction was measured before and after low temperature annealing, using a spark gap and high speed video photography. Rutherford backscattering spectrometry (RBS) was used to calibrate the deposition process and to characterize the interfacial interdiffusion induced by annealing. Increases in required initiation energy and decreases in propagation velocity were observed with increased anneal times and temperatures, in agreement with the RBS results and existing literature discussion of reaction mechanisms that show sensitivity of these to interface reactions. Initiation sensitivity and propagation velocity were both impacted by varying the stoichiometric ratio of Al to Ni/V, and the propagation rate was also affected by the nature of the substrate. These results allow for the optimization of both reliable initiation and long term, low temperature storage stability of said reactive coatings as required for Army applications. Scale-up demonstration of this process has begun, which will use a dual-source magnetron sputter system with a computerized sample manipulator, and will be capable of coating structural segments of carbon composite or steel up to 20 inches long. Once the adhesion, reactivity, and durability of these reactive coatings has been demonstrated on a component scale, such coatings are envisaged to become useful debonding agents in a number of future Army systems.

**4:40pm SE-ThA9 Dimensional Attributes of Enhancements in Nanocrystalline Ta-V Layered Structures, A.F. Jankowski, Univ. California - Lawrence Livermore National Laboratory**

The scaling of structure to the micro- and nano-scale is a known method of enhancing the physical properties of many materials. For example, the strength and hardness of nanocrystalline metals and laminates can be increased several fold. At present, we evaluate how the dimensional attribute of nanoscale affects the mechanical properties of body-centered-cubic Ta and V thin films. The samples for this study are prepared by magnetron sputter deposition and characterized using the methods of x-ray diffraction, transmission electron microscopy, and nanoindentation. Systematic increases in hardness, for example, are measured to a factor of ten or more above the comparative value of fully annealed samples. To assess underlying structural origin, single and layered structures of each metal are evaluated separately as well as in the form of layered structures. That is we examine Ta, Ta/Ta, V, V/V, and Ta/V films as deposited on silicon

substrates. At small layer-pair spacings, as 3 nm, it is found that strained layered superlattices are formed in Ta/V. Dimensional attributes of the nanoscale effects are considered in accounting for the origin of mechanical property enhancements in all these Ta and V nanostructured materials. Specifically, we assess the nanoscale features that are parallel versus perpendicular to the growth plane of the films, i.e. the relative effects of grain size versus the layer pair spacing. Although layer spacing is commonly associated with the effects of superlattice distortions in correlating effects of elastic properties, it is seen that grain size is a dominant contributor to plastic deformation associated with strength and hardness in the Ta-V films. This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

# Thursday Evening Poster Sessions, November 16, 2006

## Advanced Surface Engineering Room 3rd Floor Lobby - Session SE-ThP

### Advanced Surface Engineering Poster Session

#### SE-ThP1 Study of Mechanical Properties of Tungsten Nitride and Tungsten Carbide Hard Coatings, *E.C. Samano, W. De la Cruz, G. Soto*, CCMC-UNAM, Mexico

Transition metal nitride and carbide coatings are a good alternative to be used as protective layers against wear because transition metals are hard materials with a high melting point. Tungsten nitride and carbide coatings are an excellent choice to prevent wearing of cutting tools, structural components, etc. Their mechanical properties can be tailored by controlling the nitrogen and carbon content, in each case, during film processing. The investigation on the relationship between thin film preparation conditions and mechanical properties of tungsten nitride and tungsten carbide is presented in this work. We report the growth of tungsten nitride and carbide coatings grown on stainless steel substrates by reactive dc magnetron sputtering in the ambient of  $N_2/Ar$  and  $CH_4/Ar$  gas mixtures, respectively, at various pressures and magnetron system input powers. The composition of the films is determined by XPS and film crystallinity by XRD. The mechanical properties of the films are studied as a function of gas pressure and magnetron input power. The average hardness of the deposited coatings were found to be in the 31 to 37 GPa range for tungsten nitride and in the 30 to 41 GPa range for tungsten carbide.

#### SE-ThP3 Ti<sub>x</sub>Al<sub>y</sub>Si<sub>z</sub>N Films for Super-Hard Coatings Deposited by Reactive Co-Sputtering using Ti, Al and Si Targets, *A. Miyamura, M. Yamaguchi*, Aoyama Gakuin University, Japan; *K. Hattori*, National Institute of Advanced Industrial Science and Technology, Japan; *Y. Sato, Y. Shigesato*, Aoyama Gakuin University, Japan

Ti<sub>x</sub>N<sub>y</sub> is one of the promising hardcoating materials for its high toughness, high hardness and high chemical stability. Recent research goes to add the third element in order to make it extremely harder, higher melting point and higher thermal stability. For example, Ti<sub>x</sub>Al<sub>y</sub>N increases hardness by solid solution strengthening, whereas Ti<sub>x</sub>Si<sub>y</sub>N increases hardness by self-constructing nanocomposite structure. In order to attain more outstanding properties than the both ternary systems, we deposit Ti<sub>x</sub>Al<sub>y</sub>Si<sub>z</sub>N super hard films by three cathode co-magnetron sputtering systems. This system can adjust a composition of Ti, Al and Si in the film by controlling the input power ratio of the three cathodes mostly following the additive properties. As a result, Ti<sub>x</sub>Al<sub>y</sub>Si<sub>z</sub>N films with various compositions were deposited on silicon or glass substrates. For all the depositions, Ar was used as sputtering gas and  $N_2$  was introduced as reactive gas. Crystallinity and surface morphology of the films were analysed by X-ray diffraction (XRD) and atomic force microscope (AFM). Compositions were estimated using X-ray photoelectron spectroscopy (XPS) and electron probe micro analyzer (EPMA). A nano-indentation equipped with Berkovich diamond indenter using a continuous stiffness method was used to measure the hardness and Young's modulus along the depth of the Ti<sub>x</sub>Al<sub>y</sub>Si<sub>z</sub>N films. With increasing Si concentration, intensity of XRD peaks decreased and the films became amorphous over nearly 20% of Si concentration. It was clarified that the hardest condition could be obtained when titanium concentration was 2-3 times of aluminum concentration and silicon concentration was about 10-20%. For these films the nanocomposite structure was clearly observed by TEM. This work was partially supported by a Grant-in-Aid for the 21st COE Program from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government.

#### SE-ThP6 Pulsed AC Plasma Polymerisation for the Chemical Modification of Glassy Carbon Surfaces in Model Composite Interface Studies, *J.M. Drews*, The Technical University of Denmark, Denmark; *S. Goutianos, P. Kingshott, N. Rozlosnik*, Risoe National Laboratory, Denmark; *S. Hvilsted*, The Technical University of Denmark; *K. Almdal, B.F. Soerensen*, Risoe National Laboratory, Denmark

Pulsed AC plasma polymerization was used for surface modification of glassy carbon (GC) substrates, which are chosen as a model for the surface chemistry of carbon fibres used in composites. The pulsed AC plasma system, which is custom built, is powered by a 50 Hz 2-phase AC power supply from the grid and phase 1 is shifted 180° from phase 2. The resulting voltage between the electrodes (the plasma voltage) is the sum of phase 1 and 2. Depending on pressure and gas composition, a voltage of around 250 V is needed to ignite the plasma, resulting in a (100 Hz) pulsing plasma

current that has an effective power input of less than 1 W/L. This opens up the possibilities of generating plasma polymer layers by plasma-induced radical polymerisation. We utilise maleic anhydride (ppMAH) and 1,2-methylenedioxybenzene (ppMDOB) to generate both homo-plasma polymer and co-plasma polymer layers surfaces, in the power range from 0.3 to 1.3 W/L, to generate stable layers with varying degrees of functional integrity. X-ray Photoelectron Spectroscopy (XPS) and Attenuated Total Reflectance Fourier Transform Infrared spectrometry (ATR-FTIR) were used to monitor surface chemistries, and toluidine blue (TB) staining to determine the number of reactive acid groups after hydrolysis. Atomic Force Microscopy was used to monitor both topography and layer thicknesses using a polymeric masking method. The results show that the properties of the plasma polymer layers can be subtly varied by the plasma conditions. Unexpected results were obtained using the TB staining, and indicate that the hydrolysis of MAH groups is much more difficult to achieve than previously reported. Finally, the interfacial fracture properties were determined using a Double Cantilever Beam (DCB) method. It was found that differences in fracture energy are related to differences in surface properties, and that in all cases, the plasma polymer coatings increased the fracture energy, compared to the uncoated GC.

#### SE-ThP7 Integrating Aligned Nanorod Array onto Optical Fibers, *J.G. Fan, Y.J. Liu, Y.P. Zhao*, University of Georgia

We report a modified oblique angle deposition (OAD) method to prepare nanorod arrays onto optical fibers or cylindrical objects. By rotating the optical fiber with a proper tilting angle, aligned nanorods from materials, such as metals, semiconductors and metal oxides, have been successfully deposited onto optical fibers. With a slight modification, multi-layer film/nanorod and nanorod/nanorod structures have also been demonstrated. Surface enhanced Raman spectroscopy of trans-1,2-bis(4-pyridyl)ethane (BPE) molecules on Ag nanorod array on a fiber optical tip is demonstrated.

#### SE-ThP8 Protective Oxide Layers on Austenitic Stainless Steels (316L and D9) in Molten Lead Service: Formation and Reformation, Structure and Dynamics, *A.L. Johnson, J.W. Farley, D. Koury, B. Hostermann, J. Welsh, T. Ho*, University of Nevada, Las Vegas; *L. Ma*, Harry Reid Center; *U. Younas*, University of Nevada, Las Vegas

Liquid lead based alloys are of current interest due to their use as non-moderating coolants for fast neutron systems for power generation and nuclear waste transmutation. Unfortunately liquid lead corrodes steel by dissolution of the alloy's components. This corrosion may be mitigated by the injection of low levels of oxygen in the lead to form protective oxide layers. However the initially formed oxide layer is subject to failure and must reform when damaged under operational conditions. We have been investigating the structure and composition of the oxide layers formed on steels by oxygen controlled Lead Bismuth Eutectic (LBE) using XPS, SEM/WDS, and TEM. We find that there is an initial crystalline oxide (high Cr, low Fe) that converts to a complex bilayer (magnetite over (Fe,Cr)<sub>3</sub>O<sub>4</sub>) when damaged. Detailed investigation of the morphology and composition of these layers indicates the relative mobility of the alloy components in the near surface region and suggests a novel mechanism for the previously observed improvement in corrosion resistance due to cold working of the surface and near surface region. We will discuss this work in the context of current work with oxide layers formed by oxide generating species (Al, Si, and Y) introduced by sputter deposition or alloying.

#### SE-ThP9 Two Dimensional Micro Honeycomb and Nanoring Array, *D. Jia, C. Shaffer, J. Weyant, A. Goonewardene*, Lock Haven University of Pennsylvania

Polystyrene microspheres with 10, 2, 1 and 0.56 micron sizes were used to prepare monolayer as patterning for sputtering deposition. Gold, silver and platinum metal sources were used as sputtering deposition source. Two dimensional micro-honeycomb and nanoring metallic arrays were fabricated on glass and silicon substrate. No ring structures were obtained for platinum and silver deposition. Transition from honeycomb to ring structure was found for deposition gold. For 10 micron size microspheres, honeycomb structures were dominant and no ring structure was found. For 2 micron size microspheres, honeycomb and ring structures were found to co-exist. For size smaller 1 micron, ring structures were dominant. Surface corrugation was achieved by using these structures. Laser diffractions were studied for these structures.

# Thursday Evening Poster Sessions, November 16, 2006

**SE-ThP10 Influence of the Negative Oxygen Ions on the Structure Evolution of Transition Metal Oxide Thin Films, S. Mráz, J.M. Schneider,** RWTH Aachen University, Germany

The energy distributions of  $O^-$  ions of magnetron sputtered Nb, Ta, Zr, and Hf in an  $Ar/O_2$  atmosphere were measured as a function of the oxygen partial pressure. Three ion populations were detected in the plasma: low, medium and high energy ions. The ion energy distribution functions were compared to distributions obtained based on sputtering theory. If the surface binding energy is assumed to be equal to the heat of formation, good agreement between the experiment and theory was achieved. From correlating the measured ion energy distributions with previously published phase stability data,<sup>1</sup> it can be deduced that large fluxes of medium and high energy  $O^-$  ions enable formation of crystalline transition metal oxide thin films during low temperature growth. The here presented data may be of general relevance for understanding the structure evolution of thin oxide films. <sup>1</sup> Ngaruiya et al., Appl. Phys. Lett. 85(5), 748 (2004).

**SE-ThP11 Influence of the Normalized Ion Flux on the Constitution of  $Al_2O_3$  Films Deposited by Plasma Assisted Chemical Vapor Deposition, D. Kurapov, J. Reiss, RWTH Aachen, Germany; D.H. Trinh, L. Hultman, Linköping University, Sweden; J.M. Schneider, RWTH Aachen, Germany**

$Al_2O_3$  thin films were deposited onto tempered hot working steel substrates from an  $AlCl_3-O_2-Ar-H_2$  gas mixture by plasma assisted chemical vapor deposition (PACVD). During deposition the normalized ion flux was varied through changes in the precursor content while keeping the cathode voltage and the total pressure constant. As the precursor content in the total gas mixture was increased the deposition rate resulting in an increased normalized ion flux from 50 to 480. The constitution, morphology, impurity incorporation and the elastic properties of the alumina thin films were found to be normalized ion flux dependent. These normalized ion flux induced changes in structure composition and properties may be understood by considering surface and bulk diffusion related mechanisms.

## Advanced Surface Engineering Room 2007 - Session SE1-FrM

### Coatings with Enhanced Thermal Stability & MAX Phases

Moderator: A.A. Voevodin, WPAFB

8:00am **SE1-FrM1 Coatings for Aero Engine Applications: Current Status and New Developments, C. Leyens**, Technical University of Brandenburg at Cottbus, Germany **INVITED**

Increasing demands placed on the efficiency and performance of aero engine gas turbines have resulted in ever higher process temperatures; this requires high thermal stability of the materials systems applied. Also, with increasing temperatures, the lifetime of components becomes strongly affected by oxidation and hot corrosion processes that eventually limit the useful service temperatures. Therefore, coating systems have been developed that effectively protect gas turbine hardware against environmental attack and at the same time provide thermal insulation of the underlying superalloy component. In the cooler part of the engines, titanium alloys are used which might be complemented with the application of intermetallic titanium aluminides in the future which have a higher temperature capability. To date, no coatings for these material are available, however, current research is looking for adequate solutions. The present paper will review state-of-the art science and technology of coating systems for high temperature applications in the turbine part of aero engines. Here, thermal barrier coating systems are applied consisting of a duplex layer system which is comprised of a metallic bond coating and a ceramic top coating that provides thermal insulation. The paper will address currently used coating technologies and will deal with a number of materials-related aspects such as thermal conductivity of the ceramic coating, thermal stability, lifetime and failure. Current research for future materials systems with improved performance will be highlighted. Moreover, coatings development for titanium alloys and titanium aluminides will be addressed shedding light on an emerging field of new coating systems. Major emphasis is placed on the thermal stability of the coatings, their interaction with the reactive Ti-containing substrate and their effect on the mechanical properties of the component.

8:40am **SE1-FrM3 Effect of a BN Interlayer on the Tensile Strength of NiAl Coated Sapphire Fibers, D.E. Hajas**, RWTH-Aachen University, Germany; S. Kyrsta, CemeCon AG, Germany; J.M. Schneider, RWTH-Aachen University, Germany

Intermetallic Matrix Composites (IMCs) can be fabricated by diffusion bonding of coated fiber bundles. Continuous single crystal  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> fibers were coated with NiAl, h-BN and h-BN-NiAl using Chemical Vapor Deposition (CVD) for the h-BN interlayer and Physical Vapor Deposition (PVD) for the NiAl matrix material. The strength of the coated fibers was evaluated by tensile testing and compared to the strength of uncoated fibers. The effect of temperature during diffusion bonding on the fiber strength was studied. The influence of the coating on the fiber strength was evaluated by etching experiments. Fibers without h-BN interlayer cracked during heat treatment and testing could not be performed. This may be due to thermal stress induced fiber fracture during cooling. However, fibers coated with h-BN interlayer retained approximately 60% of their initial strength after the heat treatment. Two types of morphological features were identified which in combination with thermal stresses may be responsible for the strength degradation of annealed h-BN-NiAl coated fibers: Surface diffusion of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> into cracks in the h-BN interlayer and reaction of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> with impurities on the fiber surface.

9:00am **SE1-FrM4 Decomposition Process of Ti<sub>3</sub>SiC<sub>2</sub>(0001) Thin Films, J. Emmerlich, D. Music**, RWTH Aachen University, Germany; H. Willman, P. Eklund, H. Höggberg, Linköping University, Sweden; J.M. Schneider, RWTH Aachen University, Germany; L. Hultman, Linköping University, Sweden

MAX phases (M: early transition metal; A: group-A element (13-15), X: C and/or N), such as, Ti<sub>3</sub>SiC<sub>2</sub> exhibit metallic (e.g. well-conducting and ductile) and ceramic (e.g. oxidation resistance, high Young's modulus of ~340 GPa) properties. The main reason for the interesting set of properties is the nanolaminated crystal structure consisting of twinned Ti<sub>3</sub>C<sub>2</sub> slabs interleaved with an atomic layer of Si acting as mirror plane weakly bonded to the Ti<sub>3</sub>C<sub>2</sub> slabs. Epitaxial Ti<sub>3</sub>SiC<sub>2</sub>(0001) thin films were deposited on Al<sub>2</sub>O<sub>3</sub>(0001) substrates using DC magnetron sputtering. In our

earlier investigations, these samples were vacuum-annealed from 800-1400°C with in-situ x-ray diffraction analysis. Between ~1000 and 1100°C the onset of decomposition was observed followed by the complete decomposition of the film after 25h annealing at 1200°C. Here, we present a 4-stage decomposition model based on the findings of transmission electron microscopy and supported by ab-initio calculations. The Si out-diffusion and evaporation initiated at the surface at 1100°C is followed by the O-uptake and SiO evaporation resulting in Ti<sub>3</sub>C<sub>2</sub> relaxation, detwinning, and Ti<sub>3</sub>C<sub>2</sub> formation by C-redistribution with void formation. Initial differential scanning calorimetry measurements on as-deposited Ti<sub>3</sub>SiC<sub>2</sub>(0001) films show that the MAX phase is stable up to at least 1400°C for cases, where Si out-diffusion and O-uptake are prevented by means of Ti<sub>3</sub>SiC<sub>2</sub>(0001) films mechanically put face-to-face and heated in an Al<sub>2</sub>O<sub>3</sub> crucible in Ar atmosphere. This further supports the validity of the presented model.

9:20am **SE1-FrM5 Synthesis, Structure and Properties of New Types of M-A-X Phase Films, U. Jansson**, Uppsala University, Sweden **INVITED**

New thin film materials in the M-A-X systems have recently been given a considerable attention. In these systems M represents a transition metal, A is a so-called A-element typically from group 13-15 (e.g. Si, Al, Ge) and X is either carbon or nitrogen. An interesting group of compounds in these systems are the nanolaminated MAX-phases with a general composition M<sub>n+1</sub>A<sub>n</sub>X<sub>n</sub> where n=1,2 or 3. They can be described as nanolaminates of metal carbides or metal nitrides separated by A-layers. The nanolaminated structure gives rise to special chemical and physical properties that suggest a potential use of these materials in different thin film applications such as low-friction materials, thermal protection coatings and chemically resistant coatings. Today, these compounds can be deposited as thin films using e.g. magnetron sputtering. Depending on the process parameters, however, also other types of thin film materials can be obtained. This includes other compounds such as perovskites and metastable solid solutions of metal carbides/nitrides with extremely high A-contents. Other examples are nanocomposites of carbides and nitrides in an A-containing matrix or other types of self-organizing microstructures. During thin film growth all these different types of materials and microstructures may be formed and a careful tuning of process parameters is required. This paper will discuss how phase composition and microstructure can be controlled in e.g. the Ti-Si-C, Ti-Al-C and Ta-Al-C systems. The possibilities to design functional coatings for various applications will be discussed.

10:00am **SE1-FrM7 Growth and Characterization of Ti-Al-C Thin Films Deposited by dc Magnetron Sputtering from a Ti<sub>2</sub>AlC Compound Target, J. Frodelius, P. Eklund, H. Höggberg, L. Hultman**, Linköping University, Sweden

The ternary carbides and nitrides referred to as the MAX phases exhibit properties combining typical ceramic characteristics such as resistance to oxidation and thermal shock with electrical resistivity values comparable to those typically found in metals. These merits suggest many application areas for MAX phases both in the form of bulk material, such as heating elements and gas nozzles, as well as functional thin films in sensors and microelectronics. The synthesis of well-defined epitaxial thin films has progressed lately by the development of a magnetron sputtering process from elemental sources. This method is, however, less suited for growth under industrial conditions. In this study we present the synthesis of Ti-Al-C films on Al<sub>2</sub>O<sub>3</sub>(0001) as well as Mo substrates, using dc magnetron sputtering from a Ti<sub>2</sub>AlC target. The growth, structure and properties of Ti-Al-C films were investigated by XRD, SEM, TEM, EDS, nanoindentation and four-point-probe measurements. The films were synthesized for a wide range of substrate temperatures from ambient to 1000 °C as well as different substrate bias and target-to-substrate distances. The growth of Ti<sub>2</sub>AlC films on Al<sub>2</sub>O<sub>3</sub>(0001) substrates appear to be restricted to a narrow temperature regime around 700 °C. Below that, films consist of TiC:Al and for higher substrate temperatures, there is preferred growth of epitaxial TiC cubic phase. These films are depleted in Al, as revealed by EDS measurements. Footnote 1@ MAXTHAL 211, courtesy of Kanthal AB.

# Friday Morning, November 17, 2006

10:20am **SE1-FrM8 Reactive dc Magnetron Sputtering of Ti-A-CN (A=Si, and Ge) MAX-Phase Thin Films**, *H. Högberg, P. Eklund, J. Emmerlich, J. Frodelius*, Linköping University, Sweden; *O. Wilhelmsson, U. Jansson*, Uppsala University, Sweden; *L. Hultman*, Linköping University, Sweden

The  $M_{n+1}A_nX_n$  ( $n=1$  to 3) phases exhibit a unique set of properties, described as being a combination of metallic and ceramic, reflected by the values reported for  $Ti_3Si_2$  on good oxidation and thermal shock resistance as well as high electrical conductivity. These attributes that stem from an anisotropic hexagonal crystal structure formed by early transition metals (M), group 14-16 elements (A) and carbon or nitrogen (X) are shared by the ~60 MAX phases. However, the extent is dependent on choice of material system and stoichiometry. The structure allows for freedom in substitution of elements of all the three constituents, opening possibilities to further tailor the properties of these materials by synthesis of quaternary and higher-order phases. In this study, we present results from thin film growth of the quaternary Ti-Si-C-N and Ti-Ge-C-N systems on  $Al_2O_3$  (0001) substrates at temperatures in the range 500 to 1000 °C, using d.c. magnetron sputtering from elemental sources and growth in  $Ar/N_2$  plasmas. XRD shows a temperature-dependent growth behavior for epitaxial ternary  $Ti_3Si_2$  and  $Ti_2GeC$  as seen by the possibility to synthesize single-phase films at 850 °C, while lower temperatures result in growth of cubic phases. Higher temperatures promote surface segregation of the A-element as particularly pronounced in the Ti-Ge-C system resulting in growth of less Ge-rich stoichiometries. The addition of  $N_2$  to single-phase films in the Ti-Ge-C system results in growth of films of lower crystalline quality and thickness, and with nucleation of cubic phases as the flow of  $N_2$  is increased.

## Advanced Surface Engineering Room 2007a - Session SE2-FrM

### Wear Mechanisms, Tribochemistry and Nanotribology

Moderator: A.A. Voevodin, WPAFB

10:40am **SE2-FrM9 The Relation of Tribochemistry to Superlubricity in DLC Films**, *A. Erdemir, O.L. Eryilmaz*, Argonne National Laboratory **INVITED** Diamondlike carbon (DLC) films have attracted a great deal of interest in recent years, mainly because of their exceptional mechanical and tribological properties. Systematic studies of such films in our laboratory over the past 15 years have led to the development of a new class of carbon films that can provide friction coefficients of 0.001 to 0.005 and wear rates of 10<sup>-11</sup> to 10<sup>-10</sup> mm<sup>3</sup>/N.m when tested in inert-gas or high-vacuum environments. Comprehensive studies over broad test conditions and environments have shown that the unique friction and wear behavior of these films is very sensitive to the type and extent of tribochemical interactions that occur when certain gaseous species are present in the surrounding atmosphere. Among others, oxygen and water molecules were found to have the strongest adverse effects on their friction and wear. Using x-ray photoelectron spectroscopy and time-of-flight secondary ion mass spectrometry, we determined the chemical states of their sliding surfaces and correlated these findings with their super-low friction behavior in inert gases and high-friction behavior in oxidizing and moist environments. Synthesis of diamondlike carbon films with superlow friction and wear properties, A. Erdemir, O. L. Eryilmaz, G. Fenske, *Journal of Vacuum Science and Technology A*, 18(2000)1987-1992.

11:20am **SE2-FrM11 Synthesis and Tribological Properties of Novel 'Chameleon' Coatings**, *C.C. Baker*, North Carolina State University; *J.J. Hu, A.A. Voevodin*, Air Force Research Labs, MLBT

'Chameleon' coatings are nanocomposite coating systems adapt their tribological performance to changes in environmental conditions such as humidity and temperature. In this research we have investigated the tribological properties of two new nanocomposite 'chameleon' coating systems. One of the system includes the incorporation  $Al_2O_3$  in an Au matrix with diamond like carbon (DLC) and  $MoS_2$  nanoparticle inclusions. The coating design approach included a formation of nanocrystalline hard oxide particles for wear resistance, their embedding onto an amorphous matrix for contact toughness enhancement, and inclusion of nanocrystalline and/or amorphous solid lubricants for friction adaptation to different environments. The other coating system that we have studied includes a composite of Rhenium and hexagonal Boron Nitride. Rhenium is a unique ultra hard material that shows low coefficient of friction at

elevated temperatures to 700 °C and in vacuum environments, while Boron Nitride is also excellent for high temperatures and for humid environments. All coatings were produced using a combination of laser ablation and magnetron sputtering. Chemical and structural analysis of the coatings included x-ray photoelectron spectroscopy, x-ray diffraction, transmission electron microscopy, and micro-Raman spectroscopy. Mechanical properties such as coating hardness and toughness were investigated using nanoindentation, scratch, and indentation adhesion tests. Friction measurements were studied by cycling between humid air and dry nitrogen conditions, as well as tests at temperatures of up to 700 °C. Both of the new coating systems validate the universality of the 'chameleon' design approach.

11:40am **SE2-FrM12 Tribochemical Studies on Single Crystal Surfaces using Atomic Force Microscopy**, *J.T. Dickinson, A. McEvoy, S.C. Langford*, Washington State University

We have examined two tribochemical processes on single crystal surfaces using the atomic force microscope that result in nanometer scale modification. Using solutions appropriate for crystal growth or crystal dissolution we show that application of tribological stimulation can lead to highly localized, in some cases atomic, deposition or material removal. The samples of current study include cleavage surfaces of calcite and gypsum (for growth) and Si(100) for tip-induced dissolution. The latter study relates directly to understanding the mechanisms of chemical mechanical planarization of silicon wafers where today's requirements for topography have reached the sub-nanometer scale.

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