Advanced Surface Engineering
Room 303D - Session SE-MoM

Nanolayered and Gradient Coatings for Surface Engineering

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

8:20am **SE-MoM1 Structure and Hardening in TiN/a-SiNx Multilayers and Self Organizing Ti1-xAlxN Films*, M. Oden,*** Lulea University of Technology, Sweden **INVITED**

This talk will cover two distinctly different mechanically hard films. The first is a dual reactive magnetron sputtered mulilayer consisting of alternating polycrystalline TiN and amorphous SiNx layers. The TiN layers exhibit a preferred 200 orientation for layer thicknesses below 10 nm. For thicker layers 111 orientations are also observed. The amorphous SiNx layers provides for TiN renulcleation in each layer yielding a column free microstructure. Nanoindentation was used to evaluate the hardness which varied between 18 to 32 GPa depending on the layer modulation. For large wavelength (>20 nm), Hall-Petch dependence is observed with a generalized power of -0.4. For shorter wavelengths superhardening yields a deviation from the Hall-Petch relationship. The highest hardness is observed for mulilayers having thin SiNx -layers (< 1nm) for which HRTEM reveals a transformation from amorphous to crystalline SiNx layers growing cube on cube on the TiN crystals. The formation of crystalline SiNx and its influence on hardening is discussed. The second material system to be reviewed is arc evaporated Ti1-xAlxN with a range of compositions (x=0 to 0.74). As-deposited coatings with xï,£0.66 had metastable cubic structures. Annealing at 1100 Â°C of these films resulted in phase separation of c-TiN and h-AlN, via spinodal decomposition of c-TiN and c-AlN. The high hardness (~37 GPa) and texture of the Ti1-xAlxN coatings are retained for annealing temperatures up to 950ï,°C, which indicates a superior stability of this system compared to TiN and Ti(C,N) coatings. It is proposed that competing mechanisms are responsible for the effectively constant hardness; softening by lattice defect annihilation is balanced by hardening from formation of a nano-composite structure of c-AlN volumes by spinodal decomposition.

9:00am **SE-MoM3 Structure and Optical Behavior of As-Grown and Annealed Titania/Alumina Nanolaminate Films*, M.A. Omari,*** *R.S. Sorbello, C.R. Aita,* University of Wisconsin-Milwaukee

Titania-alumina nanocomposites are of current interest for optical, catalytic, and sensor applications. A wide range of desirable properties can be obtained by varying the amount of each constituent. A convenient way of incorporating tailored nanocomposites in thin film structures is by using a nanolaminate structure. We report here the fabrication, structure, and optical behavior of titania-alumina nanolaminates. 150 nm-thick multilayer films were grown at room temperature on silica substrates by sequential reactive sputtering of metal targets in argon/20% oxygen rf discharges. The nominal titania layer thickness was varied from 1.25 to 45 nm, and the alumina layer thickness was kept constant at 5 nm. X-ray diffraction and spectrophotometry were used for film analysis. The films were cyclically annealed at 700 and 1000 deg. C from 15 min to 10 h. Alumina was amorphous in as-grown and annealed films. Titania in as-grown films consisted of rutile nanocrystals embedded in an amorphous matrix. No anatase was present, nor was anatase formed by annealing. High temperature annealing produced a series of crystalline (Ti,Al)-oxide interface phases. Optical band gap and refractive index measurements indicate that significant interfacial mixing occurred in as-grown films, as well.

9:20am **SE-MoM4 The Growth of Depth-Graded WSi@sub 2@/Si Multilayer Linear Zone Plates**, C. Liu,*** *R. Conley, A.T. Macrander, J. Maser, H.C. Kang, G.B. Stephenson,* Argonne National Laboratory

Fresnel zone plates, consisting of alternating transparent and opaque rings designed according to Fresnel phase conditions, are widely used to focus x-rays. Zone plates are commonly made using lithographic techniques and have achieved high spatial resolution on the order of 20 nm in the soft x-ray range. For hard x-rays, to achieve an optimum efficiency, the thickness of the zone plate needs to be several microns. The required high aspect ratio is difficult for lithography and imposes a limit to the focus spot size. Techniques have been developed using sectioned multilayer-coated wires to obtain a high aspect ratio, with concentric multilayers as the zone-plate rings. We have recently explored a linear zone-plate concept, by first growing a depth-graded multilayer on a flat substrate and then sectioning the multilayer and assembling several sections to focus the x-rays. The structure of the multilayer is calculated according to the desired focus parameters with corresponding Fresnel phase conditions. We have grown a depth-graded WSi@sub 2@/Si multilayer on a Si substrate using dc magnetron sputtering to test the linear zone-plate idea. The multilayer has a total of 469 alternating layers with thickness gradually increasing from ~15 nm to ~60 nm. It has a total coating thickness of ~11.27 µm and took ~45 h to coat. The sample has been sectioned and polished and studied using a scanning electron microscope and synchrotron radiation x-rays. The challenges and solutions for the growth of this kind of depth-graded multilayer will be discussed. @FootnoteText@ @footnote *@ This work is supported by the U. S. Department of Energy, under Contract No. W-31-109-ENG-38.

10:00am **SE-MoM6 Early Stages of Oxidation at 800°C for CrAlON Superlattice Coatings used to Improve Oxidation Resistance of Steel Plates for Applications as SOFC Interconnects@footnote *@*, R.J. Smith*,** *A. Kayani, C.V. Ramana, P.E. Gannon, M.C. Deibert,* Montana State University-Bozeman*; V.I. Gorokhovsky,* Arcomac Surface Engineering, LLC*; V. Shutthanandan, D. Gelles,* Pacific Northwest National Laboratory

The requirements of low cost and high-temperature corrosion resistance for bipolar interconnect plates in solid oxide fuel cell stacks has directed attention to the use of metal plates with oxidation resistant coatings. We have investigated the performance of steel plates with superlattice coatings consisting of CrAlON (oxynitrides). The coatings were deposited using large area filtered arc deposition technology@footnote 1@, with various O/N pressure ratios, and subsequently annealed in air for up to 25 hours at 800°C. The composition, structure and morphology of the coated plates were characterized using RBS, nuclear reaction analysis, XPS and AFM techniques. Area specific resistance was measured as a function of time and temperature. By altering the architecture and composition of the coatings, the rate of oxidation was reduced by more than an order of magnitude relative to the uncoated steel plates. @FootnoteText@ @footnote 1@Vladimir I. Gorokhovsky, Rabi Bhattacharya and Deepak G. Bhat, Surface and Coating Technology, 140 (2) 2001, pp. 82-92.@footnote *@Work supported by DOI and DOE subcontract from PNNL, number 3917(413060-A). Work at PNNL (EMSL) supported through OBER (DOE) .

10:20am **SE-MoM7 Oxide Nanolaminate Coatings for Protection Against Perforated Pitting Corrosion in Stainless Steel*, W.F. Gaertner,*** *C.R. Aita,* University of Wisconsin-Milwaukee

Perforated pitting corrosion is disastrous in stainless steel (SS) medical implants where even a low released cation concentration causes rejection by the surrounding tissue. Protection by oxide nanolaminates on 316L SS in saline is reported here. The behavior of constituent oxide single-layer films is also reported. We previously found [1] that a tetragonal ZrO@sub 2@/A1@sub 2@O@sub 3@ smart nanolaminate protects a rough 316L SS substrate (15 µm finish) against pitting. We constructed a model for corrosion prevention after a pit has initiated. This model involves mesoscopic film fracture accompanied by passivation of the underlying exposed SS. Here, we apply this model to (a) films on highly polished (1 micron finish) substrates where adhesion can be a problem, and (b) to a TiO@sub 2@/A1@sub 2@O@sub 3@ nanolaminate (which is not a smart coating) on both rough and substrates. 200 to 250 nm thick films were grown at room temperature by sequential sputtering of metal targets in Ar with 20% O@sub 2@ rf discharge. Cyclic polarization was used to determine the corrosion current, i@sub o@, as a function of applied potential after a steady state open circuit potential (OCP) was established. Samples were examined by scanning electron microscopy and energy dispersive spectroscopy. The results show that: (1) Corrosion current in all samples was low, on the order of 1 to 100 nA/cm@super 2@. (2) Single layer ZrO@sub 2@ and TiO@sub 2@ films did not protect against perforated pitting in polarized samples of either surface finish. (3) Single layer A1@sub 2@O@sub 3@ did prevent pitting but catastrophically failed after a single polarization cycle.(4) Nanolaminates protected by the synergic effect of a tough (ZrO@sub 2@, TiO@sub 2@) nanolayer combined with a brittle (A1@sub 2@O@sub 3@) became important in 316L SS with a rough finish. @FootnoteText@ NSF-CMS Grant No. 9988892 is acknowledged. [1]W.F.Gaertner,et al.,JVST A 22, 272 (2004).

10:40am **SE-MoM8 Environmentally Friendly Plasma Electrolytic Processes for Corrosion and Wear Protection of Lightweight Metals*, A.L. Yerokhin,*** Sheffield University, UK, U.K.*; A. Matthews,* Sheffield University, UK **INVITED**

The paper discusses both fundamentals and applied aspects of novel Plasma Electrolytic Oxidation (PEO) processes which can be successfully used for wear and corrosion protection of Al, Ti and Mg alloys. Being a high-voltage electrochemical oxidation process, PEO is featured by a plasma discharge that occurs at the metal/electrolyte interface in the form of discrete short-lived microdischarges moving across the metal surface. This alters the kinetics of the main electrode processes, i.e. anodic oxidation and dissolution, complementing them with high rate gas evolution triggered by plasma enhanced thermochemical reactions at the metal surface. As a result, surface layers with composition and structure substantially different to those of conventional anodic oxide films can be formed in environmentally friendly diluted alkaline solutions. Electrolyte species tend to be more strongly incorporated into the surface layer, forming mixed oxide compounds. Rapid local heating and quenching of the surface during the microdischarge events promotes formation of high temperature oxide phases with fused-like structure, controllable porosity and a graded coating/substrate interface. Oxide ceramic surface layers produced by PEO as well as composite coatings based on these layers are proven to possess excellent tribological and anti-corrosion properties, which show promise for a number of industrial applications.

11:20am **SE-MoM10 Evaluation of Plasma Polymer Coatings in Corrosion Protection of Aluminum Alloys***, **Q.S. Yu,*** University of Missouri-Columbia, US*; Y.F. Chan, H.K. Yasuda,* University of Missouri-Columbia

As a pretreatment method, chromate conversion coatings are being widely used for corrosion protection of aircraft aluminum alloys. Pretreatment by chromate conversion layer is used to ensure good paint adhesion and provide corrosion inhibition. Due to the hazardous and toxic effects of chromates to environment and human heath, however, pressure from EPA has promoted research efforts focusing on the replacement of chromate conversion coatings with more environmentally friend systems. One promising alternative method is the use of plasma polymer coatings as pretreatment for metallic materials. Plasma polymerization process is a dry and â?ogreenâ?□ process which can produce high quality and chemically inert coatings with strong adherence to various substrates including metallic materials. Our recent studies have demonstrated that interface engineered plasma coating systems provide excellent corrosion protection of various aircraft Al alloys. In this study, the roles of plasma polymer coatings in interface engineering and fabrication of environmentally benign coating systems are further investigated. Electrochemical measurements including potentiodynamic polarization and electrochemical impedance spectroscopy are employed to characterize the corrosion resistance and interface properties of plasma coated Al alloys. The results obtained through this study will be presented and discussed.

11:40am **SE-MoM11 Nano-coatings for Complex Uneven Surfaces Cellular Foams & Nano-fibers of Carbon***, S.M. Mukhopadhyay, **R.V. Pulikollu,** P.P. Joshi,* Wright State University

The concept of surface coatings to enhance or prevent bonding with a second phase is not new, but when the surface in question has complex shape, and the coating needs to be effective at the nanometer scale, new challenges emerge. In this presentation, effectiveness of plasma-assisted nano-coatings (4-5nm thick) on two carbon structures will be presented. These are: (i) microcellular foam that has about 80% porosity and the surface consists of open, interconnected cell walls, and (ii) vapor-grown fibers having diameter of about 200nm. Both these structures are useful as reinforcing materials for composites. Coatings for enhancement surface wettability are obtained in microwave plasma using siloxanes. This treatment forms a strongly bound SiO2-type layer on the surface and causes noticeable enhancement of polar fluid infiltration in these materials. This results in micro-structural differences and enhancement of mechanical properties of composites formed. A different type of coating, that makes the surface inert by attaching CF2 groups on it, is effective in making these surfaces moisture-repellent. This coating appears to influence composite behavior in different ways. Additional aspects of these coatings, specific to different applications, such as bonding with metals and polymers, and possibility of creating multi-layer and multi-functional nano-coatings will be discussed.

Advanced Surface Engineering
Room 303D - Session SE-MoA

Structure Control of Hard Coatings in Sputtering Processes

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

2:00pm **SE-MoA1 Control of Nanostructure Evolution in Metastable Transition Metal Nitride Layers using High-Flux, Low-Energy Ion Irradiation during Growth*, I. Petrov,*** University of Illinois **INVITED**

We use high-flux, low-energy ion irradiation during low-temperature growth to control the kinetic pathways of phase separation in metastable transition-metal nitride layers in order to produce novel nanostructures composed of self-organized nanolamellae in δ-TaN@sub x@ or nanocolumns in Ti@sub 1-x@Ce@sub x@N. Coherent δ-TaN(111)/γ-Ta@sub 2@N(0002) nanolamellae form spontaneously in reactively-sputter-deposited TaN@sub x@ layers when using ion energy E@sub i@ ~ 50 - 65 eV with an ion-to-metal flux ratio J@sub i@/J@sub Me@ ~ 11; at lower E@sub i@ the films are phase-pure metastable δ-TaN @sub x@. The nanolayers are coherent platelets of alternating metastable cubic δ - TaN@sub x@ and thermodynamically-stable hexagonal γ-Ta@sub 2@N phases which are lattice-matched along their hexagonal closed-packed δ-TaN(111) and γ-Ta@sub 2@N(0002) planes. The formation of γ-Ta@sub 2@N nanolamellae is attributed to ion-irradiation-induced ordering of N vacancies within the (111) N planes of δ-TaN that causes hexagonal stacking of the closed-packed Ta planes. The nanolamellar TaN layers exhibit superhardness values (H = 40-45 GPa). During reactive sputter-deposition of metastable Ti@sub 1-x@Ce@sub x@N alloys, we observe nanophase films with x>0.1. Under conditions of low ion-irradiation, i.e. grounded or floating substrates, the nanostructure consists of equiaxed grains which forms due to continuous renucleation induced by CeN segregation. This is analogous to the nanostructure to the one observed in crystalline/amorphous nanocomposites, e.g. TiN/Si@sub 3@N@sub 4@. In contradistinction, a novel nanocolumnar structure forms when the alloys are grown under intense ion-irradiation with J@sub i@/J@sub Me@ ~ 15 and Ei = 45 eV. The intense ion mixing in the near surface area allows sufficient adatom mobility to form local TiN- and CeN-rich areas that propagate along the growth direction.

2:40pm **SE-MoA3 Investigation of the Solubility in (M@sub x@M'@sub 2-x@)AlC (M and M' = Ti, V, Cr) as well as the Cr-Al-C System*, J.M. Schneider,*** *D. Music, Z. Sun, R. Mertens,* RWTH Aachen, Germany*; R. Ahuja,* Uppsala University, Sweden

We have performed theoretical studies of the solubility within (M@sub x@M'@sub 2-x@)AlC, where M and M' = Ti, V, Cr by means of ab initio total energy calculations. The theoretical values of equilibrium volume and the optimized c/a ratios are in good agreement with those of experiments (within ~ ± 4% and ~ ± 1.3%, respectively). Furthermore, we show that if x is increased from 0 to 2 the bulk modulus can be increased by as much as 36%. Based on the total density of states analysis as well as the energy of formation, we suggest that the investigated systems show solubility except for the (Cr,Ti)@sub 2@AlC system. In addition to these data we have studied the effect of the chemical composition on the structure in the system Cr-Al-C by combinatorial thin film synthesis. By changing the Cr/C ratio from 1.72 to 3.48 and the Cr/Al ratio from 1.42 to 4.18 the formation of Cr@sub 2@AlC, Cr@sub 2@Al and Cr@sub 23@C@sub 6@ phases was observed. Furthermore, based on X-ray diffraction a single phase Cr@sub 2@AlC composition region is identified (Cr/C ratio between 1.72 and 1.925, Cr/Al ratio between 1.42 and 2.03) in the Cr-Al-C phase diagram. Throughout the studied composition range the lattice parameters of Cr@sub 2@AlC were independent of the chemical composition : a = 2.865 Å ± 0.2%, c = 12.80 Å ± 0.6%. Furthermore, we find that a deviation from the stoichiometric composition of up to 6.3 at % for Al still results the formation of a Cr@sub 2@AlC single phase field. Possible pathways to accommodate the observed deviation from stoichiometry are discussed.

3:00pm **SE-MoA4 Growth and Characterization of New Epitaxial MAX-Phase Thin Films from the Ti@sub n+1@(Si, Ge)C@sub n@ Systems by Magnetron Sputtering*, H. Högberg,*** *J. Emmerlich,* Linköping University, Sweden*; J.-P. Palmquist,* Kanthal AB, Sweden*; P. Eklund,* Linköping University, Sweden*; O. Wilhelmssson,* Uppsala University, Sweden*; L. Hultman,* Linköping University, Sweden*; U. Jansson,* Uppsala University, Sweden

This is a presentation of the state-of-the-art for the materials research on M@sub n+1@AX@sub n@ (n=1 to 3) phase thin films. The MAX-phases are a family of ductile inherently nanolaminated ternary nitrides and carbides with a high potential for industrial applications due to their unique combination of metallic and ceramic properties, as recently reported for the archetype Ti3SiC2. These properties stem from a highly anisotropic hexagonal crystal structure, where early transition metal (M) atoms and C or N (X) atoms form edge-sharing octrahedral MX blocks that are interleaved by layers of group 13-15 elements (A). Using DC magnetron sputtering with elemental sources we deposited epitaxial MAX-phase films from the Ti-Si-C and Ti-Ge-C systems on Al2O3(0001) or MgO(111) substrates at temperatures of 900 oC or 1000 oC, which is 500 oC lower than for conventional bulk processes. Besides demonstrating single-crystal growth of the known phases Ti3SiC2, Ti3GeC2, and Ti2GeC we have discovered two phases Ti4SiC3 and Ti4GeC3 as well as four intergrown structures of stoichiometries Ti5A2C3 and Ti7A2C5. The general trend from synthesis and characterization is that both MAX-phase systems show similarities with respect to phase distribution, mechanical, and electrical properties, reflecting the close chemical relationship between Si and Ge. However, XRD shows that the Ti-Ge-C MAX-phases are restricted to a more narrow deposition window and require slightly higher temperatures due to a more limited diffusivity of the larger Ge atoms. From the nanoindentation analysis we see the characteristic large plastic deformation with extensive pile up for both systems, but measure a slightly lower Youngs modulus of 300 GPa for the Ti-Ge-C films compared to the 320 GPa obtained from Ti3SiC2 films. The four-point probe measurements show a lower conductivity for the Ti3GeC2 films compared to their Si-counterparts with resistivity values of 50 and 25 @micro@@ohm@cm, respectively.

3:20pm **SE-MoA5 Epitaxial Growth of B1-NaCl-Structure HfN@sub x@ Layers on MgO(001) by Ultrahigh Vacuum Magnetron Sputter Deposition*, H.-S. Seo,*** *T.-Y. Lee, J.G. Wen,* University of Illinois*; D. Gall,* Rensselaer Polytechnic Institute*; I. Petrov, J.E. Greene,* University of Illinois

Group IVB metal nitrides are used in hard coating, wear-resistant, and diffusion barrier applications due to their excellent mechanical, electrical, and electrochemical properties. In the Hf-N system, unlike Ti-N where TiN is the terminal phase, several conflicting claims concerning the existence of N-rich phases have appeared in the literature. Here, we report the results of a systematic investigation of the properties of epitaxial HfN@sub x@ layers grown at 650°C on MgO(001) by ultrahigh vacuum reactive magnetron sputter deposition in mixed N@sub 2@/Ar discharges. X-ray diffraction and transmission electron microscopy analyses show that HfN@sub x@ with 0.8 @<=@ x @<=@ 1.38 grows epitaxially with a cube-on-cube orientational relationship to the substrate. HfN@sub x@ layers with x @<=@ 1.2 are single crystalline while films with x @>=@ 1.24 consist of a mixture of NaCl-structure HfN@sub x@(001) and a N-rich phase with large interplanar spacing (d = 2.7-3.0 Å). The relaxed bulk lattice parameter of HfN@sub x@(001) decreases only slightly with N/Hf ratio from 4.543 Å with x = 0.8 to 4.504 Å with x = 1.38. The room-temperature resistivity @rho@ of HfN@sub x@ varies from 14.2 µ@ohm@-cm for x = 1.0 to 2710 µ@ohm@-cm for x = 1.5, while the hardness H and elastic modulus E values of HfN@sub x@(001) with 0.8 @<=@ x @<=@ 1.5 are 28±4 GPa and 400±60 GPa, respectively. HfN@sub x@(001) layers with 0.8 @<=@ x @<=@ 1.32 are metallic with positive temperature coefficients of resistivity (TCR) between 10 and 300 K and temperature-independent carrier concentrations. They are also superconducting with the highest critical temperature, 9.18 K, obtained for layers with x = 1.0. At higher N/Hf ratios (x @>=@ 1.38), the layers exhibit significant changes in their electronic structure leading to a dramatic increase in @rho@ with a negative TCR, no superconducting transition above 2 K, and a decrease in H and E.

3:40pm **SE-MoA6 Surface Morphological Evolution of Epitaxial CrN(001) Layers***, J.R. Lynch, J. D'Arcy-Gall, S.V. Kesapragada,* ***D. Gall,*** Rensselaer Polytechnic Institute

CrN layers, 7 to 300 nm thick, were grown on MgO(001) at 600-800 @degree@C by ultra-high-vacuum magnetron sputter deposition in pure N@sub 2@ discharges at 20 mTorr. Microstructural and surface morphological evolution were found to depend strongly on the growth temperature T@sub s@. Layers grown at 600 @degree@C nucleate as single crystals with a cube-on-cube epitaxial relationship with the substrate. However, above a critical thickness of ~50 nm, misoriented CrN grains nucleate and develop into cone-shaped grains that protrude out of the epitaxial matrix to form triangular faceted surface mounds. These mounds lead to a dramatic increase in the root-mean-square surface roughness, from 3 to 19 nm, for a 300-nm-thick layer. CrN grown at T@sub s@ = 700 and 800 @degree@C are complete single crystals. Their surfaces exhibit dendritic mounds with fingers extending along orthogonal directions. In addition, the T@sub s@ = 700 @degree@C layer also shows square shaped "super"-mounds which protrude out of the underlying matrix and are attributed to a growth instability related to atomic shadowing effects which were purposely enhanced by non-normal deposition. For all layers, the surface roughness follows a power law with t. The exponent @beta@ is 1@+-@0.2 for the matrix-part of the surfaces, that is, the surfaces excluding the triangular and square shaped mounds for the T@sub s@ = 600 and 700 @degree@C layers, respectively. In contrast, @beta@ increases to 1.8@+-@0.3 when including the protruding grains. The two distinct @beta@-values are related to two roughening mechanisms: kinetic roughening, which is associated with an adatom motion towards ascending step edges due to a kinetic barrier for diffusion over descending steps, and atomic shadowing roughening, which is due to an increased local growth rate of surface protrusions caused by a higher capture rate of the incoming deposition flux.

4:00pm **SE-MoA7 Stress Reduction in Sputter Deposited Tungsten Films Using Nanostructured Compliant Layers by High Working-Gas Pressures***, **T. Karabacak**, J.J. Senkevich, G.-C. Wang, T.-M. Lu,* Rensselaer Polytechnic Institute

We present a new strategy of stress reduction in sputter deposited films by a nano-compliant layer at the substrate using physically self-assembled nanostructures obtained at high working-gas pressures prior to the deposition of a continuous film. This technique is all in-situ, and the nanostructures are made of the same material as the deposited thin film and requires no lithography process. This nanostructured layer has a lower material density and can act as a compliant layer to reduce the stress of the subsequently deposited continuous film grown under low gas pressure. By using this approach we were able to reduce stress values significantly in sputter deposited tungsten films and the strategy of alternating high and low Ar gas pressures leads to the growth of much thicker films without delamination.

4:20pm **SE-MoA8 High Powered Pulsed Magnetron Sputtering of Metallic Films in Ar, Ne, and He Plasmas***, S.L. Rohde, J. Li, **D.M. Mihut**,* University of Nebraska-Lincoln

High Powered Pulsed Magnetron Sputtering (alternatively, HIPIMS) can yield peak plasma densities >10@super 13@ cm@super -3@, three orders of magnitude higher than conventional sputtering, and also results in a higher fraction of ionized sputtered material. For sputtering of Ti almost 100% ionization has been observed, while for Cu around 70% of the metal was ionized, as compared with 5 to 10% for conventional magnetron sputtering. In the present study, the ionization efficiency of HPPMS has been investigated as a function of working gas using Ar, Ne, and He to sputter a variety of metallic targets (Cr, Al, Ti, and Cu). Successful deposition was achieved using all three working gases, and it was determined that the percentage of ionized metal reaching the substrate surface in each case varies with gas pressure, pulse energy, target metal, and gas species. Even using He as the working gas, it was possible to generate a highly ionized Al-flux - a very unexpected result. Additionally, there are preliminary indications that this highly ionized flux may be utilized in interface engineering during etch and pre-deposition stages. Selected films were studied both in-situ and ex-situ using spectroscopic ellipsometry (SE) to determine their optical properties and provide correlation between the optical properties and chemical/structural changes in the films, and thus providing a valuable resource for future work. In addition, some of these films were characterized post-deposition using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), atomic force microscopy (AFM), and nanoindentation. XPS, AES, and SE were used in tandem to reveal the crystal structure of the films observed under specific growth conditions.

4:40pm **SE-MoA9 The Dominance of Oxygen in Two-Gas Reactive Sputtering of Oxynitride Films***, **W.D. Sproul**, D.C. Carter, D.J. Christie,* Advanced Energy Industries, Inc.

Reactive sputtering with two reactive gases and one target material presents special problems. Both reactive gases affect the state of the target surface and the plasma conditions, which means that both affect common feedback control signals such as the cathode voltage and optical emission signals. Modeling has shown that the way to control the two-gas reactive sputtering process is to produce individual control signals for each gas and to control the partial pressure of each reactive gas. Experiments have confirmed the model. When oxygen and nitrogen are the two reactive gases, oxygen usually dominates the reaction. A small change in the amount of oxygen results in large changes in the properties of the films, whereas it usually takes a large change in the nitrogen partial pressure to change the film properties. These results were found during two-gas reactive sputtering of the oxynitrides of aluminum, silicon, and titanium where a differentially pumped mass spectrometer was used to produce individual partial pressure feedback signals for the oxygen and nitrogen. For these three oxynitride systems, oxygen strongly dominated the reaction. Very slight changes in the oxygen to nitrogen partial pressure ratios result in large changes in rate and optical properties for these oxynitrides. The dominance of oxygen is particularly acute when flow control is used for the oxygen and the nitrogen is in partial pressure control. In this situation, it is possible for the oxygen to trap the target in a poisoned state that cannot be reversed until both gases are removed. To avoid this problem, partial pressure control should be used to control both reactive gases. Experimental results showing the dominance of oxygen over nitrogen for the two-gas reactive sputtering of AlOxNy, SiOxNy, and TiOxNy will be shown and discussed.

5:00pm **SE-MoA10 Ion Assisted Deposition of Zirconium Nitride using Balanced and Unbalanced Magnetron Sputtering***, **S. Guruvenket**,* Indian Institute of Science, India, India

Zirconium nitride thin films were deposited on Si (111) substrates by balanced and unbalanced magnetron sputtering. The change in the preferred orientation of the deposited films was studied as a function of substrate bias voltage. ZrN films deposited by magnetron sputtering with out any bias voltage showed a preferred orientation of (111) where as, those deposited at higher bias voltages (above â?"60Volt) showed (200) as the preferred orientation. ZrN films deposited by unbalanced magnetron also showed a similar kind of transformation in the preferred orientation but the bias voltage required in this case was about -40V. Better quality films have been obtained with a resistivity value of 50 @micro ohm cm 1@ in unbalanced magnetron sputtering, where as, a resistivity of 63@micro ohm cm 2@ was obtained in case of magnetron sputtered ZrN thin films. The change in the surface roughness as the function of the bias voltage was also studied. @FootnoteText@ 1. @micro ohm cm 1@ 2. @micro ohm cm 2@.

Advanced Surface Engineering
Room 303D - Session SE-TuM

Hard and Low Friction Coatings with Advanced Designs

Moderator: D. Gall, Rensselaer Polytechnic Institute

8:20am **SE-TuM1 Tribological Coatings: Synthesis, Structure, and Properties***, **D.V. Shtansky**,* Moscow State Institute of Steel and Alloys, Russia **INVITED**

Various approaches to design and evolution of tribological coatings are review and refer to our recent results on the deposition, characterization, testing, and application of multicomponent nanostructured thin films. The targets for PVD based on the systems TiN+TiB@sub 2@, Ti@sub 5@Si@sub 3@+Ti, Ti@sub 5@Si@sub 3@+TiN, TiB@sub 2@+Si, TiB@sub 2@+SiC, TiB+Ti@sub 9@Cr@sub 4@B+Cr@sub 2@Ti, CrB@sub 2@, TiB@sub 2@+TiAl+Ti@sub 2@AlN, TiC+Ti@sub 3@SiC@sub 2@+TiSi@sub 2@, TiC@sub 0.5@+ZrO@sub 2@, TiC@sub 0.5@+CaO, Ti@sub 5@Si@sub 3@+ZrO@sub 2@, and TiC@sub 0.5@+Nb@sub 2@C were manufactured by means of self-propagating high-temperature synthesis (SHS). Multicomponent films were deposited by DC magnetron sputtering of composite targets either in an atmosphere of argon or reactively in a gaseous mixture of argon and nitrogen. The BN and WSe@sub x@ films were deposited using a sintered hexagonal BN and a cold compacting WSe@sub 2@ target, respectively. The WSe@sub x@ films were deposited by pulsed laser deposition (PLD) and ion-assisted PLD technique. The microstructure and chemical composition of films were studied by means of AES, EDXS, XRD, SEM, TEM, high-resolution TEM, XPS, and EELS. The films were characterized in terms of their hardness, elastic modulus, elastic recovery, adhesion, surface topography, friction, and wear. The biocompatibility of the medical films was evaluated by both in vitro and in vivo experiments. Three groups of films are considered: 1) nanostructured hard, tribological coatings Ti-B-N, Ti-Cr-B-N, Ti-Si-N, Ti-Al-B-N, Ti-Si-C-N, Ti-Si-B-N, BN, and Cr-B-N; 2) double-layer self-lubricating/hard coatings WSe@sub x@/TiC, WSe@sub x@/TiCN, WSe@sub x@/TiSiN, and 3) biocompatible hard coatings for medicine Ti-Ca-C-O-(N), Ti-Zr-C-O-(N), Ti-Zr-Si-O-(N), and Ti-Nb-C-(N). Particular attention is paid to the analysis of the structure of the films in the nanometric scale and the evaluation of the properties of the individual nanostructures.

9:00am **SE-TuM3 New Concepts for Low-friction Coatings***, **C. Mitterer**,* University of Leoben, Austria

Hard coatings deposited by plasma-assisted vapor deposition are widely used to reduce tool wear. The presently applied transition metal nitride coatings show high friction against steels, which restricts their applicability with reduced or without coolant. Tool temperatures for different machining operations are extremely different ranging from relatively low temperatures for deep drawing to above 1000°C for dry cutting. Presently applied low-friction coatings are essentially based on diamond-like carbon and MoS@sub2@, which often begin to fail with increasing temperature, in humid atmosphere or due to oxidation. The aim of the present contribution is thus to present now concepts for low-friction coatings for different temperature ranges. Examples for low-temperature lubrication approaches to be described include Cl-alloyed TiN coatings, where low-friction coefficients are provided by the Cl-induced formation of rutile layers on top of the coating in humid air, and CrC/a-C:H, where graphitization of the a-C:H phase is responsible for low friction coefficients. Approaches for lubricant phases at high temperatures (i.e. above 600°C) are based on the formation of Magneli phase oxides, in particular V@sub2@O@sub5@, due to oxidation of VN in Ti@sub1-x@Al@subx@N/VN superlattices or V in V-alloyed Ti@sub1-x-y@Al@subx@V@suby@N coatings. Using these concepts, friction coefficients of 0.2-0.4 against steel can be obtained for temperatures of 700°C, where lubrication is achieved by melting of the V@sub2@O@sub5@ phase. Another high-temperature low-friction approach is the application of thin top layers based on intermetallic phases on hard coatings. In particular, the Al@sub2@Au phase is stable up to 850°C without oxidation, shows a pink color and yields friction coefficients of 0.45 at 700°C. These nanoscale design approaches allow the utilization of functional properties facilitating the development of next generations hard coatings.

9:20am **SE-TuM4 Why do DLC and MoS@sub x@-based Amorphous Coatings Have Similar Friction and Wear Behavior?***, **I.L. Singer**,* Naval Research Laboratory **INVITED**

Amorphous coatings based on MoSx and hydrogenated carbon (a-C:H) exhibit dry sliding friction and wear behavior that qualifies them as ideal solid lubricating coatings. Both exhibit friction coefficients of 0.05 or less in dry air; in load-dependent friction tests, both coatings show interfacial shear strengths around 25 MPa in dry air. Both can have lifetimes of the orders of millions of cycles even though the coatings are one micrometer or less thick. However, their tribological behavior could not have been predicted based on common understanding of solid lubricants. The lubricity of MoS@sub 2@ is associated with easy shear of the basal planes, yet the MoSx-based coatings are amorphous. Often called diamond like carbon, a-C:H is a very hard material (12 - 16 GPa), with no easy shear planes. These discrepancies - between materials properties and tribological properties - can be reconciled by recognizing the role that third bodies play in the friction and wear of the two coatings. The low friction is associated with a film that transfers from the coating to the (counterface) slider and the velocity accommodation mode - interfacial sliding - between the transfer film and the parent coating. The higher friction coefficients of both in humid air is also explained by interfacial sliding and attributable to a higher interfacial shear strength in the presence of humidity. Earlier studies demonstrated that third body recycling from reservoirs contributed to the long life of MoS@sub 2@ coatings, and recent in situ tribometry studies also suggest ways in which the transfer film contributes to long life of diamond-like carbon, as well. Thus, both the friction behavior and the long life of these two otherwise different coating materials can be accounted for by third body effects on sliding contacts.

10:00am **SE-TuM6 In-situ Quantitative Nano-scale Metrology of Thin Coatings***, **N. Gitis**, A. Daugela, A.K. Sikder, M. Vinogradov, A. Meyman,* Center for Tribology, Inc.

Quantitative nano-metrology tools have become a standard in semiconductor, data storage and other hi-tech industries where products are tested for coating properties. Though it is critical to characterize advanced thin films and coatings, todayâ?Ts off-line nanoscale metrology tools can capture only limited number of manufacturing process stages. A quantitative nano/micro-instrument mod. UNMT with both SPM and optical microscope imaging integrated into it was developed to characterize mechanical properties of thin films and coatings and monitor their changes during indentation, scratching, reciprocating, rotating and other tribology tests. Both the materials properties and surface topography can be assessed at various stages of the tests. A 5-um thick copper layer on a silicon wafer was tested for changes in material properties during tribology test. Integrated SPM type imaging and nano-indentation tests revealed changes in elastic modulus, hardness and surface topography at nanometer scale. Dynamics of the copper layer hardening was recorded at several hundreds time steps during the entire tribology test.

10:20am **SE-TuM7 Effect of Impurities and Deposition Condition on the Mechanical Properties of Superhard Nanocomposites with High Thermal Stability***, **S. Veprek**,* Technical University Munich, Germany **INVITED**

Nano-Sized and Nano-Structured materials represent the leading edge of the research and technological development in many different areas from inorganic to biological ones. This paper will address the preparation and properties of superhard nanocomposites with a high thermal stability and an unusual combination of mechanical properties which were developed on the basis of our generic design concept that was published in 1995. These superhard nanocomposites were recently introduced into a large-scale industrial production. Because many researchers have recently claimed a lack of reproducibility of our results, the emphasis of my lecture will be on the deposition conditions needed for a reproducible preparation of these nanocomposites. A special attention will be paid to the detrimental role of impurities in these and other nano-structured coatings. It will be shown that minor oxygen impurities of @>=@0.4 at. % are the most probably reason why a number of researcher were unable to reproduce our data.

11:00am **SE-TuM9 Development of Hybrid Deposition Techniques for Nanocomposite Coating Growth***, **A.A. Voevodin**, J.G. Jones, J.S. Zabinski,* Air Force Research Laboratory

Development of hybrid processes, combining filtered vacuum arc deposition, magnetron, sputtering, and laser ablation for synthesis of functionally gradient and nanocomposite materials are discussed. Hybrid techniques facilitate a high degree of structural control and allow growth of nanostructured materials at low temperature by mixing plasma streams from various sources. Special attention was given to process instrumentation for plasma chemistry and energy control. Spectroscopic, imaging and time of flight analysis techniques are discussed. Interesting plasma interactions were found in a hybrid of laser ablation and ion beam deposition, where short-lived interactions between two plasma sources were explored to produce alumina oxinitride films. In addition, studies of a combination of laser ablation with magnetron sputtering (MSPLD) are presented. In this hybrid process, highly energetic plasma plumes from laser ablation were intersected with a magnetron-generated plasma containing sputtered metal atoms. Another hybrid process combined filtered vacuum arc and magnetron sputtering. All processes were tuned to produce advanced tribological coatings for wear protection of engineering components, combining metals, oxides, carbides, and dichalcogenides into various nanocomposite coating designs.

11:20am **SE-TuM10 Growth and Characterization of Zirconium Nitride/Inconel Nanocomposite Structures***, **S.M. Aouadi**, M. Debessai,* Southern Illinois University*; J. Xu, S.R. Mishra,* University of Memphis*; D.M. Mihut, S.L. Rohde,* University of Nebraska

This paper reports on the first study of the physical, chemical, and mechanical properties of reactively sputtered zirconium nitride/inconel nanocomposite films as a function of chemical composition, and substrate bias. Several sets of samples were deposited on Si(111) substrates at room temperature with bias voltages in the -45 to -160 V range. The chemical composition was deduced from X-ray photoelectron spectroscopy and energy dispersive X-ray fluorescence measurements, and was found to be influenced by the sputtering power and substrate bias. The phase composition and the grain size were determined using X-ray diffraction. The grain size was found to decrease with the increase in power to the inconel gun. The optical constants were measured using spectroscopic ellipsometry. A correlation between film structure/composition and optical constants was established. The hardness and elastic modulus of each sample were measured by nanoindentation. The resistance to plastic deformation, as measured by the ratio H3/E2, was optimized (H3/E2=1.0) with a substrate bias of -100 V. Finally, the tribological behavior of these films was studied using a nanowear tester. Nanowear results correlated well with the resistance to plastic deformation deduced from nanoindentation measurements.

11:40am **SE-TuM11 Microstructure and Properties of Ti-Al-Si-N Coatings Prepared by r.f.-Reactive Sputtering in Facing Targets-type Sputtering (FTS) System***, **M. Nose,*** Takaoka National College, Japan*; W.A. Chiou,* Univ. of California at Irvine*; H. Suzuki,* Toyama Univ., Japan*; E. Honbo,* Toyama Industrial Research Center, Japan*; S. Ikeno, H. Anada,* Toyama Univ., Japan*; S. Nogi,* Osaka Univ., Japan

Ti-Al-N films have been widely used in the coating industry as a superior wear protection material in comparison with its predecessor, TiN; however, the discovery of Ti-Si-N nano-composite film (by Veprek et. al. in 1995) has sparked recent interest in the study of quaternary system coatings such as Ti-Al-Si-N. Research on the influence of Si content on the mechanical properties of the quaternary system has been reported, however, the studies of microstructure and properties of Ti-Al-Si-N films containing high Al content are scarce. The effect of Si concentration on the microstructure and on high aluminum-content systems (such as (Ti@sub0.5@A1@sub0.5@)@sub50@-N@sub50@ film), remain unclear. Thin Ti-Al-Si-N films were synthesized by r.f. reactive sputtering in a facing target-type sputter (FTS) system on the hight speed steel substrates. A pair of composite targets consisting of a Ti@sub50@-Al@sub50@ plate and Si chips was used. During the deposition the substrate was heated from room temperature up to 300° C. The crystallite size of the deposited film without bias voltage decreased from 14 nm to 7 nm with the increase of Si content up to about 7 at. %. XRD patterns of Ti-Al-Si-N films suggested two phases, the cubic B1 NaCl type structure and an amorphous phase, were presented in the film. XPS analysis exhibited a peak that corresponded to the Si@sub3@N@sub4@ phase. TEM investigation of (Ti@sub48@-Al@sub0.48@-Si@sub0.04@)@sub50@-N@sub50@ films revealed a nano-column structure. The nano-column structure has a long aspect ratio ranging from 3 to 10 with an average around 7 to 9. Without applying substrate bias, the hardness of the films increased from 35 GPa for Ti-Al-N films, reaching a maximum of 38GPa for Ti-Al-Si-N films containing approx. 4 at. % Si. Based on thermal-gravity measurement by oxidation of films at 900° C in the air, the oxidation ratio of the Ti-Al-Si-N films was only a quarter of that in Ti-Al-N films. These special characteristics of the Ti-Al-Si-N films are potential results from the formation of an amorphous Si@sub3@N@sub4@ phase.

Advanced Surface Engineering
Room Exhibit Hall B - Session SE-TuP
Poster Session

SE-TuP1 Ab-Initio Structural Properties and Stress-Deformation Analysis by Rheological Modeling of Fracture of Diamonds-Containing Nanocomposites*, M.V. Kireitseu,* University of New Orleans*; **I.O. Nedavniy,*** Institute of Strength Physics and Materials Science, Siberian Branch of Russian Academy of Sciences, Russia

The principal goal of the paper is to study fundamentally pure interfaces diamond-like C / metal or polymer structure (matrix). Diamonds nanoclusters with effective sizes between 2 nm and 50 nm were used. The present work describes study of stable atomic structure of diamond-like nanoclusters embedded into metal or polymer matrix. Diamond nanoparticles have spherical, fullerene or pyramidal-type shapes and diamonds fibers as well. Local structure deformation (rearrangement) of diamonds/metal interfaces was principal object of researches. Energy or band structure and density of electronic states analysis were investigated. Possible defect or surface states were described. Ab initio LCAO (HF or DFT) schemes, LASTO (Linear augmented Slater-type orbital method), MLASTO (Modified linear Slater-type orbital method), ab initio DFT LDA (FLAPW, LASTO, pseudopotential) super cell schemes and semi empirical LCAO (AM1, PM3, PM5, etc.) methods were used for diamonds nanoclusters with effective size less than 2 nm. It was found that embedded diamonds might be reconstructed in a fullerene-like manner. Fundamental parameters for tight-binding and molecular dynamics calculation schemes were further based on computer simulation at each direction can be easily developed for better understanding and faster calculations. Study of size dependent mechanical and structural properties revealed at what scale principal fundamentals may give reliable explanations at examining fracture mechanics of nanostructured composites. We also present was to present the modified linear augmented Slater-type orbital method (LASTO) for solving Schrodinger's equation in nanodiamonds crystals with arbitrary atoms per unit cell. It follows to expect this method will allow more efficiently calculating an electronic band structure and structural energy difference for vary transition nanocomposites. As a result overlap matrix and hamiltonian matrix elements were derived in details.

SE-TuP2 Field Emission Enhancements from C-implanted Molybdenum*, **N.D. Theodore**, R.A. Outlaw, B.C. Holloway, D.M. Manos,* College of William and Mary

The vacuum microelectronic industry is developing large, compact field emitter arrays in high-brightness devices for flat panel displays and microwave tubes. Refractory carbides are materials of interest due to their reduced work function, stable emission, high current capability, and robustness. The purpose of this study was to better understand field emission enhancements observed in molybdenum carbide by comparing it to pure molybdenum. According to Fowler-Nordheim (FN) theory, field emission is determined by two parameters, the work function of a material and its surface roughness. Slope-intercept plots of the resulting FN data are then used to separate the effects of these variables. In this experiment, we deposited molybdenum onto both flat silicon samples and triangular silicon gratings that possessed a tip radius of approximately 10 nm. We then created molybdenum carbide by implanting carbon using plasma immersion ion implantation. Carbide formation was verified using XPS; both the C1s peak and the Mo3d peaks were shifted. Depth AES analysis determined that the carbon-implant extended ~45nm from the surface. The field emission results quantify the observed differences in work function and in emission current stability, and correlate these to variations in surface layer compositions and geometry. Moreover, flat samples did not exhibit repeatable electron emission. We conclude that in flat samples, field emission from surface defects dominates the measured emission current, and this mechanism is not explained by Fowler-Nordheim theory.

SE-TuP3 Chemisorption to the Oxide Surface of Aluminium Metal: The Competing Roles of Hydroxide Formation and Adventitious Contamination*, **M.R. Alexander**,* The University of Nottingham, UK*; G.E. Thompson,* UMIST, UK

An understanding of the interaction of organic functionalities with the surface of aluminium is required for development of a range of application areas including environmentally friendly adhesion promoters, superhydrophobic architecture, MEMS and NEMS. Formation of numerous types of organic monolayer on aluminium has been reported in the literature, the first of which predates that of alkane thiols on gold.@footnote 1@,@footnote 2@,@footnote 3@ Whilst the instability of the aluminium oxide surface in ambient conditions is widely recognised, quantification of the changes in surface hydroxyl group concentration and carbonaceous contaminant from the ambient atmosphere have only recently been achieved using X-ray photoelectron spectroscopy (XPS).@footnote 4@,@footnote 5@ Previous work has identified the significant influence of an ambient laboratory atmosphere on assembly of alkyl carboxylic and phosphonic acid monolayer.@footnote 6@,@footnote 7@ Here, we investigate the influence on chemisorption from dilute solutions of such molecules using controlled atmospheric exposure prior to assembly. The order of the resultant SAMs is used as a relative measure of the reactivity of the surface to the headgroups. Water contact angle, IRRAS and XPS are used to provide information on the chemistry of the oxide surface and the order the monolayer assembled onto this surface. Differences are rationalised using the competitive processes of hydroxyl adsorption site formation and adventitious contamination blocking of such sites developed in the earlier work. @FootnoteText@ @footnote 1@ Bigelow, W et al. Colloid Sci 1946; 1: 513.@footnote 2@ Timmons, C, Zisman, W. JPhysChem 1965; 69: 984.@footnote 3@ Allara, DL, Nuzzo, RG. Langmuir 1985; 1: 45.@footnote 4@ Alexander et al. SIA 2000; 29: 468.@footnote 5@ Alexander et al. SIA 2003; 35: 649.@footnote 6@ Alexander, MR et al. ASST:ATB Metallurgie, Brussels, 2004; 60.@footnote 7@ Pertays, K et al. SIA In Press.

SE-TuP4 Microstructure and Properties Changes in CrN Films Influenced by an Implanted Cr Interlayer*, H.-Y. Chen,* National Tsing Hua University, Taiwan*; **S. Han,*** National Taichung Institute of Technology, Taiwan*; H.C. Shih,* National Tsing Hua University, Taiwan

A chromium interlayer was implanted in (100) silicon using a metal vapor vacuum arc ion implanter, and then CrN films were deposited by cathodic arc plasma deposition. Two types of the CrN films denoted as CrN/Cr/Si (with an implanted Cr interlayer) and CrN/Si (without an implanted Cr interlayer). XRD patterns revealed the presence of CrN (220) preferred orientation for both cases, indicating that regardless of whether the films included a Cr interlayer, the preferred orientation and the columnar structure of CrN films were unchanged. But the interlayer induced finer grain structure and reduced the residual stress of the films from -8.1 GPa to -2.8 GPa, which relaxed by up to 65%. Moreover, the CrN films with a Cr interlayer were less hard and exhibited a higher electrical resistivity than those without. Both specimens were annealed at 500°C for 2 h in an N@sub 2@/H@sub 2@ atmosphere to elucidate the thermal stability of the CrN film. The CrN/Si revealed a phase transformation from CrN to Cr@sub 2@N during annealing, which is due to largely stress relaxation in the film. A implanted Cr interlayer can effectively relax the residual stress in CrN films and prevent a occurrence of phase transformation during annealing. The correlation between the properties and microstructure of the CrN film is also discussed.

SE-TuP5 Oxidation Behavior of Titanium Nitride Films*, **H.-Y. Chen**, H.C. Shih,* National Tsing Hua University, Taiwan

TiN films have been a universal coatings due to their high melting points, extreme hardness, high chemical stability, golden color and so on, and the oxidation of films occurs in the hostile environmental. The oxidation mechanism of TiN films has investigated by their crystal structure and morphology using XRD and Raman scattering spectroscopy and FESEM. TiN films were synthesized by using cathodic arc plasma deposition technique because its high ionization ratio, fast deposition rate. After films deposition, the films were annealed in static air at 500°C to 800°C for 2 h. The XRD and Raman spectra indicated that the rutile TiO@sub 2@ was identified above 600°C and its relative intensity rapidly increased with temperatures. The films completely oxidized into rutile phase above 700°C. The as-deposited TiN films were columnar structure. Nevertheless, the oxide layer appeared on the top of columnar TiN films above 600°C. Furthermore, the microstructure of the oxide was porous with the pore size of several nanometers within the oxide layer at 600°C. As increasing annealing temperature, the oxide morphology possessed elongated grain structure with the aspect ratio of ten and the pore size within the oxide layer ranged in several ten nm, which indicated the densification occurring. Form the results, the oxide layer obvious grow inward with temperatures, which indicates the oxidation of TiN films is inward oxidation, meanwhile the oxide thickness was measured with temperature and the active energy for the oxidation was deduced, which was 110±10 kJ/mol.

SE-TuP6 Effect of Ion Irradiation during Deposition on the Structure of Alumina Thin Films Grown by Plasma Assisted Chemical Vapour Deposition*, **D. Kurapov**, O. Kyrylov, J.M. Schneider,* RWTH Aachen, Germany

Alumina thin films deposited by plasma assisted vapour deposition were studied with respect to the structure and composition by X-ray diffraction and electron probe microanalysis, respectively. Alumina thin films were deposited on hot work tool steel AISI H11 at a growth temperature of 500 to 600 °C. The ion energy was affected by controlling the substrate power density from 2.7 to 6.6 W/cm@super 2@, which corresponds to the bias potential range from 720 to 905 V. Within the investigated process window the following characteristic phases could be identified : amourphous alumina, @gamma@-alumina, @alpha@-alumina as well as mixtures thereof. The alumina phase formation was found to be strongly influenced by deposition temperature and power density at the substrate. The influence of the power density is discussed with respect to the ion energy distribution, which is estimated based on the charge exchange model of Davis and Vanderslice.

SE-TuP7 Microstructural Evolution on the Oxidation of Arc Ion-plated TiN/(Ti,Al)N Superlattice Coatings*, **M.H. Shiao**,* National Science Council, Taiwan*; C.C. Wang, F.S. Shieu,* National Chung Hsing University, Taiwan

TiN/(Ti,Al)N superlattice coatings with a TiN interlayer were prepared by a dual-cathode arc ion plating system on AISI 304 stainless steel. Two targets of Ti and Ti@sub 50@Al@sub 50@ were used for the vertically opposited cathodes. Oxidation of the nitride-coated steel was carried out at the temperature of 800°C in air for 60 min. The microstructure and chemistry of the as-deposited and oxidized specimens was characterized by X-ray diffraction, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Auger electron spectroscopy (AES). XRD result shows that nitride coatings have strong (111) preferred orientation, and TiO@sub 2@ phase appeared in the oxidized specimen. Cross-sectional TEM reveals a TiN/(Ti,Al)N superlattice structure with a period of 7.7 nm examined by the selected area diffraction (SAD). In the oxidized specimen, there are dense amorphous Al@sub 2@O@sub 3@ layer and underlying porous TiO2 layer on the surface of the coating. Auger depth profiling of the oxidized specimens reveals that the Al element concentration near the surface layer is much higher than that in the nitride coating, and further confirmed the cross-sectional TEM results.

SE-TuP8 Development of Amorphous Layered Structures by Laser Irradiation for Enhanced Corrosion Resistance*, J.G. Hoekstra, P.M. Mackey, N. Ünlü, G.J. Shiflet, J.R. Scully, **J.M. Fitz-Gerald**,* University of Virginia

Al and Fe based amorphous materials attract attention for their desirable mechanical hardness and corrosion resistance. This study investigated the atomic scale relationships of amorphous layer formation as a function of chemistry and pulsed laser irradiation conditions in Al-Co-Ce and Fe-Mo-Cr-Mo-C-B alloys. The primary objective was to laser surface modify a continuous, homogenous, amorphous layer on a crystalline substrate. Irradiation of a material with a short laser pulse, 3-100 ns, establishes rapid melting and solidification velocities at the surface, 10@super 7@-10@super 8@ K/s and 10@super -1@-10@super 1@ m/s respectively. A KrF excimer laser (@lambda@=248 nm, 25 ns at FWHM, 15 Hz) operating with fluences ranging from 0-10 J/cm@super 2@ irradiated a target surface with corresponding velocity between 0-50 mm/s in a controlled atmosphere ranging from 50-500 mTorr. Characterization was performed by SEM, EDS, XRD, and electrochemical analysis. The resulting microstructures were correlated with electrochemical analysis and devitrification behavior.

SE-TuP9 Nanomechanical Testing Using Noncontact Acoustic Technique*, **O.G. Lysenko**, N.V. Novikov, V. Grushko,* Institute for Superhard Materials, Ukraine

The new techniques for noncontact measurements of acoustic waves and vibration parameters, such as atomic force acoustic microscopy and tunneling accelerometer have been developed the last years. We present the experimental technique that uses noncontact acoustic method to nanoscale surface characterization. A pulse laser is used to generate surface acoustic waves in a sample. Two SPM tips detect phase and amplitude of the acoustic waves. This approach makes it possible to measure acoustic transit time within small areas of a samles. From the velocity of the surface waves the elastic modulus can be culculated. Also it is possibly to identify the onset of plastic flow in the thin films. A theoretical model embracing the most significant features of wave phenomena at nanoscale level is described. Laboratory experiments have displayed results that are in agreement with those obtained from theoretical model.

SE-TuP10 Characterizations of the Surfaces of Shocked-Bi-Pb-Sr-Ca-Cu-O Superconductor Particles for a Magnetic Sensor*, **H.K. Kezuka**,* Tokyo University of Technology, Japan*; K.Y. Yamagata, M.I. Itoh,* Kinki University, Japan*; T.S. Suzuki,* Tokai University, Japan*; M.K. Kikuchi,* Tohoku Fukushi University, Japan*; T.A. Atou, M.K. Kawasaki, K.F. Fukuoka,* Tohoku University, Japan

Recently, there has been an increased need for a highly sensitive magnetic sensor. Bi-Pb-Sr-Ca-Cu-O(BPSCCO) oxide superconductors are very attractive material as a highly sensitive magnetic sensor in which magnetic sensitivity of the sensor is found to be about 27 %/(10 @super -4@ T) using BPSCCO powders pasted for constructing the magnetic sensor. Characteristics of BPSCCO superconductor depend sensitivity on the grain growth temperature. Researches for applications of high-T@sub c@. BPSCCO superconductor particles have been made to overcome the weak-link problem around the grain boundaries for higher J@sub c@. Shock compaction for BPSCCO superconductor particles have been investigated by shock compaction technique. After the shock compaction characterizations of as-shocked BPSCCO superconductor particles are investigated by X-ray diffraction(XRD)-analysis for the measurements of lattice parameters and SQUID-measurements for the susceptibility. The grain growth with growth steps of as-shocked BPSCCO superconductor particles are observed by AFM(Atomic Force Microscope) and SEM(Scanning Electron microscopy). The particle size distribution was measured by a laser diffraction size analyzer, which employed laser diffraction and scattering methods. In this measurement, use was made of an isopropyl alcohol for dispersing the BPSCCO particles. The average particles is found to be about 4.2 µm. The specimens were pressed into pellets with 10 mm in diameter and around 1 mm in thickness. These pellets were tightly encased in stainless containers. Shock compaction experiments were carried out under the shock pressure of around 2-5 GPa by using a propellant gun-system. From XRD-analysis, it is found that Bi-2223 phase is appeared clearly after the shock compaction process under 2-5 GPa with Bi-2212 phase. The Amplitude Mode image shows the surface details better than the unfiltered Height Mode images for BPSCCO particles. Tapping AFM image of the surface and edges for annealed BPSCCO particles at 850 °C for 96 hr after shock compaction. It is found from the section analysis that the vertical distance around edge area varies from 86 to 478 nm. BPSCCO superconductors, the Bi-2223 structures of as-shocked BPSCCO probably have shock-induced defects by the shock compaction. The ΔM (the difference of susceptibility at 5 K obtained from the temperature dependency of field cooling and zero field cooling at 20 Oe) which is proportional to J@sub c@, is measured by SQUID magnetometer. As a result, from the measurements of the susceptibility by SQUID magnetometer, it is found from the susceptibility measurements as a function of temperatures that ΔM clearly increases to 0.073 (emu/g) for as-shocked BPSCCO after annealed at 850°C for 48 hr,which seems to indicate the new pinning centers around the grain boundaries caused probably by the new defects of vacancies. The shocked specimens was compacted in platelet disk with a high crystal density over 97 %. The as-shocked specimen showed an oriented crystal structure with large grains of 3-5µm in length partly for shocked specimen by 2-5GPa. The ΔM (0.073 emu/g) of shocked specimen after annealing at 850° C for 48 hr became higher than that of starting specimen. These increase of ΔM indicate the introduction of a new pinning center through the shock compaction and annealing processes. The Amplitude Mode image of AFM show large edge effects which reflect the amplitude changes. Also form the section analysis of AFM, the vertical distance of 86-478 nm is obtained around the edge area in grains for annealed BPSCCO after shock compaction.

Biomaterial Interfaces
Room 210D - Session BI+AS+SE-ThM

Surface Modification of Biomaterials

Moderator: D.G. Castner, University of Washington

8:20am **BI+AS+SE-ThM1 Strategies for the Biofunctionalization of Surfaces using Functional Polymer Layers**, ***J. Ruehe,*** University of Freiburg, Germany **INVITED**

The modification of surfaces with polymers for the promotion of cell outgrowth either in a dense layer or following a distinct pre-determined pattern is a challenging field of research with possible applications in the field of medical implants as well as for specific sensor devices. We present results from various studies in our group that range from the modification of bioimplant surfaces (e.g. glutar aldehyde treated porcine heart valves) with polymer monolayers in order to allow for a re-endothelialization of these devices to the arrangement of neuronal cells on a substrate by depositing synthetic and natural polymers on these chips in the form of a microarray. We will put a strong emphasis on synthetic approaches for establishing a strong, i.e. usually covalent interaction between the polymeric coating and the substrate in order to guarantee a sufficient long-term stability of the layer assemblies. These assemblies may be polymer monolayers as well as networks and we will also report on strategies for the incorporation of biological functions such as cell adhesion motifs or peptides. Finally, approaches for the laterally patterned deposition of these layers will be discussed.

9:00am **BI+AS+SE-ThM3 Interfacial Biomaterials: Guiding Biology on Synthetic Surfaces**, *E.B. Walsh, X. Huang,* Duke University*; M.W. Grinstaff,* Boston University*;* ***D.J. Kenan,*** Duke University Medical Center **INVITED**

Interfacial biomaterials represent a novel coating technology capable of directing biological processes at the interface between a biologic and a synthetic surface. The approach relies on screening combinatorial libraries to identify unique peptides that adhere to a synthetic target such as a plastic or metal, or to a biological target such as a protein or cell. Next, two or more adhesion peptides are synthetically coupled to create an interfacial biomaterial that mediates the interaction of the protein or cell with the synthetic material. Other interfacial biomaterials may be created by coupling known signaling molecules to peptides that bind synthetic materials. Mixtures of interfacial biomaterials may be applied to a surface to achieve a particular desired biological outcome, such as adhesion of a given cell type to the surface, followed by induction of one or more signal transduction pathways. These interfacial biomaterials are amenable to numerous coating and patterning techniques suggesting their use for diverse applications ranging from biomedical device coatings to anti-infectives to tissue engineering.

9:40am **BI+AS+SE-ThM5 Antibacterial Surfaces of Covalently Immobilized Dendrimers**, *D. Weber, N.R. Choudhury,* University of South Australia*;* ***H.J. Griesser,*** University of South Australia, Australia

The need to limit bacterial adhesion to surfaces of biomedical implants, contact lenses, and other devices has prompted considerable recent research into antibacterial compounds and coatings. To ensure long-term efficacy and eliminate concerns about potential adverse biological effects on sensitive organs remote from the implant site, release strategies seem less suitable, and the covalent surface immobilization of antibacterial compounds is the approach of choice in our work. However, the question then becomes whether a covalently immobilized antibacterial is still biologically active, and can maintain activity over extended service life spans. In this study we have principally explored the surface immobilization of dendrimers, which have previously been shown to be antibacterially active in solution (eg CZ Chen and SL Cooper, Biomaterials 23 3359 2002). Another approach involves extracts of some Australian plant species, but their chemical characterization and synthesis is less developed. We have immobilized amine-terminated dendrimers onto aldehyde plasma polymer interlayers via reductive amination and characterized the coatings by XPS, ToF-SIMS, and AFM. Using various plasma conditions the surface density of aldehyde groups can be varied. The surface density of immobilized dendrimers is determined from XPS elemental ratios, using the dendrimer-specific N signal. Following surface immobilization, the remaining amine groups are quaternized in order to produce a cationic surface. The distinct signal arising from quaternary N in the XPS N 1s spectrum enables assessment of this reaction. The plasma approach also enables us to apply this coating strategy onto a wide variety of substrates both polymeric and inorganic (ceramic and metallic).

10:00am **BI+AS+SE-ThM6 Biomimetic Vascular Engineering: Exploiting Concepts from Nature to Create New Biomaterial Interfaces**, ***R.E. Marchant,*** Case Western Reserve University **INVITED**

The abundance of complex supramolecular structures in Nature provides lessons in structural hierarchy and functional efficiency that are being explored and exploited in the development of novel biomimetic strategies for creating new biomaterial interfaces for biomedical applications. Mimicking and adapting structural concepts from Nature to create tissue compatible interfaces for biomaterials that incorporate molecular recognition and self-assembly will be the central theme of this presentation. We have developed a biomaterial architecture using "surfactant polymers" that undergo surface and self-induced assembly on hydrophobic surfaces. Our biomimetic designs benefit from understanding the structural and functional properties of the corresponding system in Nature. One example is the external region of a cell membrane, known as the glycocalyx, which is dominated by a complex milieu of glycosylated molecules. The glycosylated molecules direct specific interactions such as cell-cell recognition, and provide an important physical basis for maximizing steric repulsion that prevents undesirable non-specific cell and molecular adhesions. Conversely, understanding the nature of a cellâ?Ts adhesive interactions with the extracellular matrix facilitates design of biomimetic materials with cell adhesion properties. Using these biomimetic concepts, we have designed and studied oligosaccharide and peptide surfactant polymers that provide suppression of non-specific protein interactions and facilitate well-controlled interactions with endothelial cells.

10:40am **BI+AS+SE-ThM8 Stability of Polypeptide Multilayers as Studied by in situ Ellipsometry: Effects of Drying and Post-Buildup Changes in Temperature and pH**, *T.J. Halthur,* YKI AB, Institute for Surface Chemistry, Sweden*; P. Claesson,* KTH, Royal Institute of Technology, Sweden*;* ***U. Elofsson,*** YKI AB, Institute for Surface Chemistry, Sweden

Polyelectrolyte Multilayers (PEM) of poly(L-glutamic acid) (PGA) and poly(L-lysine) (PLL) with a initial layer of polyethyleneimine (PEI) were built on silica and titanium surfaces using the Layer-by-Layer (LbL) technique. The stability of the film during drying/rewetting, temperature cycles and pH shifts was studied in situ by means of ellipsometry. The filmthickness was found to decrease significantly (approximately 70%) upon drying, but the original film-thickness was regained upon rewetting and the buildup could be continued. The dry thickness was found to be extremely sensitive to ambient humidity, needing several hours to equilibrate. Changes in temperature and pH was also found to influence the multilayer thickness, leading to swelling and de-swelling of as much as 8% and 10-20% respectively. The film does not necessarily regain its original thickness as the pH is shifted back, but instead shows clear signs of hysteresis.

11:00am **BI+AS+SE-ThM9 PCA of TOF-SIMS Spectra from p(AAm-co-EG/AAc) IPNS on Quartz**, ***D.J. Graham,*** University of Washington*; G.M. Harbers, K.E. Healy,* University of California, Berkeley*; D.G. Castner,* University of Washington

PCA of TOF-SIMS has been carried out on many well defined model surfaces in structured experiments. These studies have shown the utility of PCA in extracting information from TOF-SIMS experiments from a wide variety of substrate surfaces. This work reports on the application of PCA to a more complex interpenetrating polymer network system. The goal of this project was to verify each step in the IPN synthesis procedure on a quartz substrate. This system presents a challenge to PCA due to the similarity of the polymers used in the IPN and the addition of a peptide chain. PCA of the entire data set (including all synthesis steps for the IPN) showed that PC1 was able to separate most samples. The PC1 loadings were dominated by the overall differences between the hydrocarbons on the bare quartz and the PEG related peak fragments after the addition of the IPN onto the quartz surface. This is likely due to the high PEG content of the IPN polymers. PCA comparing each successive synthesis step gave further insight into the success of the IPN chemistry. PCA was able to distinguish each surface modification up until the addition of the peptide precursor and peptide. The presence of the peptide was verified in subsequent experiments where it was shown that RGD-peptide modified p(AAm-co-EG/AAc) surfaces supported rat calvarial osteoblast adhesion, proliferation, and matrix mineralization. Consequently,surfaces without the RGD peptide or with a control RGE peptide did not support cell attachment. PCA also gave insight into the uniformity of the surface modifications by way of the scores plots. Increasing scatter was seen in the last few synthesis steps suggesting that a less uniform surface chemistry was achieved. The trends seen in the PCA of the TOF-SIMS data were consistent with those seen by XPS.

11:20am **BI+AS+SE-ThM10 Development of an Antimicrobial Polymer Surface Coating for the Prevention of Staphylococcal Infections***, **M. Anderle**, L. Pasquardini, L. Lunelli, R. Canteri, P. Villani, C. Pederzolli,* ITC-irst, Italy

The proliferation of pathogenic microorganisms on polymer surfaces is one of the most widespread causes of failure of biomedical devices such as catheters, medical implants, vascular graft and joint prostheses. The inhibition of pathogenesis and subsequent mechanisms of protection are possible by killing bacteria in the first steps of colonization. This work describes a polymeric surface coating with liposomes as method to provide a sustained delivery of antibiotics into the local micro-environment of the implant. In this study liposome formulations composed of Phosphatidylcholine (PC), Distearoyl-sn-Glycero-3-Phosphoethanolamine-N-MethoxyPolyethylene glycol (DSPE-PEG) and cholesterol are utilized. Liposomes, different in size, are attached to an amine activated substrate through the formation of covalent bonds with the distal end of the PEG (Polyethylene glycol) derivative molecules. Data on the surface coating using large unilamellar vesicles (LUV) and multilamellar vesicles (MLV) will be shown. The AFM analysis is performed to study the nanoscale structure of the coated surface while the fluorescence spectroscopy and microscopy are engaged to determine the immobilisation efficacy adding a fluorescent lipid (L-@alpha@-Phosphatidylethanolamine-N-lissamine rhodamine B sulfonyl) to the liposome composition. The MLV coating on polystyrene shows a more uniform distribution with a lipid concentration of about 2x10@super 15@ mol/cm@super 2@. Finally drug (rifampicin) release and bacterial colonisation rates with their correlation will be reported.

11:40am **BI+AS+SE-ThM11 Spectroscopic Characterization of Surface-Immobilized Antibacterial Furanone Coatings***, **S. Al-Bataineh**, H.J. Griesser,* University of South Australia, Australia*; M. Willcox,* University of New South Wales, Australia*; L.G. Britcher,* University of South Australia, Australia

The colonisation by bacteria of biomedical devices presents a serious concern for human implant surgery. In this study, we explore how bacterial colonisation can be prevented by the appropriate design and fabrication of antibacterial coatings, with a major focus on surface-immobilised furanone molecules. These compounds are produced naturally by the marine algae, Delisea pulchra and are used as defence agents to prevent fouling on their surface@footnote 1@. Several studies have shown that brominated furanones as well as synthetic analogues possess potent antimicrobial activity against bacteria@footnote 2@@super ,@@footnote 3@. The previously used azide protocol was adopted to prepare furanone coatings@footnote 4@. XPS and ToF-SIMS results showed successful surface modifications and furanone immobilisation. Detailed analysis of the C 1s and N 1s XPS spectra using constrained curve fitting showed that they are more complicated than anticipated from the theoretical reaction scheme. In addition, the presence of a Br@super-@ peak partially overlapped with a C-Br peak indicated that furanones are partially degraded on UV illumination. More surface characterisations are needed for full understanding of the chemical reactions that occurred. Seven furanone compounds used in this study were tested for their ability to inhibit biofilm formation and growth of two bacterial strains, Staphylococcus aureus (Saur19) and Pseudomonas aeruginosa (Paur6206). Initial results are promising; detailed investigation of the efficacy of the coatings is ongoing. Furthermore, none of the compounds used in this study showed any cytotoxicity potential at the tested concentrations. @FootnoteText@ @footnote 1@ de Nys R. et al., 1995, 4:259-71.@footnote 2@ Kjelleberg S. et al., Patent No. PCT/AU99/00284, 1999.@footnote 3@ Read R. et al. PCT international application PQ6812, 2001.@footnote 4@ Muir B. et al., Proc. 6th World Biomat. Congr., Hawaii, May 2000, p. 596.

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