### Monday Morning, October 15, 2007

**Advanced Surface Engineering** 

#### Room: 617 - Session SE-MoM

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

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

8:00am SE-MoM1 Thermal Stability of TiAlSiN and CrAlSiN Thin Films, Y.-Y. Chang, C.-P. Chang, Mingdao University, Taiwan, S.-M. Yang, National Chung Hsing University, Taiwan, D.-Y. Wang, Mingdao University, Taiwan, W. Wu, National Chung Hsing University, Taiwan Binary CrN and ternary TiAlN coatings attracted considerable industrial interest, because of their excellent tribological performance and high oxidation resistance at high temperature. Recently, TiAlSiN and CrAlSiN coatings have been developed in order to possess high hardness and good chemical stability at temperature exceeding 1000 °C. These properties are very important in developing new generation superhard and wear-resistant coatings for high speed and dry machining applications. In this study, a series of CrN, TiAlN, TiAlSiN and CrAlSiN coatings were deposited onto silicon substrate by a cathodic arc evaporation system using a lateral rotating arc source. Owing to the different oxidation behavior and decomposition of CrN, TiAlN, TiAlSiN and CrAlSiN coatings, the asdeposited films were annealed at 900 °C and 1100 °C in air atmosphere for duration of 2 hours. During the annealing process, Ti, Al, and Si would diffusion outward to form the oxidative layers of Al2O3, TiO2, and SiO2 or others at high temperature. Cr, Al, and Si would diffusion outward to form the oxidative layers of Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub> or others at high temperature. Therefore, the mechanical property varied with the phase segregation via heat-treatment caused the deposited films destruction. The correlation between oxidative layer and the deposited films will be discussed. The chemical depth profile of the deposited coatings was determined by Secondary Ion Mass Spectrometry (SIMS). X-ray diffractometry was performed using PANalytical X'pert Pro diffractometer with a high resolution ? goniometer and Cu radiation in both glancing angle and highangle configurations for phase identification. The microstructure was investigated by field emission gun high resolution transmission electron microscopy (FEG-HRTEM, FEI Tecnai G<sup>2</sup> 20 S-Twin) equipped with an energy-dispersive x-ray analysis spectrometer (EDS), operated at 200 keV for high-resolution imaging.

8:20am SE-MoM2 Si Influence on Thermal Stability, Microstructure, and Hardness of Arc Evaporated Ti-Si-N Thin Films, A. Flink, Linköping University, Sweden, J. Sjölen, T. Larsson, L. Karlsson, SECO Tools AB, Sweden, L. Hultman, Linköping University, Sweden

Ti<sub>1-x</sub>Si<sub>x</sub>N<sub>y</sub> (0≤x≤0.22) thin solid films were deposited by arc evaporation onto WC(Co) and c-BN substrates. Elastic recoil detection analysis revealed an N increase with increasing Si content. X-ray diffraction and transmission electron microscopy showed that as-deposited films contain a NaClstructure phase with a lattice parameter similar to TiN, 4.24 Å. The films exhibited a competitive columnar growth mode where the structure transits to a defect-rich feather-like nanostructure with increasing Si content. Asdeposited TiN exhibited random crystallographic orientation, which gradually changed to an exclusive <200> texture for x>0.05. The highest hardness, 42.8±2.1 GPa, was achieved for x=0.14, which was significantly higher than 29.8±1.5 GPa for TiN. The hardness increase is attributed to solid-solution and defect hardening. The hardness was retained for an annealing temperature of 1000°C for 0.05≤x≤0.10, but decreased to below 28 GPa for all other compositions due to recrystallization within the cubic state together with Co and W interdiffusion from the substrate via the grain boundaries. Furthermore, the Si content decrease for the films annealed at 1000°C to x=0.14. Residual stresses were measured with the  $\sin^2\psi$ -method and differential scanning calorimetry was performed in order to investigate phase transformations.

#### 8:40am SE-MoM3 Nanostructured PVD Hard Coatings in Industrial Research and Application, J. Vetter, Sulzer Metaplas GmbH, Germany INVITED

The improvement of the overall coating performance of wear protecting PVD coatings concentrates to achieve lower friction values, better thermal stability , optimization of hardness and toughness and higher oxidation stability. The aim of these improvements is to get a higher performance of

tools and parts of components. Nowadays composite materials having structures in the nanometre dimensions are in the scope of industrial applications. Different coating architectures were developed in industrial scale: isotropic composites coatings, gradient nano composite coatings and nano multilayer coatings. Modern industrial PVD systems are designed to deposit these types of sophisticated coating architectures. Both are evaporation and magnetron sputtering and its combinations are suitable to create nano structures. The coating processes to deposit nano structured coatings will be discussed in more detail and it will be shown that the analytical methods for coating development and production control have to be shifted toward a nanostructure compatible level.

#### 9:20am SE-MoM5 Lubricant-Friendly MoN-Cu Coatings for Extreme Tribological Applications, A. Erdemir, O.L. Eryilmaz, Argonne National Laboratory, M. Urgen, M.K. Kazmanli, Istanbul Technical University, Turkey

In this paper, we describe molecular level design and synthesis of a series of nanocomposite coatings providing extreme resistance to wear and scuffing and very low friction in lubricated test environments. The ingredients or chemistry of nanophases in these films were selected strategically so that during lubricated contacts, they can form low-shear and protective boundary films by favorably reacting with some of the additives in formulated oils. Among others, MoN-Cu coatings had the greates beneficial effects in lowering friction and increasing resistance to wear and scuffing. In fact, these films were impossible to scuff even under the maximum loading and sliding conditions that we could establish in our test machines. In this paper, we will present the main characteristics of these nanocomposite coatings and discuss in details the fundamental tribological mechanisms that control their superior friction, wear, and scuffing behaviors under severe sliding conditions.

#### 9:40am SE-MoM6 Effect of the Microstructure on the Mechanical and Tribological Properties of Cr-Si-N Coatings Prepared by Reactive Sputtering, M. Benkahoul, P. Robin, L. Martinu, J.E. Klemberg-Sapieha, Ecole Polytechnique, Canada

Cr-Si-N thin films were deposited by pulsed DC reactive dual magnetron sputtering with different concentrations of Si. Microstructural evolution and mechanical properties of these thin films were studied using XRD and nanoindentation measurements. Three regions of different Si concentration [Si] were distinguished: For [Si] < 2.3 at.%, the grain size (D) doesn't significantly change with increasing [Si]. For 2.3 < [Si] <7 at.%, D decreases as [Si] increases. At higher [Si], a relatively rapid decrease of D is observed with increasing [Si]. Nanohardness (H) behaviour of these thin films as a function of [Si] is comparable to that observed in the Me-Si-N (Me: Ti, Nb, Zr,...) nanocomposite materials. For [Si] ~2.3 at.%, H is 24 GPa, H3/Er2 ~ 0.24 GPa, and the elastic recovery, We ~ 60%, is comparable with CrN, for which H  $\sim$  18 GPa, H3/Er2  $\sim$  0.1 GPa, and We  $\sim$ 35%. Based on the evolution of the microstructure of these films, solid solution hardening is proposed as the main mechanism to explain the changes observed for [Si] < 2.3 at.% in the Cr-Si-N films, rather than the nanocomposite structure. Subsequently, we systematically studied the deposition of Cr-Si-N films on SS410 steel using a duplex treatment consisting of surface nitriding and deposition of a Cr bond coat. The influence of [Si] on the tribological properties of the Cr-Si-N coatings was found to lead to a reduction of the wear coefficient by a factor of 100 compared to bare SS410 substrate.

### 10:20am SE-MoM8 Infrared-Reflecting Thin Film Coatings, A.N. Ranade, M.E. Graham, Y.W. Chung, Northwestern University

The heating of vehicles such as cars and planes is directly dependent on the absorption of solar radiation. Approximately half of the energy that is incident upon vehicles can be attributed to near infrared (IR) radiation of wavelengths in the range of 800-1600 nm. Reflecting instead of absorbing IR radiation would lower cabin temperatures considerably, thereby improving passenger comfort and fuel economy. An inorganic coating that is transparent to visible, absorbing to UV, and reflecting to IR radiation is desired to meet these goals. Doping a TiO<sub>2</sub> matrix with well-dispersed metal atoms produces a film that acts as a plasma with specific electromagnetic properties. By controlling the metal atom concentration, one can tune the wavelength at which electromagnetic radiation is reflected. This paper discusses the properties of TiO<sub>2</sub> films doped with varying metal atom concentrations. The films are made by reactive magnetron sputtering and evaluated by AFM (surface roughness), XRD (structure), and UV-VIS-IR spectroscopy (optical properties).

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10:40am SE-MoM9 Optically Transparent Nanocomposite Thin Films: the System Al-Si-N, A. Pelisson, M. Parlinska-Wojtan, P. Schwaller, H.J. Hug, J. Patscheider, EMPA, Switzerland

Transparent nanostructured coatings of Al-Si-N were deposited by reactive DC magnetron co-sputtering of Al and Si targets in an Ar/N2 atmosphere at substrate temperatures between 200 and 500°C. The elemental composition was varied from pure AlN to Al-Si-N with 30 at.% of Si. The coatings were characterized by XPS, TEM, XRD, nanoindentation and UV-Visible spectroscopy. X-ray diffraction results suggest that the coatings consist of nanocrystalline h-AlN with substitutionally incorporated silicon for Si concentrations below 13 at%. At Si concentrations exceeding 13 at% the coatings are X-ray amorphous. In contrast to known silicon-containing ternary nitrides and to available thermodynamical data for the Al-Si-N system, this material shows no clear phase segregation during deposition into AlN and SiNx; instead an Al1-xSiNx solid solution is formed that coexists with SiNx for silicon concentrations above 6 at% Si. XRD and TEM analysis show that the crystalline material consists of elongated grains; the crystallite size decreases from 60 nm to about 10 nm upon addition of silicon. The average optical transparency of 1 micron thick coatings in the visible range of light approaches 100%. The hardness exceeds 30 GPa, with a weak maximum at 8-12 at.% of Si which corresponds to the lowest internal stress in the coatings (= 0.5 GPa). At this composition the elastic strain to failure H/E, or resilience, is increased by 50% by the addition of silicon to AlN.

#### 11:00am SE-MoM10 Atomistic Processes during Synthesis of Hard Coatings Revealed by STM and LEEM, *I. Petrov*, University of Illinois at Urbana-Champaign INVITED

Transition-metal nitrides, such as TiN, have a wide variety of applications as hard, wear-resistant coatings, as diffusion barriers, and as scratchresistant and anti-reflective coatings in optics. Understanding the surface morphological and microstructural evolution of these materials is crucial for improving the performance of devices. Studies of surface step dynamics enable determination of the rate-limiting mechanisms, corresponding surface mass transport parameters, and step energies. However, most models describing these phenomena are limited in application to simple elemental metal and semiconductor surfaces. We summarize recent progress toward elucidating the interplay of surface and bulk diffusion processes on morphological evolution of compound surfaces. Specifically, we analyze the coarsening/decay kinetics of two- and three-dimensional TiN(111) islands and the effect of surface-terminated dislocations on TiN(111) steps. Further, in an attempt to gain better understanding of the origin of TiN-SiNx superhardness, we use in-situ STM and LEED to investigate the atomic-scale structure of the SiNx/TiN interface, of which very little is known. SiNx overlayers were grown onto single-crystal TiN(001) or TiN(111) substrates at temperatures between 700 and 900 °C. We show both topographic (STM) and diffraction (LEED) evidence that (a) SiNx overlayers on TiN are crystalline with reconstructions including 2x2, c-3x3, and 1x5, depending upon SiNx coverage, surface orientation, and annealing temperature; and (b) TiN grows epitaxially on top of the SiNx layers. Specifically, our results show that for SiNx coverages near 1ML, where maximum TiN-SiNx hardness is attained, the SiNx layer is not amorphous as deposited. Finallly, we will describe a design of a tandem instrument combining a low-energy electron microscope (LEEM) and a negative ion accelerator. This instrument provides video rate imaging of the dynamics of surface microtopography evolution during irradiation by energetic ions, at temperatures up to 1500 K. We will present in-situ real-time atomic-scale studies of energetic epitaxial film growth and etching.

#### 11:40am SE-MoM12 A Novel Form of Hard Hydrogenated Amorphous Carbon Grown under High Rate Conditions, S.V. Singh, M.A. Creatore, Eindhoven University of Technology, The Netherlands, R. Groenen, K. van Hege, NV Bekaert SA, Belgium, M.C.M. van de Sanden, Eindhoven University of Technology, The Netherlands

A novel form of diamond-like hydrogenated carbon deposited utilizing the expanding thermal remote Ar/C2H2 plasma is reported. The plasma is generated in a cascaded arc at subatmospheric pressure in argon. The discharge expands into a low pressure (remote) chamber where acetylene is introduced downstream by means of an injection ring. The downstream plasma is characterised by a low electron temperature which leads to ion driven chemistry and negligible physical effect like ion bombardment (< 2 eV) on the substrate. Distinct from previous works, relatively low argon to acetylene gas flow ratio has been used in this study. Infrared absorption shows a reduced concentration of CH stretching and in addition, it is also evident that the endgroups  $(sp^2 - CH_2 \text{ and } sp^3 - CH_3)$  are absent in the films. Theses films posses relatively low optical band gap and hydrogen content, high refractive index and a nanohardness exceeding 16 GPa. Further characterizations by means of Raman spectroscopy, spectroscopic ellipsometry (SE) and Rutherford back scattering (RBS) indicate that the films are well cross-linked graphite like hydrogenated amorphous carbon.

The film properties will be interpreted in view of the specific plasma chemistry taking place in the expanding thermal plasma.

## Monday Afternoon, October 15, 2007

**Advanced Surface Engineering** 

#### Room: 617 - Session SE+PS-MoA

#### **Pulsed Plasmas in Surface Engineering**

Moderator: J. Patscheider, EMPA, Switzerland

2:00pm **SE+PS-MoA1 Modulated Pulse Power Deposition of Nanometer-Scale Multilayered Coatings**, *R. Chistyakov*, *B. Abraham*, Zond, Inc./Zpulser, LLC, *W.D. Sproul*, Reactive Sputtering, Inc., *J.J. Moore*, *J. Lin*, Colorado School of Mines

Modulated pulse power (MPP) sputtering is a variation of high power pulse magnetron sputtering that overcomes the rate loss issue through modulation of the pulse shape, intensity, and duration. In MPP, the pulse shape and duration and plasma perturbations directly affect the degree of ionization of the sputtered material. In this study, the MPP plasma generator was controlled by a special electronic device that allowed the generation of two different plasma discharges within the same deposition cycle. Nanometer scale layers of material deposited under the two different plasma condition were alternately deposited, and the thickness and structure of each nanolayer was controlled by varying the output voltage pulse shape of the MPP plasma generator. Films of carbon and reactively deposited itianium nitride and chromium nitride were sputtered, and the film structure, orientation, and mechanical properties were analyzed and measured. These variations in the plasma conditions directly affect the film properties, and results of the film property measurements will be presented.

#### 2:20pm SE+PS-MoA2 Reactive High Power Impulse Magnetron Sputter Deposition of Alumina, E. Wallin, S. Swedin, M. Lattemann, U. Helmersson, Linköping University, Sweden

Alumina, Al<sub>2</sub>O<sub>3</sub>, is one of the technologically most important ceramic materials. Due to the existence of a variety of different polymorphs, it finds use in a wide range of applications. In the present work, alumina thin films have been deposited using high power impulse magnetron sputtering (HIPIMS) of an Al target in Ar/O<sub>2</sub> gas mixtures. HIPIMS is a new and promising technique for ionized physical vapor deposition (I-PVD), in which a high degree of ionization of the deposition flux as well as an inherently high energy of the depositing species can be achieved at relatively low average power, by applying high power pulses with a low duty factor (typically around 1 %) to a conventional sputtering target (see, e.g., Helmersson et al., Thin Solid Films 513, 1 (2006)). Stoichiometric alumina films could be grown in a stable and essentially arc free process at rates which are high compared to the deposition rate for pure Al metal and comparable to, or even higher than, what can be achieved with traditional DC deposition methods. A model qualitatively describing and giving explanations for this behavior of the reactive process will be presented. The resulting films were investigated by x-ray diffraction, as well as scanning and transmission electron microscopy. Films deposited directly onto Si substrates at a substrate temperature of 400 °C were found to have a microstructure consisting of small, equiaxed grains with a diameter of the order of 10 nm, and with y-alumina as the only detectable crystalline polymorph. The results demonstrate the potential of depositing dielectric films at relatively high rates using HIPIMS. In addition, HIPIMS deposition of such films opens the possibility of utilizing the ionized deposition flux to improve the film quality and affect the structure of the coatings, also at reduced substrate temperatures.

#### 2:40pm SE+PS-MoA3 Effect of Sub-Surface Reactions on the Growth of Nano-Structured Functional Thin Films Deposited under Energetic Ion Bombardment, A. Amassian, M. Dudek, P. Jedrzejowski, R. Vernhes, O. Zabeida, P. Desjardins, J.E. Klemberg-Sapieha, L. Martinu, Ecole INVITED Polytechnique, Canada Recent advances in science and technology stimulate the development of new coating materials, surface and interface engineering processes and thin film systems that provide an ever increasing performance in numerous areas ranging from optical and optoelectronic to aerospace, automotive, biomedical, microelectronic, and other applications. Many successful solutions in these particular fields have been identified when using ionassisted deposition of thin films and thin film systems with tailored functional characteristics including the complex refractive index, the mechanical properties such as stress, hardness, friction coefficient and wear, the electrical conductivity, the gas and vapour permeation, and many others. In this context, we have recently investigated ion-surface interactions in a plasma environment (biased-controlled PECVD and PVD) using a

methodology combining in situ real-time spectroscopic ellipsometry (RTSE), dynamic Monte-Carlo simulations, and different complementary methods such as ERD, HRTEM, SEM, AFM and others. These have the capability to detect and simulate subplantation-related processes, such as sub-surface structural and compositional modifications, and interface broadening, on time and depth scales relevant to functional coatings deposition. The ion-induced effects result in (i) rapid structural (<< 1 s) and compositional (< 2 s) changes as deep as ?10 nm below film or substrate surfaces, as well as (ii) significant ion mixing and interface broadening, and (iii) relocation of a large proportion of deposited atoms below the growth surface. Specifically, following a description of the principal physical processes, we will show examples when the above-mentioned methodology helped to enhance our understanding of the film growth and interface evolution for numerous single and multilayer functional coatings comprising TiO2, SiO2, Si3N4, ITO and the nanocomposite superhard TiN/SiN and TiCN/SiCN systems. We will also discuss the ion-controlled growth mechanisms in the context of new deposition approaches such as plasma pulsing.

#### 3:40pm SE+PS-MoA6 Microstructure Evolution in High Power Magnetron Sputter Deposited Titanium Nitride, M. Lattemann, D. Jädernäs, U. Helmersson, Linköping University, Sweden

Transition metal (TM) nitrides are well known for their remarkable physical properties including high hardness and mechanical strength, chemical inertness, high temperature stability, low resistivity, and good optical properties. As a result they have become of high technological and scientific importance and are used in a wide range of applications. NaCl δ-TiN has received by far the most attention and is therefore often used as a model system. In this work, TiN thin films were deposited onto MgO(100) and MgO(111) substrates in an Ar/N2 atmosphere using high power impulse magnetron sputtering (HIPIMS). HIPIMS has earlier been proven to produce a highly ionized metal flux exhibiting a broad ion energy distribution with energies up to 100 eV advancing surface processes. It was shown that these ion energies are sufficient to produce fully dense films even at ambient temperature. However, the high amount of metal species with an energy around 1 eV promote the formation of underdense grain boundaries as the energy only allows the ions to interact with the nearest neighbor sites by single hop events. At ambient temperature and grounded substrate, the TiN thin films show a columnar structure with almost random orientation of the crystals as a result of combination of arriving species with high and low mobility as well as highly energetic ions creating defects and nucleation sites. The window for epitaxial growth of TiN for a variety of different process parameters was investigated. E.g. a more monoenergetic ion energy distribution can be achieved by tailoring the substrate bias and process conditions. In addition to the metal ion energy and substrate temperature, also the effect of assisting gas ion irradiation was investigated both during the pulse and in between the pulses, where no deposition occurred. In this way, the onset and breakdown of structure relation towards polycrystalline morphology can be monitored. The resulting structure of the TiN thin films was investigated by x-ray diffraction and high resolution transmission electron microscopy.

# 4:00pm SE+PS-MoA7 High Power Impulse Magnetron Sputtering (HIPIMS): Scaling Up to the Industrial Level, G. Greczynski, J. Bohlmark, Chemfilt Ionsputtering AB, Sweden

High Power Pulsed Magnetron Sputtering (HIPIMS or HPPMS) is a novel magnetron sputtering technique that draws increasing interest due to the ability to form the droplet-free films out of highly ionized vapor of the target material. Invented by Kouznetsov in 1999 (US patent US6296742) HIPIMS has gone the long way and is nowadays entering the stage of commercial applications. The focus of the work presented here is the basic parameter study performed on the industrial system equipped with HIPIMS power supply capable of delivering up to 10 kW average power in MW pulses. The target material used is Ti/Al and Ti. Purely metallic films, as well as, reactively sputtered TiAlN and TiN films were grown. The deposition rate and film quality were studied as a function of the energy per pulse (up to 20J), pulsing frequency (up to 500Hz), working gas pressure and the substrate bias. The degree of ionization, that was simultaneously monitored with optical emission, reached 90% under optimum conditions. Results are compared to the films produced with the state-of-the-art industrial DC coater. It is apparent from this study that the technique can be successfully used in the industrial applications.

#### 4:20pm SE+PS-MoA8 Mechanisms of Adhesion Enhancement by High Power Impulse Magnetron Sputtering, A.P. Ehiasarian, Sheffield Hallam University, UK INVITED

Adhesion to steel and carbide substrates is one of the primary factors determining coating performance under environmental attack such as wear in cutting and automotive engine operations, errosion-corrosion, and high temperature oxidation. Technologies that improve adhesion aim to sputterclean the substrate by high energy ion bombardment with energy >500 eV. These energies are sufficient for ions to be implanted into the bulk of the substrate to a depth of several monolayers (1-3 nm). Therefore the chemical composition of the bombarding flux can have a strong influence on the structure of the coating-substrate interface. Technologies that use gas ion bombardment typically incorporate Ar as interstitial or at vacancy sites generated in the steel or carbide lattice by the high energy of irradiation. The inert nature of Ar means that it does not form bonds with the surrounding atoms and thus greatly disturbs atomic ordering and increases stress. In the case of high power impulse magnetron sputtering (HIPIMS) plasmas operating at peak current of 2 Acm<sup>-2</sup>, the ion bombardment flux contains high fractions of metal ions. For HIPIMS of Cr and Ti, the ratio  $Ar^{l+}$ :  $Me^{l+} = 1$ : 1 was observed with energy-resolved mass spectroscopy, whilst the metal ion-to-neutral ratio was  $Me^{l+}$ :  $Me^0 = 1$ : 1 as determined from atomic absorption spectroscopy. Scanning transmission electron microscopy-energy dispersive spectroscopy (STEM-EDS) analysis of 304 stainless steel bombarded at 600 V by HIPIMS of Cr showed a layer of implanted Cr ions with depth of 5-8 nm, resulting from ballistic implantation as confirmed with TriDyn simulations. High-resolution TEM revealed that this region is highly crystalline with low defect density, probably due to the substitutional incorporation of Cr ions in the steel lattice. Incorporation and retention of Cr is improved by irradiation- and temperature- enhanced diffusion. As a result of the crystalline interface, the coating nucleated in local epitaxial growth mode which was maintained over several microns in lateral direction. A number of susbtrate-coating combinations demonstrated such epitaxy, for example for steel substrates: CrAIN, CrN, VN, TiAIN, and for γ-TiAl substrates - CrAIN, and CrN. This resulted in significant improvements to the adhesion and performance in wear and cutting of Ti and Al tests.

#### 5:00pm SE+PS-MoA10 Deposition Rate of High Power Pulsed Magnetron Sputtered Cu, J. Emmerlich, S. Mráz, R. Snyders, K. Jiang, J.M. Schneider, RWTH Aachen University, Germany

In high power pulsed magnetron sputtering (HPPMS), several kW target power are dissipated during µs pulses resulting in a high degree of ionization of the sputtering gas as well as the sputtered target material.<sup>1</sup> A major drawback of this deposition process is reported to be the low deposition rate compared to d.c. magnetron sputtering (dcMS). Selfsputtering, due to a metal-ion dominated plasma later in the pulse, and plasma conductivity may play a large role in the deposition rate loss. However, the high target potential (up to ~2kV) applied during HPPMS influences the sputtering yield induced by both, the sputtering gas and the target ions (self-sputtering). The effect of the energy dependent sputtering yield on the deposition rate is discussed for Cu. Using transport-of-ions-inmatter (TRIM) software, we simulated the sputtering yield for a Cu target bombarded with energetic Ar<sup>+</sup> and Cu<sup>+</sup> ions for dcMS and HPPMS target potentials. The results show that the deposition rate of HPPMS compared to dcMS based on an energy dependent sputtering yield is in the range of 77% to 43%.

<sup>1</sup>K. Macák, V. Kouznetsov, J. Schneider, and U. Helmersson, J. Vac. Sci. Technol. A 18, 1533 (2000). **Advanced Surface Engineering** 

#### Room: 617 - Session SE-TuM

#### **Glancing Angle Deposition**

Moderator: D. Gall, Rensselaer Polytechnic Institute

#### 8:00am SE-TuM1 Temperature Effect on the Glancing Angle Deposition of Si Nanostructures, *C. Patzig, B. Rauschenbach*, Leibniz Institute of Surface Modification, Leipzig, Germany

It is well-known that combining a glancing angle deposition (GLAD) process with suitable substrate rotation offers the ability to grow nanostructures with various shapes, including spirals, screws or vertical posts. When depositing on bare substrates, different growth phenomena are often encountered: Starting of as single fibers at the substrate, adjacent structures will merge together at a certain stage of growth. Also, dying out of structures due to a competitive growth of neighboured structures, and a broadening of the structures diameter with increasing structure height is often observed. However, for most applications, well-aligned, non-merged structures with comparable diameters are needed. Therefore, it is important to understand the influence of the deposition parameters on the nano-scaled structures in order to be able to control their growth. Here, the effect of the substrate temperature Ts on the growth of different Si nanostructures is studied. An ion-beam induced GLAD process was used to grow Si nanostructures at different substrate rotational velocities and at different substrate temperatures T<sub>s</sub> ranging from room temperature (RT) up to 360°C, while all other deposition parameters where held constant. Due to the different rotational velocities, spirals, screws and vertical posts could be deposited. Analyzing the structures by means of scanning electron microscopy , it is found that Ts strongly influences the morphology of the grown structures. For the spirals and the screws, T<sub>s</sub> effects the critical structure height  $\boldsymbol{h}_{crit}$  at which the single fibers start merging together. From RT to  $T_s = 300^{\circ}$ C,  $h_{crit}$  is increased with increasing  $T_s$  from  $h_{crit}(RT) =$ 150nm to  $h_{crit}(300^{\circ}C) = 350nm$  (for the spiral structures), thus giving the possibility to grow spirals consisting of single fibers without merging together over a larger thickness range. However, it was found that increasing the temperature over  $T_s = 300^{\circ}C$  results in a sudden drop of the critical height  $h_{crit}$  (360°C) = 130nm. Moreover, the total structure height was found to be dependent on T<sub>s</sub> as well, indicating a change of the film density. For the posts, it was found that Ts influences the total number of posts and the inter-post-distance as well as the total structure height, showing a change of the film density as found for the spirals and screws.

### 8:20am SE-TuM2 Gold Nanorod Arrays for Surface Enhanced Raman Scattering Imaging of Micro-objects, *M. Suzuki*, *K. Nakajima*, *K. Kimura*, Kyoto University, Japan, *T. Fukuoka*, JST Kyoto Pref. CREATE, Japan, *Y. Mori*, Doshisha University, Japan

Recently, we have demonstrated the direct formation of Au nanorods with a quasi-parallel major axis on a template layer of SiO<sub>2</sub> having a strongly anisotropic surface morphology. Those Au nanorods show excellent surface enhanced Raman scattering (SERS) properties.1 Since the number density of nanorods is considerably high, we tried to apply our nanorod arrays to SERS imaging of micro-objects. Template layers of SiO<sub>2</sub> were prepared by the serial bideposition technique (SBD) on a glass substrate. During the SBD, the deposition angle measured from the surface normal was fixed at an angle of 79°, while the azimuthal angle was changed rapidly by 180° with each deposition of a 10-nm-thick layer. After repeating 30 cycles of the serial bideposition, Au was evaporated at a deposition angle of 73° onto the fabricated template layer. Owing to the self-shadowing, Au nanorods aligned in such a way where their major axes are parallel with each other. On the Au nanorod arrays, surface-modified polystyrene (PS) beads (5 µm in diameter), which have pyridyldithio group on their surface, were distributed. Raman spectra were measured by scanning the laser ( $\lambda$ =785 nm) with 1 µm step in a 40x40 µm<sup>2</sup> region. Raman peaks those originate from pyridyldithio group were detected only at the points where the PS beads and Au nanorods coexist. By assigning the Raman intensity levels to colors, SERS images were obtained. The PS beads were successfully resolved. Therefore, Au nanorod arrays are useful for the imaging of microobjects such as cells and dusts without any labeling by other chemicals.

<sup>1</sup> M. Suzuki, K. Nakajima, K. Kimura, T. Fukuoka, and Y. Mori, Analytical Sciences (2007) in press.

#### 8:40am SE-TuM3 Applications of Porous Thin Films Fabricated by Glancing Angle Deposition, *M.J. Brett*, University of Alberta, Canada INVITED

Considerable efforts have been made by a number of research groups to advance the Glancing Angle Deposition (GLAD) technique in order to achieve precisely engineered and porous thin film structures. Carefully controlled substrate motion and glancing incidence evaporative flux enable fabrication of regular and random arrays of metals, semiconductors and insulators in architectural shapes such as posts, chevrons and helices. After a brief overview of the GLAD process and some advanced fabrication algorithms, this presentation will highlight some recent advances in applications of these coatings, in particular their use in sensor devices. Porous nanostructures of insulator materials have been deposited over planarized interdigitated electrodes and demonstrate fast (100 ms) response in conjunction with capacitive detection. Optical filters have been fabricated with the GLAD process to produce spectral hole or narrow bandpass characteristics ideal for optical detection through shift of the transmission peak. These filters have also been chemically functionalized to alter their sensitivity. Ag nanostructures will be presented that utilize surface plasmon resonance absorption for optically based sensing of biochemical compounds. For these and other applications, GLAD provides the advantages of broad material choice and precise control of microstructure shape and degree of porosity.

### 9:20am SE-TuM5 Periodic Nanostructures by Glancing Angle Deposition, C.M. Zhou, D. Gall, Rensselaer Polytechnic Institute

Periodic Ta nanopillar arrays were grown by glancing angle deposition onto patterned substrates. Both the effects of pattern size and surface diffusion on morphological evolution were studied by varying the pattern length-scale and by growing at temperatures Ts ranging form 200 to 900 °C. The surface patterning experiments show a direct scaling, indicating that the overall nanopillar morphologies are determined by geometric shadowing and are for  $T_s = 20$  °C independent of material parameters such as the characteristic length-scale for surface diffusion. However, at high growth temperatures, the increased adatom diffusion length causes Ta nanopillars to grow in a competitive growth mode, which in turn results in the breakdown of the regular array morphology. Glancing angle deposition has also been extended to fabricate novel Ta/Si two component nanostructures onto selfassembled close-packed silica nanosphere arrays. The two component nanostructures are shaped into zigzags or nanopillars by adjusting the deposition angle and/or the substrate rotation. By manipulating the sequence of the deposition, that is, by sequential or simultaneous deposition from two sources, complex nanostructures are formed where the two components are stacked vertically, laterally, or in a checker board arrangement. Scanning electron microscopy, back scattered imaging, and transmission electron microscopy provide clear compositional and microstructural contrast and show sharp vertical and horizontal interfaces.

#### 9:40am SE-TuM6 Electrically Actuated Alq<sub>3</sub> Nanospring Arrays, G.D.

Dice, M.J. Brett, D. Wang, J.M. Buriak, University of Alberta, Canada We report the fabrication and characterization of an electrically variable Fabry-Perot interferometer constructed from a nanospring array placed between partially reflective mirrors. Electrostatic compression of the nanosprings provides peak transmission wavelength control. Previous work studied the compression of SiO<sub>2</sub> nanosprings,<sup>1</sup> and individual Si nanospring actuation through electric current applied via a contact mode atomic force microscope (AFM).<sup>2</sup> High quality nanostructures have recently been created using the organic material tris (8-hydroxyquinoline) aluminum (Alq<sub>3</sub>), which has a significantly smaller Young's modulus than inorganic films. Glancing Angle Deposition (GLAD) is a single step physical vapour deposition (PVD) technique utilizing an oblique deposition angle to create porous thin film helical structures.<sup>1</sup> Our device is constructed from three films deposited on a conductive indium tin oxide electrode. A 25 nm thick aluminum film forms both a partially reflective mirror and one parallel capacitor plate. A two turn helical Alq<sub>3</sub> nanospring film (300 nm pitch)is then deposited via GLAD PVD. A patterned 25 nm thick layer of aluminum forms the final mirror layer and top capacitor plate. Spring compression as a function of applied voltage was measured through a conducting contact mode AFM. The measured compression varies from 0 nm at 0 V, to  $\sim 1.2$ nm at 6 V. We calculate the Young's modulus of the deposited Alq<sub>3</sub> to be ~ 0.93 GPa. A shift in the peak transmission wavelength from 582.4 nm to 580.8 nm was measured utilizing a fiber-coupled white light source and spectrometer as the applied voltage was raised from 0 V to 10 V. This 1.6 nm wavelength shift corresponds to a physical spring compression of 1.73 nm for the nanospring structure which has an effective refractive index of 1.42.

<sup>1</sup> M. W. Seto, K. Robbie, D. Vick, and M. J. Brett, "Mechanical response of thin films with helical microstructure," J. Vac. Sci. Techol. B, vol. 17, pp. 2172-2177, Sep. 1999.

<sup>2</sup> J. P. Singh, D. L. Liu, D. X. Ye, R. C. Picu, T. M. Lu, and G. C. Wang, "Metal-coated Si springs: Nanoelectromechanical actuators," Appl. Phys. Lett, vol. 84, pp. 3657-3659, Apr. 2004.

<sup>3</sup> P. C. P. Hrudey, K. L. Westra, and M. J. Brett, "Highly ordered organic Alq3 chiral luminescent thin films fabricated by glancing-angle deposition,"Adv. Mater., vol. 18, pp. 224-228, Jan. 2006.

10:40am SE-TuM9 Effect of Thermal Oxidation and Annealing on the Structure and Morphology of Glancing Angle Deposited TiO<sub>x</sub> Films, W.J. Kiether, C.R. Guarnieri, H.T. Nagle, North Carolina State University The typical Glancing Angle Deposited (GLAD) structure is an isolated, self-similar construct on a nanometer scale. Therefore, each structure can react to external influences independently of the other structures, as a separate, albeit similar system. This small scale system independence allows the nanostructures to exhibit different material characteristics than conventional thin films. As with other nanoscale structures, the large surface-volume ratio enhances surface effects, but the isolated GLAD structures are also effectively pinned on the substrate suppressing crossstructure grain growth and other microstructure propogation phenomena. Therefore, they provide an excellent surface engineering template to investigate the effects of annealing and thermal oxidation on thin film structure and morphology. Oxidation of titanium, with the existence of the metastable anatase and stable rutile polymorphs within the titania system, is significantly influenced by the microstructure obtained by GLAD films. Simple GLAD structures (pillars and chevrons) were deposited using reactive e-beam evaporation with a titanium source at various partial pressures of oxygen and argon. Additional process variables included deposition rate, flux angle of incidence, rotation speed, and substrate. Post deposition anneals were conducted in oxidizing, inert, and reducing atmospheres from 150-1200 °C. XRD patterns and SEM images served as the primary forms of film characterization. The combination of reactive evaporation at higher oxygen partial pressures and lower temperature anneals formed films with the highest percentage of the anatase phase. Depositions at lower oxygen partial pressures yielded films with a higher percentage of the rutile phase, which supports the role of oxygen vacancies as nucleation centers for the anatase to rutile transformation. Higher temperature annealing produced rutile films as expected from the thermodynamics of the titanium dioxode system, however the thermal stability of anatase phase structures was significantly enhanced by the GLAD microstructure. The titanium films also exhibit highly ordered crystallographic textures dependent on the flux angle of incidence for both ss-deposited films and after subsequent thermal oxidation. Finally, SEM images provide an interesting perspective on the dynamics of oxidation, grain growth, and sintering for a surface reaction dominated oxidation process.

#### 11:00am SE-TuM10 Glancing Angle Deposition of Organic Molecules, M.D. Fleischauer, G.D. Dice, S. Tsoi, University of Alberta, Canada, B. Szeto, M.J. Brett, University of Alberta / NRC National Institute for Nanotechnology, Canada

Glancing Angle Deposition (GLAD) has developed in to a widely-used nanostructuring technique because of the wide range of possible structures and material choices. Efforts to understand the fundamental mechanisms central to GLAD, including self-shadowing and limited surface diffusion, have largely focused on metals and oxides. Hrudey et al.<sup>1</sup> recently demonstrated that the GLAD technique can also be used for organometallics such as the luminescent material tris (8-hydroxyquinoline) aluminum (Alq3). Unlike their inorganic counterparts, GLAD-fabricated Alq3 nanostructures are smooth, show a self-ordered periodicity, and do not broaden or bifurcate. A solid wetting layer was also observed to form below the Alq<sub>3</sub> structures whose thickness varies with deposition conditions. Alq<sub>3</sub> molecules differ from metal atoms in that they are larger (1 nm dia.), heavier (ca. 460 a.m.u.), approximately planar, and possess an electronic quadrupole moment. A better understanding of how these properties lead to wetting layer formation, self-ordering, and smooth feature morphology, as a function of deposition conditions, is critical to the future realization of GLAD-nanostructured optical and optoelectronic organic devices. Here, we will present our investigations of the growth of Alq3 nanostructures during GLAD. Methods to control film morphology (including wetting layer thickness) via deposition conditions and substrate preparation will be presented. Special attention will be paid to the initial stages of Alq3 film growth during GLAD, especially compared to initial growth mechanisms observed at normal incidence by Brinkmann et al.,<sup>2,3</sup> with an eye towards predicting the behaviour of other organic and organometallic materials in the glancing angle regime.

<sup>1</sup>P.C.P. Hrudey, K.L. Westra, and M.J. Brett, Adv. Mater. 18, 224 (2006).

<sup>2</sup>M. Brinkmann, S. Graff, and F. Biscarini, Phys. Rev. B 66, 165430 (2002).

<sup>3</sup>M. Brinkmann, F. Biscarini, C. Taliani, I. Aiello, and M. Ghedini, Phys. Rev. B, 61, R16339 (2000).

11:20am SE-TuM11 Scaling Behavior of the Surface Roughness of Platinum Films Grown by Oblique Angle Deposition, A. Dolatshahi-Pirouz, M.B. Hovgaard, University of Aarhus, Denmark, K. Rechendorff, Ecole Polytechnique Federale de Lausanne, Switzerland, M. Foss, F. Besenbacher, University of Aarhus, Denmark

Recently there has been an increasing focus on the growth of thin films and nanostructures with rough surface morphologies on the nanometer length scale for applications in biotechnology, cell/tissue engineering, and catalysis, since the surface morphologies and the absolute value of the surface roughness on the nanometer scale may influence the performance in these areas. In this work, thin platinum films were grown by e-gun evaporation with oblique angle of incidence between the deposition flux and the substrate in order to generate surfaces with well controlled rough morphologies. Atomic force microscopy (AFM) was used to determine the root-mean square (rms) value, w, of the surface roughness. From the scaling behavior of w for the thin platinum films, we observe that while the roughness exponent  $\alpha$  remains unchanged, the growth exponent  $\beta$  changes from  $0.49 \pm 0.04$  to  $0.26 \pm 0.01$  as the deposition angle approaches grazing incidence. The change in the growth exponent  $\beta$  indicates that the kinetics of the film growth is influenced by both surface diffusion and shadowing effects under oblique incidence deposition.

#### 11:40am SE-TuM12 Tailoring the Wettability of Vertically Aligned Si Nanorod Arrays by Glancing Angle Deposition, J.G. Fan, A. Collins, Y.P. Zhao, University of Georgia

We report a facile method to tailor the wettability of vertically aligned Si nanorod arrays by glancing angle deposition. As-prepared Si nanorod array surface is hydrophilic, while after coating a fluorocarbon layer, it becomes hydrophobic. For vertically aligned nanorod arrays, when increasing the nanorod height from tens of nanometers to several microns, the as-prepared samples become more hydrophilic while fluorocarbon coated samples become more hydrophobic. A wetting transition from a rough surface to a composite surface is observed at the same critical nanorod height (~ 150 nm for deposition angle of 86°) for both hydrophilic and hydrophobic surfaces. This critical height decreases when increasing the sample deposition angle, i.e., reducing the surface coverage of the nanorods. With a deposition angle of  $88^\circ$ , both superhydrophilic (contact angle = 0) and superhydrophobic (contact angle =  $170^{\circ}$ , and contact angle hysteresis  $< 10^{\circ}$ ) surfaces are obtained. For tilted nanorod arrays, strong anisotropic wetting behavior is observed in the plane formed by the vapor incident direction and the substrate normal. After hydrophobization, the difference between the left and right (nanorod tilting direction) contact angles of a water droplet could be as large as 30°. Such a droplet is able to move along the nanorod tilting direction under external disturbances. This tilting nanorod array provides a new morphological manipulation method for liquid delivery in microfluidic or nanofluidic devices.

# 12:00pm SE-TuM13 Chemical Modification of Nanocomposite Si-SiOx Films Obtained by Oblique Deposition, *I.Z. Indutnyy*, *V.A. Dan'ko*, *I.Yu. Maidanchuk*, *V.I. Min'ko*, *P.E. Shepeliavyi*, V. Lashkaryov Institute of Semiconductor Physics NAS of Ukraine

Nanocrystalline silicon (nc-Si) embedded in SiOx matrix recently have attracted much interest due to perspective of application in optoelectronics and photonics. One of the methods that allow forming nanocomposite Si-SiOx films is vacuum deposition of amorphous SiOx with further anneal in vacuum or inert atmosphere. It leads to formation of nc-Si with diameter about 3-5 nm. Photoluminescence (PL) at room temperature is observed in such structures, position of PL band is in range of 700-950 nm. In recent papers we offered new method that allow to control nc-Si size and spectral range of PL by forming porous SiOx film using oblique deposition of silicon monoxide. Film obtained by oblique deposition has columnar structure (diameter of columns 10-50 nm). Annealing of such film leads to formation of nc-Si in volume limited by column size, that is nc-Si of smaller size are forming. Film obtained by oblique deposition is porous (porosity up to 57%). In this work we investigated the influence of chemical treatment in ammonia and acetone vapor on PL spectra of porous nc-Si-SiOx structures. Oblique deposited films were treated by saturated vapour of acetone or ammonia before anneal. This chemical treatment leads to the considerable changes in PL spectra effecting as on the band shape as on intensity. A new intensive PL band (with peak position near 590 nm) appears after annealing in samples treated in ammonia, and with peak near 600-610 nm in samples treated in acetone vapor. IR transmission spectra of treated and annealed films demonstrates appearance of silicon nitrides bands (for samples treated in ammonia) and bands connected with carbonization (for samples treated in acetone). It is assumed that the changes in PL spectra is caused by modification of nc-Si-SiOx interface with N or C atoms. Replacement of oxygen in Si-SiOx interface by N or C modifies electronic structure of excitons involved in light emitting process. Shortwave band (590-610 nm) that appears after chemical treatment is blueshifted for 0,6 eV in comparison with nontreated samples. The value of

0,6 eV is in good agreement with other works where oxide matrix with embedded nc-Si was replaced by nitride or carbon matrix. Thus chemical treatments in ammonia and acetone vapor are efficient methods that allow to increase PL intensity of the silicon nanocrystals embedded in the oxide matrix and vary PL peak position in wide range from 560 to 950 nm.

# Tuesday Afternoon, October 16, 2007

**Advanced Surface Engineering** 

#### Room: 617 - Session SE-TuA

#### Naturally and Artificially Nanolaminated Coatings

Moderator: D. Gall, Rensselaer Polytechnic Institute

#### 1:40pm SE-TuA1 Optical Characterization of ZnO/Ag/ZnO Multilayer Films with Ag Layer Deposited by High Power Pulsed Magnetron Sputtering, J. Li, S.R. Kirkpatrick, S.L. Rohde, University of Nebraska-Lincoln

ZnO/Ag/ZnO multilayer films can be used in Low-E glass, solar cells and flat panel displays. Thin silver layers sandwiched between layers ZnO have been deposited by High Power Pulsed Magnetron Sputtering (HPPMS). By varying the deposition conditions during HPPMS, a thin, dense and uniform silver layer with low resistivity, high transmittance in visible light range have been obtained. The optical properties of ZnO/Ag/ZnO multilayer films with silver layer deposited by HPPMS have been studied using spectroscopic ellipsometry and infrared spectroscopic ellipsometry. The results have also been compared with multilayer films with silver layers deposited by conventional DC magnetron sputtering. For ZnO/Ag/ZnO multilayer films, the Ag-HPPMS multilayer films showed lower resistivity, lower IR transmittance than DC magnetron sputtered films. The optical properties of ZnO/Ag/ZnO multilayer films with different silver layer thickness deposited by HPPMS have also been investigated, with respect to their potential in an array of optical applications.

2:00pm SE-TuA2 Synthesis and Elastic Properties of MAX Phases, J.M. Schneider, D. Music, RWTH Aachen University, Germany INVITED  $M_{n+1}AX_n$  phases (space group P6<sub>3</sub>/mmc), where M is a transition metal, A is mostly IIIA or IVA group element, X is either C or N and n = 1-3, can be referred to as nanolaminates, where MX layers are interleaved with A layers. We have investigated the valence electron concentration induced changes in the elastic properties of M<sub>2</sub>AlC phases (M = Sc, Y, La, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W) using ab initio calculations.<sup>1,2</sup> In terms of bulk moduli [1], we have suggested that M2AlC phases can be classified into two groups based on the coupling between MC and Al layers: M2AlC phases with M = VB and VIB are strongly coupled, while M<sub>2</sub>AlC with M = IVBare weakly coupled. In terms of shearing,<sup>2</sup> we have proposed that these phases can also be classified into two groups: one group comprises M = VB and VIB, where the C<sub>44</sub> values are independent of the corresponding MC. The other group includes M = IIIB and IVB, where the C<sub>44</sub> shows a linear dependency with the corresponding MC. This may be understood based on the electronic structure: shear resistant bands are filled in M2AIC phases with M = VB and VIB, while they are not completely filled when M = IIIBand IVB. These classification proposals exhibit identical critical valence electron concentration values for the group boundary. Experimental efforts have been dedicated towards exploring the correlation between the valence electron concentration, constitution, and the elastic properties of M2AlC phases (M = Ti, V, Cr). Ti<sub>2</sub>AlC can be deposited onto sapphire substrates at a growth temperature of 800 °C using a compound target and an additional source of Ti.<sup>3</sup> V<sub>2</sub>AlC was grown at a substrate temperature of 850 °C. We report that 450 °C is sufficient to grow crystalline Cr<sub>2</sub>AlC thin films. This is the lowest deposition temperature ever reported for a MAX phase and is significantly lower than the crystallization temperature of an amorphous Cr<sub>2</sub>AlC thin film based on our differential scanning calorimetry data.

<sup>1</sup>D. Music, Z. Sun, R. Ahuja, J.M. Schneider, Phys. Rev. B 73 (2006) 134117.

<sup>2</sup>D. Music, Z. Sun, A.A. Voevodin, J.M. Schneider, Solid State Commun. 139 (2006) 139.

<sup>3</sup>C. Walter, C. Martinez, T. El-Raghy, J.M. Schneider, Steel Research Int. 76 (2005) 225.
 <sup>4</sup>C. Walter, D.P. Sigumonrong, T. El-Raghy, J.M. Schneider, Thin Solid Films 515 (2006) 389.

2:40pm SE-TuA4 Deposition of  $M_{n+1}AX_n(n=1-3)$ Phase Coatings by Magnetron Sputtering from Compound Targets and High Velocity Oxy-Fuel Spraying. *H. Högberg*, Linköping University, SwedenINVITED Magnetron sputtering has proven to be a favorable route for synthesis of films of the ternary carbides or nitrides referred to as the  $M_{n+1}AX_n(n=1-3)$ phases. Sputtering from elemental targets has enabled the growth of several materials systems; predominately carbidic phases with Ti as the carbideforming transition metal (M) and with either Al, Si, Ge or Sn as the Aelement, but with extensions to other metals as in the V-Ge-C system or to nitride based systems as in the Ti-Al-N system. The majority of the films have been deposited on Al<sub>2</sub>O<sub>3</sub>(0001) substrates to promote epitatial growth at temperatures typically above 700 °C, but for V<sub>2</sub>GeC as low as 450 °C. In addition to deposition of the known phases in each of the studied systems this type of process also enables the growth of new phases such as Ti<sub>3</sub>SnC<sub>2</sub> and so-called intergrown structures in the Ti-Si-C and Ti-Ge-C systems. Using sputtering from compound targets of Ti<sub>3</sub>SiC<sub>2</sub> and Ti<sub>2</sub>AlC in either Ar or Ar/N2 plasmas we are currently investigating the growth conditions for the respective phases as well as potentially quaternary Ti-Si-CN and Ti-Al-CN phases. The studies show that sputtering of the compound targets in pure Ar plasmas favors epitaxial growth conditions for Ti<sub>3</sub>SiC<sub>2</sub> and Ti<sub>2</sub>AlC when the sources are co-sputtered with Ti. The as-deposited coatings consist predominately of MAX phase, but with intergrown layers of TiC. This behavior is attributed to higher carbon content in the deposited films compared to the target composition. Addition of N2 during growth of both systems results in films of lower crystalline quality, and with preferential nucleation of TiC or TiCN for higher N2 flows. XPS shows that up to 30 at. % N2 is incorporated in the Ti-Al-CN films, and that the content of nitrogen in the deposited films scales with the amount of nitrogen available in the plasma. For deposition of thick (appr. 200  $\mu$ m) Ti<sub>2</sub>AlC coatings, we have applied high velocity oxy-fuel (HVOF) spraying. Characterization shows that dense and well-adherent coatings can be deposited on steel. Structural analysis shows that the HVOF coatings consist of Ti2AlC (the powder phase) together with Ti-Al melting phases and residual TiC and Ti<sub>3</sub>AlC<sub>2</sub>. Vickers indentation experiments and scanning electron microscopy imaging of the indented area showed a hardness of appr. 6 GPa, with concentric cracks at the indent.

4:00pm SE-TuA8 Effect of Swift Heavy Ion Irradiation on the Hardness of Chromium Nanorods, *R. Nagar*, Indian Institute of Technology Delhi, India, *K. Sai, D. Gall, Rensselaer Polytechnic Institute, D. Jain, UGC-DAE, CSR, India, B.R. Mehta, J.P. Singh, Indian Institute of Technology Delhi, India* 

This presentation discusses the use of ion irradiation to controllably tailor the hardness of Cr columnar thin films. Regular arrays of slanted Cr rods, 2 µm long and 250 nm wide, were grown by glancing angle dc magnetron sputter deposition on patterned Si(100) substrates. The patterns consist of 500-nm-diameter polystyrene spheres that self-assemble to form hexagonal close-packed monolayers. The Cr rod arrays were irradiated with 100 MeV Ag<sup>+8</sup> ions at three different fluences of  $10^{13}$ ,  $5x10^{13}$  and  $10^{14}$  ions/cm<sup>2</sup>, while maintaining the sample at a constant temperature of 80K. The ionirradiation induced defect formation is dominated by electronic energy losses, with a very small contribution (approximately 0.5%) from the nuclear energy losses and negligible Ag-implantation. The average nanohardness of pristine Cr rods, as determined using a Berkovich diamond tip attached to an atomic force microscope, was found to be 0.6 GPa. Irradiation of the rods with 10<sup>13</sup> ions/cm<sup>2</sup> does not lead to a measurable change in the hardness. However, for the fluence of  $10^{14}$  ions/cm<sup>2</sup>, the hardness increases to about 4 GPa, leading to an about eight-fold increase. The fluence-dependent hardness in these Cr rods is attributed to the ionirradiation induced defect formation that may lead to dislocation pinning which is particularly effective due to the nanoscale dimensions of the Cr rods. These results are very promising as they demonstrate the use of swift heavy ion irradiation to tune the hardness of nanorod coatings.

4:20pm SE-TuA9 Formation of Surface Relief of As2S3 Films using Glancing Deposition, *M.V. Sopinskyy*, V. Lashkaryov Institute of Semiconductor Physics, Ukraine, *V.I. Min'ko*, V. Lashkaryov Institute of Semiconductor Physics NAS, Ukraine, *I.Z. Indutnyy*, *O.S. Lytvyn*, *P.E. Shepeliavyi*, V. Lashkaryov Institute of Semiconductor Physics, Ukraine

In this report we present the first results on the surface morphology and optical properties of 1-3 mkm thick As2S3 films that were thermally evaporated on the glass and silicon substrates within 70-80° range of the vapor incidence angles. The AFM has revealed the details of the surface relief of glancing-deposited films showing quasi-regular grating-like structure, with the spatial frequency of quasi-gratings being in the 3000-6000 mm<sup>-1</sup> range, and relief depth of 10-60 nm range. Ordering degree also depends on the substrate. The preliminary deposition of thin Cr film on the glass substrate results in more pronounced surface self-ordering of glancing-deposited As2S3 films. Multiangle ellipsometric measurements have been performed to determine the refractive index, and check the anisotropy of the films. It has been found that the refractive index values in these films are lower compared to the values for the films with the normal (perpendicular) deposition. In addition, there is anisotropy of refractive index in the plane of the film. This indicates that the structure of the films is columnar, with the columns tilted relative to the substrate normal. The most probable explanation for the observed effect is the surface stress that plays significant role in the self-organized ordering of nanostructures at the mesoscopic length scales (several nm - hundreds of nm). It is the known fact that the thermally deposited As2S3 films are mechanically stressed, especially in the near-surface area. Thus, due to the structural anisotropy of the obliquely deposited As2S3 films, the stress forces are also anisotropic. The more pronounced columnar structure of these samples provides a lot of free space where the bond breaking and atomic movements are facilitated. Both of these factors result in anisotropic plastic shears in the film' near-surface region. The effect is a cheap and easy way to create quasi-gratings on the surface of amorphous chalcogenide films and could be used for fabrication of nano- and microdevices.

### **Tuesday Afternoon Poster Sessions**

Advanced Surface Engineering

#### Room: 4C - Session SE-TuP

#### **Advanced Surface Engineering Poster Session**

#### SE-TuP1 Protective Coatings of Extensible Biofibers, N. Holten-Andersen, F. Zok, J.H. Waite, University of California, Santa Barbara

As thin film coatings are increasingly finding their way in engineering and biomedical applications, the demand for unique combinations of their material properties is increasing as well. A coatings protection of the underlying substrate against wear relies on its resistance to penetration, i.e. its hardness. Increasing hardness of the coating however, significantly lowers its extensibility. Protecting substrates undergoing large strains against wear is therefore a challenge beyond the reach of current engineering coating applications. By investigating natural coating materials adapted to high- and low-stress environments we have studied nature's solution to this problem. In the protective cuticles of mussel holdfast threads (self-assembled biological fibers), high wear resistance have in wave-exposed species been combined with high extensibility. Here, we demonstrate that the inclusion of deformable micro-particles within a stiff protein matrix allows the cuticle of these holdfast threads to exhibit sufficient hardness against wear without encumbering the elasticity of the thread. This unique composite design results in an impressive damage tolerance by arresting developing micro-cracks thereby preventing catastrophic failure of the coating up until an astounding 70% strain. Cuticles from mussel species in deeper and calmer habitats lack these deformable particles and fracture below 30% strain. This increase in extensibility of the granular composite cuticle parallels the behavior observed with rubber toughened polymers such as High Impact Poly-Styrene. However, whereas the inclusion of rubber particles significantly compromises the hardness of these synthetic composites, our study shows that only a small reduction in hardness is observed in the biological coating composite. Interestingly, the interior morphology of the micro-particles in the cuticle shares a striking similarity with the bi-continuous network morphologies observed in polymer micro-emulsions and block copolymer systems. The superior mechanical properties together with the selfassembling nature of the material, makes this study significant for the broad materials community.

#### SE-TuP2 Optimization of Process Parameters using Matrix Assisted Pulsed Laser Evaporation (MAPLE) for Deposition of Carbon Nanoparticles, *M.H. Check*, University of Dayton, *A.A. Voevodin, C.N. Hunter*, Air Force Research Laboratory, *J.J. Hu*, University of Dayton Research Institute

Matrix Assisted Pulsed Laser Evaporation (MAPLE) is a thin film deposition technique that can be applied to a large range of polymeric and biological substances. The advantage of using MAPLE compared to other laser techniques is that deposition can be accomplished with little or no damage to the transported material. The technology was explored for preparation of tribological coatings with carbon nanopearls (~150 nm in size) encapsulated in metal (Au and Ag) and ceramic (TiN) matrices. The focus was placed on understanding how to control transport and uniformity of nanopearls on the deposition surface. The controlling parameters included laser fluence (200-800 mJ), repetition rate (1-30 Hz), solvent material (methanol and isopropanol), and background gas composition and pressure (5-30 mTorr of Ar and N2 mix). The characteristics of the synthesized 1-2 micron thick carbon/metal and carbon/ceramic composite films were correlated with area fraction of the nanoparticles, degree of dispersion of the nanoparticles and effect of the transport process on the properties of the nanoparticles. Results from electron microscopy, optical profilometry, and XPS are discussed.

# SE-TuP3 High Rate Deposition of Photocatalytic TiO<sub>2</sub> Films with High Activity by Hollow Cathode Gas-Flow Sputtering, Y. Kubo, Aoyama Gakuin University, Japan, Y. Iwabuchi, M. Yoshikawa, Bridgestone Co., Japan, Y. Sato, Y. Shigesato, Aoyama Gakuin University, Japan

Titanium dioxide (TiO<sub>2</sub>) has been well known as a photocatalyst because of the strong oxidizing power of photo-generated holes. Reactive sputter depositions using a Ti metal target should be one of the most promising techniques for uniform coatings in large area with high packing density and strong adhesion. However, the deposition rate is very small of 2~5 mm/min for the conventional reactive magnetron sputtering to deposit fully oxidized TiO<sub>2</sub> films because the films should be deposited at the "oxide mode" where the target surface is oxidized and the sputtering yield is very smal.<sup>1</sup> In order

for the high deposition rate of 30~90 nm/min, we have been reported on dual cathode sputtering system<sup>2</sup> or unipolor pulsing system<sup>3</sup> with plasma emission control systems<sup>2-3</sup>. As the much simpler and lower cost system, TiO2 films were deposited on unheated alkali-free glass substrates by gasflow sputtering using two Ti metal targets which were mounted parallel with each other. Ar (sputtering gas) was supplied between these two targets.O<sub>2</sub> (reactive gas) was supplied in the vicinity of the substrate. Ar and O<sub>2</sub> flows were 3.0 SLM and 10~50 sccm, respectively, and total gas pressure during the depositions was maintained at 45 Pa. In such pressure mean free path of gas atoms is very small and a gas flow is in viscous regime, that is why the process has been named gas-flow sputtering.<sup>4</sup> The photocatalytic activity was evaluated by photo-decomposition of acetaldehyde and contact angle for water after UV illumination (black light lamp, 0.4 mW/cm<sup>2</sup>). Both of the as-deposited films and the post-annealed films at 300 °C in air performed the photocatalytic decomposition. Especially the post-annealed films performed extremely high photocatalytic activities. The highest deposition rate to deposit such photocatalytic TiO2 films were 162 nm/min.

<sup>1</sup> M. Yamagishi, S. Kuriki, P. K. Song and Y. Shigesato, Thin Solid Films, 442 (2003) 227.

<sup>2</sup> S. Ohno, D. Sato, M. Kon, Y. Sato, M. Yoshikawa, P. Frach, Y. Shigesato, Jpn. J. Appl. Phys., Vol. 43, No.12 (2004) 8234.

<sup>3</sup> S. Ohno, N. Takasawa, Y. Sato, M. Yoshikawa, K. Suzuki, P. Frach and Y. Shigesato, Thin Solid Films 496 (2006) 126.

4 K. Ishii, J. Vac. Sci. Technol., A7 (1989) 256.

SE-TuP4 High Rate Deposition of Photocatalytic WO<sub>3</sub> Thin Films with Visible Light Activity by Gas-Flow Sputtering, *M. Fukuyama*, *M. Kikuchi*, Aoyama Gakuin University, Japan, *Y. Iwabuchi*, *M. Yoshikawa*, Bridgestone Corporation, Japan, *Y. Sato*, *Y. Shigesato*, Aoyama Gakuin University, Japan

In recent years, we have been reported on the visible-light induced photocatalytic properties on polycrystalline WO3 films deposited by reactive dc magnetron sputtering on heated glass substrate at around 600 oC.<sup>1,2</sup> However deposition rate was very low of about 10 nm/min for the conventional reactive magnetron sputtering to deposit fully oxidized WO<sub>3</sub> films because the films should be deposited at the "oxide mode" where the target surface is oxidized and the sputtering yield is very small. In this study, polycrystalline WO<sub>3</sub> films were deposited by on fused quartz glass substrate by gas flow sputtering using two W metal target which were mounted parallel with each other. Ar was used as sputtering gas and O2 was used as reactive gas, which were supplied between these two targets. Total gas pressure was maintained at 70Pa. Ar and O<sub>2</sub> gas flows were 5.0 SLM and 50 sccm, respectively. WO3 films were deposited on the substrate without heating or heated upto 500 oC, 600 oC or 700 oC. The films deposited on the unheated substrate were post-annealed at 500 oC, 600 oC or 700 oC for an hour in the air. The crystal structure of the WO<sub>3</sub> films were analyzed by X-ray diffraction (XRD). The transmittance and reflectance of the films in UV-VIS region were measured using spectrophotometer in order to estimate absorption coefficient by Newton-Raphson's method. The photocatalytic activity was evaluated by decomposition of acetaldehyde and contact angle for water after UV (black light lamp : 0.4mW /cm<sup>2</sup>, center wavelength : 352 nm) light and VIS (Xe lamp with a 410-500 nm band pass filter : 1.0, 7.0 mW/cm<sup>2</sup> respectively, center wavelength : 450 nm) light irradiation. Both of the films deposited at 500-700 oC and the films postannealed at 500-700 oC performed the visible-light induced photocatalytic activity. The highest deposition rate to deposit such photocatalytic WO<sub>3</sub> films was 230nm/min.

<sup>1</sup> M.Ebihara, Y.Shigesato, et al., Proceedings of the 3<sup>rd</sup> ICCG), (2000) 137.

<sup>2</sup> M. Kikuchi, Y. Shigesato, et al., Proceedings for 6<sup>th</sup> International Conference on Coatings on Glass and Plastics (ICCG-6), (2006) 365.

### SE-TuP5 Photocatalysis of Dense and Porous Bilayers of Cuprite and Titania, *M.H. Wu*, *M.S. Wong*, National Dong Hwa University, Taiwan

Titanium dioxide with anatase phase couples with different materials contributing better or worse photocatalysis. Transferring of electrons and holes in junction is caused by the different energy levels of conduction band and valence band. Dense and porous bilayers of cuprous oxide and titanium dioxide with various microstructures and thickness were prepared by magnetron sputtering and electron beam evaporation with glancing-angle deposition technique. The photocatalysis of the films was tested via photodegradation of methylene blue. Porous columnar titania films covered with Cu2O layer allow good carrier transfer and high specific surface area, where the photo-generated electrons and holes can be separated and function at different area of the columnar structure, resulting better photocatalytic performance. SE-TuP6 Preparation of TiO<sub>2</sub> Thin Films by Laser Ablation for Photocatalytic Applications, W.-T. Chang, J.-Y. Ciou, National Dong Hwa University, Taiwan, S.-J. Wang, National Taipei University of Technology, Taiwan, M.-K. Wei, M.S. Wong, National Dong Hwa University, Taiwan

Thin titanium dioxide (TiO2) films were deposited by KrF excimer laser ablation deposition system using a titanium oxide target. The effects of substrate temperature and oxygen partial pressure on the phase formations of various microstructures were investigated by X-Ray diffraction (XRD), scanning electron microscopy (SEM), Raman scattering spectroscopy and UV-Vis spectrophotometer, respectively. Increasing the substrate temperature can improve the quality of anatase phase of crystalline TiO2 films that were obtained from the amorphous structure hybridized with rutile and anatase phases. However, the oxygen pressure in the range between 15 to 60 mTorr shows a single anatase phase in TiO2 films that the rutile and anatase phases were observed elsewhere. The bandgap of TiO2 films varied from 2.72eV to 3.27 eV with more oxygen partial pressure in the film deposition indicates the phase changed from rutile phase to anatase phase. The surface area of TiO2 films was increased as more oxygen partial pressure involved in the fabrication. The photocatalytic effect measured by exposing the methylene blue in UV light that was distinguishable in the TiO2 films with high anatase phases and surface area.

#### SE-TuP7 Effect of Internal Pressures for TiO<sub>2</sub> based Colloidal Sols during Hydrothermal Process, C.R. Yoon, H.J. Oh, N.H. Lee, Y. Guo, S.J. Kim, Sejong University, Korea

Transparent TiO<sub>2</sub> sols were prepared by hydrothermal synthesis to heat Ti precursor solutions, from Ti hydroxides obtained with neutralizing aqueous TiOCl<sub>2</sub> solutions having various concentrations of NaCl by aqueous NaOH solution, in the autoclave at 120°C, and then their photocatalytic abilities using glass beads coated with the sol for gaseous benzene were evaluated. Because it was possible to prepare brookite phase TiO<sub>2</sub> sol by external pressurization into the autoclave during the synthesis, the internal pressure in the autoclave was controlled using a technique with capturing Na ions in the lattice of Ti hydroxide. As a result, it was found that due to the increase of brookite phase in TiO<sub>2</sub> by controlling the concentration of Na ion the optical absorption of TiO<sub>2</sub> increases toward long wavelength but that in the range of short wavelength becomes relatively low and consequently the photocatalytic performance of TiO2 thin film for benzene gas rather decreases, compared to that of composite film of anatase and brookite phases. These results suggest that in order for coated TiO<sub>2</sub> thin film to have high dissociation performance for benzene gas it is effective to form anatase and brookite phases compositely in TiO2.

#### SE-TuP8 Photoinduced Friction Force Variation of Polycrystalline Anatase Thin Films, N. Arimitsu, A. Nakajima, Y. Kameshima, K. Okada, Tokyo Institute of Technology, Japan

Titanium dioxide (TiO<sub>2</sub>) thin film has attracted much attention as a photocatalyst. TiO<sub>2</sub> surface exhibits conventional photocatalytic oxidation reactions and photoinduced highly hydrophilic conversion. These reactions result in useful properties such as antibacterial functions, self-cleaning, and antifogging. The photoinduced reaction on TiO2 surface has been well studied by various techniques. According to a friction force microscopy (FFM) study using a Si<sub>3</sub>N<sub>4</sub> cantilever, it was revealed that rutile single crystal produce a unique microdomain structure in the surface with a contrast difference by UV illumination.<sup>1</sup> Since the tip of the cantilever is hydrophilic, the image contrast implies the difference in hydrophilicity on the surface. Recently, it is reported that the contrast difference after UV illumination was also obtainable on polycrystalline anatase thin film as in the case of rutile single crystal.<sup>2</sup> In the present study, we prepared polycrystalline anatase thin films on Si substrates using sol-gel process and O2 plasma treatment<sup>3</sup> and investigated the relationship between photoinduced friction force change and photoinduced hydrophilicity of the film. The photoinduced friction force change was evaluated by FFM with a Si<sub>3</sub>N<sub>4</sub> cantilever. Upon UV illumination, the average friction force decreased gradually with decreasing water contact angle until it reached the lower limit. Then, the friction force began to increase with increasing UV illumination time. Detailed relationship among contact angle change, UV illumination period, and friction force change will be discussed.

<sup>1</sup>R. Wang et al., Nature 388 (1997) 431.

<sup>2</sup>K. Katsumata et al., Surf. Sci. 579 (2005) 123.

<sup>3</sup>N. Arimitsu et al., Surf. Coatings Technol. 201 (2006) 3038.

#### SE-TuP9 Pretreatment by High Power Impulse Magnetron Sputtering - Interface Structure and Stress Evolution, D. Jädernäs, M. Lattemann, U. Helmersson, Linköping University, Sweden

Substrate pretreatment using metal ion bombardment is an effective way of promoting film-substrate adhesion. In this work we have used high power impulse magnetron sputtering (HIPIMS) to produce the Cr-ions that are bombarding the high speed steel substrates with an applied negative substrate bias, U<sub>b</sub>, between 200 and 1100 V. During pretreatment and subsequent film growth, the stress evolution was measured and the adhesion of the films was evaluated using scratch testing. Some samples were also post-annealed at a temperature of 900 K. The results showed that all pretreatment conditions result in a compressive stress that can be correlated to U<sub>b</sub>. The stress induced during pretreatment was also shown to affect the growth of the subsequently grown film. For U<sub>b</sub> below 600 V significant etching did not occur and a Cr-layer was formed. In this case, the native oxide on the steel remained. For higher U<sub>b</sub> values the oxide layer was removed. For the non-annealed films a strong correlation between U<sub>b</sub> and adhesion was observed. Substrates with the oxide layer intact showed low film adhesion. After annealing all samples showed an increased adhesion and no clear trend between different pretreatments and adhesion could be observed. The interfacial chemistry and structure were examined in order to find the correlation between structure, chemistry and adhesion. The results show that strong interfaces, capable of resisting an applied force, can be produced even though an oxide is still present.

SE-TuP10 Nanostructure and Properties of TiAlN/a-C Composite Coatings, M. Nose, T. Kawabata, University of Toyama, Japan, S. Khamthe, Graduate School of Science and Engineering, Japan, K. Matsuda, T. Nagae, S. Ikeno, University of Toyama, Japan, K. Nogi, Osaka University, Japan

Aluminum/magnesium pressure die-casting needs protective coatings to the molding dies in order to extend die life. When applied to cast liquid aluminum or magnesium alloy into molding parts, die surface faced harsh conditions such as soldering and erosion at temperatures over 600 °C. DLC (diamond like carbon) or a-C (amorphous carbon) coating has been widely applied to machine-tools for aluminum, due to enhanced tribological properties in terms of low friction, high hardness and non-affinity to aluminum. However, DLC or a-C becomes thermally unstable at temperatures higher than 300 °C when coating hardness drastically drops with temperature. Nanocomposite coatings consisting of transition metal nitride/carbide and amorphous carbon are expected to be stable at higher temperatures and to reduce adhesion of nonferrous alloy. In this study, TiAlN/C nano-composite coatings synthesized by PVD process were examined the effects of sputtering conditions on the microstructure and mechanical properties, and evaluated as potential applications in molding dies. Coating films were synthesized by the co-sputtering of TiAl (pulsedd.c. sputtering) and C (d.c. sputtering) targets using a Facing Target-type Sputtering system (FTR-2, Osaka Vacuum Co., Ltd.) under an environment with a mixture of Ar and N2 on square plates of Si and high speed steel (ANSI M2). The structure of the films was investigated by means of XRD, XPS and HRTEM with GIF (Gatan Imaging Filter). Mechanical properties of coating films were measured in detail by a submicron indentation system (H-100, Fischer). Although TiAlN or a-C films showed hardness of about 30 or 10 GPa, one of TiAlN/a-C films containing several % of a-C showed higher hardness of 43 GPa. The Zero-loss image indicated that a change of contrast accompanies the change of composition of Ti and Al. Nanometersize of Al agglomerates were observed and Ti distribution corresponded to that of Al. XPS analysis of C1s spectrum revealed that carbon in the films bound almost as C-C with a few bondings of Ti-C or Al-C and C-N. Ti2p and Al2p spectrum indicated that these transition metals bound mostly with nitrogen. These results indicated that nano-composite structure consisting of complicated mixture of nanocrystalline Ti-Al-N phase and a-C phase (with a small amount of C:N phase and metal carbide phase) existed in the TiAlN/a-C films.

SE-TuP11 Wear Behavior of Unbalanced Magnetron Sputtered Multilayer CrN/TiAlYN Coatings Deposited on Plasma Nitrided Steels, *M. Flores, E. Rodriguez,* Universidad de Guadalajara, México, *E. De las Heras, P. Corengia,* Instituto Nacional de Tecnología Industrial, Argentina, *L. Huerta,* Universidad Nacional Autonoma de México

The influence of pretreatment on the wear behavior of tool steels coated with TiN, CrN and CrN/TiAIYN multilayers were experimentally investigated. The substrate materials were nitrided using plasma nitriding. The thin films were deposited using unbalanced magnetron sputtering technique. A comparison between the wear resistances of nitrided, coated, nitrided and coated samples were made. The nitrided coatings and CrN/TiAIYN multilayer grown on pulse plasma nitriding steels have been characterized by using X-ray diffraction (XRD), scanning electron microscope (SEM), micro-indentation and abrasive wear tests. The depth profiles were studied by X-ray photoelectron spectroscopy (XPS) and Rutherford Backscattering spectroscopy (RBS). The duplex coatings showed a low wear respect to the coated samples. The out-performance of the prenitrided TiN, CrN and CrN/TiAIYN coatings can be attributed to the presence of a nitrided subsurface.

SE-TuP12 Power Supplies to Enable High Power Impulse Magnetron Sputtering, *D. Ochs*, HÜTTINGER Elektronik GmbH, Freiburg, Germany, *R. Spencer*, Alacritas Consultancy Ltd., Leicestershire, U.K.

High Power Impulse Sputtering (HIPIMS or HPPMS) receives more and more attention as a technique to produce very dense films. It relies on the creation of high density plasma in front of the sputtering source and by that way a large fraction of the sputtered atoms are ionized. These ionized atoms can be used for surface pretreatment and deposition as well. The interfaces and layers so produced show superior properties in many applications. Currently the most investigated and promising application is use for hard coatings as wear and corrosion protection. Popular layers are for example CrN and TiN. To enable the HIPIMS process a specially designed power supply for powering the magnetron cathode is needed. This power supply consists of 3 modules. The DC module contains a converter which charges a capacitor bank in the pulse module. A semiconductor switch is activated by the pulse control unit. The third module is an impedance matching circuit to shape the output current pulse in order to match the requirements of the cathode. Several power supply configurations have been realized in order to fulfill the different process needs. HIPIMS power supplies with a max. pulse power of up to 18MW, a voltage of 1kV to 3kV and a current of 1kA to 6kA will be presented with practical results from industrial coating applications.

## Wednesday Morning, October 17, 2007

**Advanced Surface Engineering** 

#### Room: 617 - Session SE-WeM

#### **Photocatalytic Coatings**

Moderator: A. Erdemir, Argonne National Laboratory

8:00am SE-WeM1 High Rate Deposition of Photocatalytic TiO<sub>2</sub> Films by dc Magnetron Sputtering using a TiO<sub>2-x</sub> Target, Y. Sato, A. Uebayashi, N. Ito, Aoyama Gakuin University, Japan, T. Kamiyama, Asahi Glass Ceramics Co.,Ltd., Japan, Y. Shigesato, Aoyama Gakuin University, Japan

Sputter deposition should be the most promising technique for the uniform coatings in large area with very high durability and strong adhesion. However, the deposition rate of  $TiO_2$  films by conventional reactive sputtering using a Ti metal target is very low, because the target surface should be fully oxidized (in "oxide mode") in order to deposit stoichiometric TiO<sub>2</sub> films. Recently, a slightly reduced TiO<sub>2-x</sub> target (2-x = 1.986, Resistivity: 0.27 Ωcm) has been developed. Using this TiO<sub>2-x</sub> target TiO<sub>2</sub> film deposition by dc sputtering with rater high rate and high durability should be possible. TiO<sub>2</sub> films were deposited on alkali-free glass substrate at RT-400°C by dc magnetron sputtering using the TiO<sub>2-x</sub> target under 3.0 Pa. O2 flow ratio during deposition was controlled from 0 to 100%. The variation in the deposition as a function of O<sub>2</sub> flow ratio did not show hysteresis curve at "transition region" as can be seen in the case of using Ti metal target, indicating that the TiO2-x target surface was gradually oxidized with increasing O2 flow ratio. The deposition rate using TiO2-x target under 100% Ar gas was about 5 times higher than that using Ti metal target in "oxide mode". XRD patterns of the films deposited at O2 flow at 0-5% showed entirely amorphous structure. After postannealing in air at higher than 200°C for 1 hour, these films changed to polycrystalline anatase TiO<sub>2</sub> and showed excellent photocatalytic activities such as photodecomposition of acetaldehyde (CH<sub>3</sub>CHO) or photo-induced hydrophilicity. Furthermore, we carried out in-situ analyses on the sputtering processes using the different sputtering target. A quadrupole mass spectrometer (QMS, AQ-360, ANELVA) combined with a specially designed energy analyzer revealed that high-energy O ion flux was detected clearly even in the sputtering with 100% Ar gas in the case of using the TiO<sub>2-x</sub> target. Whereas in the case of using Ti metal target the O<sup>-</sup> ion flux was detected only in the "oxide mode". The sputtered fragments mass analyses showed that Ti<sup>+</sup> and TiO<sup>+</sup> existed as sputtered particles in case of using the TiO<sub>2-x</sub> target under O<sub>2</sub> flow ratio from 0 to 100 %, which was the same result as in the case of using the Ti metal target in the "oxide mode".

# 8:20am SE-WeM2 Flat-Flame Chemical Vapor Deposition Synthesis of Nanostructured Titania for Visible Light Photocatalyst, *Y.J. Chen, J.M. Wu, M.S. Wong*, National Dong Hwa University, Taiwan ROC

Anatase is known as the favorable phase of titania as photocatalyst over rutile. However, several reports suggest that a mixed phase of anatase and rutile possesses even better photocatalytic efficiency. In this paper, we report that a mixed phase of anatase and rutile synthesized by low-pressure flat-flame metalorganic chemical vapor deposition does show such phenomenon that the mixed phase with proper proportion has higher photocatalytic efficiency over single phase anatase. Using acetylene and oxygen as fuel and oxidizer for the flame, the titanium isopropoxide was decomposed and oxidized, and the nanoparticles of titania were formed. The phase of titania powder can be manipulated from almost pure anatase through mixed phases and to pure rutile phase by varying the inert precursor-carrying gas flow rate. The higher the carrier gas flow, the higher the rutile content. From the methylene blue decomposition study we found that the powder with almost pure anatase phase possesses best photocatalytic efficiency under illumination of UV light. However, mixed phase shows best efficiency under visible light illumination. Furthermore, for powder annealed in nitrogen atmosphere at 150 Celsius for 3 hours, the sample of mixed phase further enhanced its methylene blue photodecomposition efficiency. The reaction rate constant is even higher than that of ST-01 titania powder, which is commercially available for photocatalytic applications. While proper annealing process increases the photocatalytic activity of the powder, prolonged or elevated temperature annealing leads to degradation of its power, even the mixed-phase configuration is still retained. It suggest that carbon species play important role in enhancement of mixed-phase photocatalytic activity, since the carbon species will be oxidized during annealing, leaving uncontaminated titania powder, which lose its enhanced catalytic power. Evidence will be provided to show that the carbon species does evolve with annealing, and the presence of carbon species is in coincident with the presence of visible light absorption.

# 8:40am **SE-WeM3 Preparation and Characterization of TiO2/Ferrite Nanocomposites**, *K.S. Lin*, *W.R. Chen*, *C.F. Wu*, Yuan Ze University, Taiwan, R.O.C.

A core-shell structured composite, nanophase titania coated Ni-, or Znferrites nanoparticles, not only reserve the characteristics and advantages of TiO2 but also have the strong ferromagnetism of the ferrites. Therefore, the main objective of this study was to synthesize TiO2/nickel or zinc ferrite nanocomposites with spinel structure. In addition, it focused on the magnetic characteristics of the TiO2 surface-modified Zn or Ni-ferrite nanoparticles, which was expected to prepare a magnetically separable TiO2 photocatalyst. Experimentally, nickel or zinc ferrite core nanoparticles were synthesized under hydrothermal conditions by precipitating from metal nitrates with aqueous ammonia. TiO2 coated on the surface of the nickel or zinc ferrites were then prepared by hydrolysis of titanium chloride in the presence of ferrite nanoparticles. The optimal synthetic conditions included pH values of 8~9 and sintering at 673-773 K. The obtained ferrites or TiO2/Ni-, Zn-ferrites samples were characterized by XRD, FE-SEM, and TEM techniques. The results indicated that the size of nanoshell of TiO2 with anatase structure was 20-50 nm. X-ray absorption near edge structure (XANES) or extended X-ray absorption fine structure (EXAFS) was performed to identify the fine structures and oxidation state of Ni- or Znferrites and anatase-typed TiO2 coated ferrites nanoparticles. By using XANES spectra, Ni- or Zn-ferrites may exhibit an absorbance feature for the 1s to 3d transition can reveal the occupation of tetrahedral sites within the lattice, it showed that Ni ferrite had the same reverse spinel structure with Fe3O4 and the valence of hydrogenated ferrites were between 2 and 3. When the sintered temperature arrive 723 K, the nanoshell of TiO2 would transform from amorphous to anatase, and the nanoshell of TiO2 photocatalysts were all Ti (IV). The EXAFS data revealed that the nanoshell TiO2 photocatalyst had first, second shell of Ti-O, and third shell of Ti-Ti with bond distances of  $1.96 \pm 0.01$ ,  $2.01 \pm 0.01$ , and  $3.05 \pm 0.01$  Å, respectively.

# 9:00am SE-WeM4 The Substrate Effect on the TiO2 Photocatalytic Thin Films, J.-Y. Ciou, S.-J. Lin, M.-K. Wei, M.S. Wong, National Dong Hwa University, Taiwan

Titanium dioxide thin films were deposited on two different substrates of ptyped Si (100) and LaAlO3 (001) single-crystal in a pulsed laser deposition system via KrF excimer laser ablation of a pure titania target of 99.95% purity. The substrate temperature and oxygen partial pressure were varied at 400-600?C and 0-9.3 Pa, respectively. The mismatch of lattice constant between anatase TiO2 and LaAlO3 (001) is less than 0.2%, but that between anatase TiO2 and Si (100) is much larger. TiO2 films deposited on LaAlO3 have much better crystallinity than those deposited on Si. The films on LaAlO3 also revealed strong preferred orientation, but the films on Si did not. At all substrate temperatures the films on LaAlO3 compose of only a single anatase phase, while the film on Si composes of mixed phases of anatase and rutile at 600?C, but the crystallinity of the films on both substrates increases with rising substrate temperature. For the surface morphology, the films on LaAlO3 show mosaic structures of epitaxial growth, but the films on Si are polycrystalline in nature with smaller random grains. The photocatalytic performance is determined by the relative amounts of precipitated silver aggregates on the deposited films from AgNO3 aqueous solution under illumination of ultraviolet or visible light. The most precipitated silver aggregates were found at the steps or grain edges on the film surfaces. At lower substrate temperatures, the film deposited on Si has better catalytic performance than those deposited on LaAlO3. It may be due to much more grain edges of the films on Si. At higher substrate temperatures, however, the film deposited on LaAlO3 has better performance than the film on Si, which may be due to pure anatase phase with better crystallinity in the film on LaAlO3.

#### 9:20am SE-WeM5 Structuring Highly Active, Nano-scale Photocatalytic Films using Reactive Sputtering, K.A. Gray, L. Chen, M.E. Graham, G. Li, Northwestern University INVITED

Since Fujishima and Honda developed the photoelectrochemical cell for  $H_2O$  splitting in 1972, heterogeneous photocatalysis has attracted much attention. TiO<sub>2</sub> is among the most extensively studied semiconductor photocatalysts. It is chemically and biologically inert, photocatalytically stable, commercially available, and inexpensive. In the past three 30 years, most of the effort in the photocatalytic field has been focused on energy and environmental applications, which require materials with the following properties: (1) hindered charge recombination and improved photocatalytic

efficiency; (2) targeted reactivity and selectivity that match band energies to the desired reaction, and (3) extended photoresponse into the visible light region. Masakazu Anpo first introduced the notion of "second-generation" TiO<sub>2</sub> photocatalysts, which can absorb visible light and also operate effectively as photocatalysts. We hypothesize that the solid-solid interface in TiO2-based nanocomposites is key to overcoming these three challenges and are a promising candidates for 2nd-generation photocatalysts. Recent findings in our laboratory and others throughout the world reveal a number of surprising insights as to why TiO2 nanocomposites tend to display higher photoactivity than pure-phases and point to the critical role of the solidsolid interface as the location of catalytic "hot spots". Yet, efforts to probe the role of the solid-solid interface in photocatalytic activity are stymied by an inability to synthesize under sufficiently controlled conditions and in sufficient quantities the "interface", which would then allow structural characterization and functional interrogation. Advances in photocatalyst synthesis using sputtering technologies promise to revolutionize our ability to engineer the solid-solid interface at the molecular level and thus, to fabricate photoactive nanostructured composite materials having high densities of "defects" designed for energy harvesting and storage. We prepare highly active TiO2 nanocomposites using chemical and physical methods in our laboratory. By varying key fabrication conditions (target power, substrate bias, oxygen partial pressure, and deposition angle) in reactive DC magnetron sputtering, we synthesize TiO2 thin films with different microstructures. This paper will report the synthesis and characterization of photocatalytic films and their use to generate solar fuels and oxidize gas phase contaminants.

# 10:40am SE-WeM9 Photocatalytic Coating: Present Situation and Future Direction, A. Fujishima, Kanagawa Academy of Science and Technology, Japan INVITED

The recent decade has witnessed the birth and development of photocatalytic coatings.<sup>1</sup> In the early 1990s, we proposed the concept of photocatalytic thin film coatings for deodorizing, self-cleaning, and antibacterial uses.<sup>2</sup> In 1997, we reported the photo-induced superhydrophilic effect of  $TiO_2$  surface,<sup>3</sup> and proposed the concept of antifogging surface, and the concept of self-cleaning based on the photocatalytic and superhydrophilic actions of TiO2.4 Nowadays, these concepts have all born out real products. In Japan, self-cleaning building materials have covered tiles, glass, coatings, polymer films, aluminum sidewalls, and so on. Aircleaners, equipped with photocatalytic filters, have got recognition of consumers. Antibacterial tiles have been used in hospitals, hotels, and restaurants. Recent news is the carriage of high-speed railway system of Japan will be coated with photocatalytic self-cleaning coating. Besides these matured techniques, we are now studying new applications of photocatalytic coatings; these include anticorrosion coatings,<sup>5</sup> multichromic coatings,<sup>6</sup> low reflection self-cleaning coatings,<sup>7</sup> and heat-transfer applications,<sup>2</sup> etc. We are also thinking of the development visible-light responsive photocatalytic coatings and the standardization of photocatalytic coatings.<sup>1</sup> Our photocatalyst museum, which started three years ago, provides exhibition for companies' products as well as information service for consumers and researchers.

- <sup>1</sup> A. Fujishima, X. Zhang, C. R. Chimie 9 (2006) 750.
- <sup>2</sup> K. Hashimoto, H. Irie, A. Fujishima, Japn. J. Appl. Phys. 44(2005) 8269.
- <sup>3</sup> R. Wang, K. Hashimoto, A. Fujishima, et al. Nature 388 (1997) 431.
- <sup>4</sup> R. Wang, K. Hashimoto, A. Fujishima, et al. Adv. Mater. 10 (1998) 135.
- <sup>5</sup> T. Tatsuma, S. Saitoh, Y. Ohko, A. Fujishima, Chem. Mater. 13 (2001) 2838.
- <sup>6</sup> Y. Ohko, T. Tatsuma, A. Fujishima et al., Nature Mater. 2 (2003) 29.
- <sup>7</sup> X.-T. Zhang, A. Fujishima et al., J. Phys. Chem. B 110 (2006) 25142.

# 11:20am SE-WeM11 Composition-Spread Carbon-Incorporated Titania Films for Visible Light Photocatalysis, C.W. Weng, P.W. Chou, K.K. Rao, M.S. Wong, National Dong Hwa University, Taiwan

We adopted a combinatorial approach to develop a series of carbonincorporated titania (TiOxCy) films titania films with composition spread up to 40 at.% of carbon. The films were deposited on silicon and quartz substrates by co-sputtering a metallic titanium target and a graphite target simultaneously onto a stationary long-strip of substrate in a gas mixture of argon and oxygen. The location of substrates in relation to targets and the power of targets are found to be very crucial for the desired result. As the carbon content increases, the film structure and crystallinity transform from anatase to amorphous-liked phase and its morphologies and microstructures change from rough surface of columnar grains to smooth surface of nanocomposite. The carbon is present both in the form of substituted Ti-C bonds in anatase grains as well as free graphitic along grain boundaries or in matrix. With increasing carbon content, the film optical absorption in visible region decreases first and then increase, while the film optical bandgap energy varies from 2.6 up to 3.2, and then descends to 2.5 eV. On photocatalysis under visible light, the film with about ~10% carbon exhibits the largest photoreduction of silver-ions to form Ag particles and nanowires, while the film of the best anatase crystallinity with about 3 at% of carbon has the most degradation of methylene blue. The content and the Wednesday Morning, October 17, 2007

nature of carbon as well as the titania crystallinity dominate the visible-light induced photocatalytic activity of the TiOxCy films.

#### 11:40am SE-WeM12 High Rate Deposition of TiO<sub>2</sub> Films by using Two Sputtering Sources, Y. Hoshi, O. Kamiya, T. Sakai, Tokyo Polytechnic University, Japan

Deposition of TiO<sub>2</sub> films by reactive sputtering of titanium metal target has been reported by many researchers. However, it is very difficult to realize the high rate deposition of TiO2 films by conventional reactive sputtering, since the surface of the target is covered with titanium oxide layer, which leads to a significant reduction of the sputtering yield of titanium atoms. If we can suppress the formation of titanium oxide layer on the target surface and promote the oxidization of titanium atoms on the film surface during sputtering, high rate deposition of titanium oxide films can be realized by using the reactive sputtering method. In this point of view, we designed a new sputter-deposition system with two sputtering sources. One source, 33mm diameter magnetron sputtering source, is used as the source of titanium atom, and works at the metal mode sputtering condition and supplies the titanium atoms to the substrate. The other source of 100 mm in diameter works as an oxygen radical source and supplies oxygen radicals to the substrate surface to promote the oxidization of the titanium atoms during film deposition. Each sputtering sources are separated from deposition chamber and Ar gas and oxygen gas was introduced through the 33mm sputtering source and 100mm source, respectively. When Ar gas flow rate is fixed at 50 sccm and oxygen gas flow rate was below 8mTorr, the 33mm titanium sputtering source works in metal mode at a discharge current of 1 A. Whereas, the 100 mm oxygen radical source works in an oxide mode at an oxygen gas flow rate below 8 sccm and the sputtering current below 1.5 A. In this deposition method, most of the titanium atoms deposited on the substrate are supplied from the 33 mm sputtering source, and oxygen radicals supplied from 100mm source promote the oxidization of titanium atoms on the substrate. As a result, deposition rate more than 30 nm/min can be easily realized for the deposition of transparent TiO2 film with transmittance above 90%. These results indicate that the reactive sputtering method with two sputtering sources is effective to realize a high rate deposition of TiO2 films.

12:00pm SE-WeM13 Enhancement of Hydrophilicity and Photo Catalytic Activities of Nanocrystalline TiO<sub>2</sub> Thin Film Doped with Ruthenium, *R.R. Pandey, K.K. Saini, M. Dhayal, Chanderkant, S.C. Jain,* National Physical Laboratory, India, *M. Singh*, University of Delhi, India In this study  $Ru^{+3}$  ion doped nanocrystalline TiO<sub>2</sub> thin films has been fabricated using dip-coating technique on glass substrates. Surface structure and chemistry of the films was characterized using X-ray diffraction, transmission / scanning electron microscopy, UV-visible spectroscopy, X-ray photoelectron spectroscopy and FTIR. The  $Ru^{+3}$  ion doping in the film have significant influence on the morphology and surface chemistry. These nanocrystalline films have shown improved activity on the oxidation of organic pollutants possibly due to enhanced surface area with more active site in presence of  $Ru^{+3}$ .

### Friday Morning, October 19, 2007

Tribology

#### Room: 617 - Session TR4+SE-FrM

#### Friction and Wear of Engineered Surfaces Macro- to Nanoscale Approaches

**Moderator:** N.D. Theodore, Naval Research Laboratory, North Carolina State University

# 8:00am TR4+SE-FrM1 Mechanical, Chemical, and Tribochemical Etching of Silicon Studied by Atomic Force Microscopy<sup>1</sup>, *F. Stevens, S.C. Langford, J.T. Dickinson*, Washington State University

Commercial silicon nitride tips for atomic force microscopy (AFM) were used as model asperities to study the mechanical and tribochemical wear of a Si(110) surface. Aqueous sodium hydroxide and tetraethyl ammonium solutions were employed as chemical etchants. Under these conditions, tip wear is a significant issue; a new tip was employed for each wear measurement. Changes in tip contact stress were estimated by characterizing tip shapes before and after wear. In basic solution, the native oxide can be patterned by the AFM tip to expose the more vulnerable underlying Si to the chemical etchant.<sup>2</sup> Features 20 nm deep, with lateral dimensions less than 100 nm, are readily produced. The rate of oxide wear is a strong function of force applied to the AFM tip; even at low contact forces, scanning significantly accelerates oxide wear. Initial penetration of the native oxide is not uniform and produces deep pits-presumably at pinholes or similar defects in the oxide. Once the oxide is fully penetrated in the scanned region, subsequent tribochemical etching produces depressions with flat, smooth bottoms. For a given contact force and solution, the final wear depth relative to the surrounding, chemically etched material depends only on the number of times the AFM tip has passed over the surface; changing the tip velocity has no significant effect. Thus the tribochemical component of wear is not limited by chemical reaction rates under the conditions of this work. To characterize mechanical wear apart from chemical effects, hydrogen-terminated Si surfaces were scanned in inert solutions and atmospheres; images after wear in argon show wear debris, consistent with abrasive wear. The observed abrasive wear is sufficient to account for 5-10% of the Si wear observed in the presence of basic solution. Tribochemical effects during Si wear at a contact force of 300 nN in 0.1 M NaOH can easily enhance the total etch rate by a factor of two over the sum of the chemical and mechanical wear rates.

<sup>1</sup>This work was supported by the US National Science Foundation under Grant CMS-0409861. <sup>2</sup>S. Miyake and J. Kim, Nanotechnology 16, 149 (2005).

8:20am TR4+SE-FrM2 New Techniques for the Quantitative Determination of nm/hr Wear Rates of Materials, *P.R. Norton, G. Pereira, Y.-R. Li*, University of Western Ontario, Canada, *A. Lachenwitzer,* Cameco Corporation, *A. Alpas,* University of Windsor, Canada, *W. Capehart*, General Motors

Much effort has been spent on the chemical and mechanical characterization of antiwear films formed from ZDDP additives in automobile engines and on the mechanisms of their formation. By contrast, much less effort has been devoted to evaluating the wear itself. This is largely because the wear rates required in the engine are of order nm/hr, and accelerated testing under high loads is unacceptable because of the ubiquity of wear-rate transitions which make extrapolation to low loads difficult or impossible. The absence of relevant low-load (ultra-mild) wear data means that it is currently not generally possible to correlate the film characterization and wear rate studies, creating a huge gap in our understanding of wear. We are addressing this unsatisfactory situation by developing new techniques for directly measuring wear rates down to nm/hr in tests lasting a few hours. These techniques must be capable of measuring both the initial and longterm wear rates, be valid in the presence of surface films and take account of retention of material during wear. The strategy involves the implantation of Au atoms into the near-surface 100 nm region of a material (currently 52100 steel or an Al-Si alloy), and the determination of the loss of gold from the samples by means of Rutherford Backscattering (RBS) and Heavy Ion Backscattering (HIBS), and the accumulation of gold in the lubricant by Neutron Activation Analysis (NAA). The initial profiles can be either unimodal or multi-modal with depth, to provide sensitivity to short and longterm behaviour. The analysis of both sample and lubricant/debris quantitatively accounts for all implanted gold, and the depth resolution of HIBS permits determination of the location of the residual gold in the samples.

8:40am **TR4+SE-FrM3** Nano-scale Friction and Wear of Carbon-Based Materials, *R.W. Carpick*, University of Pennsylvania, *D.S. Grierson, A.R. Konicek, P.U.P.A. Gilbert*, University of Wisconsin-Madison, *A.V. Sumant, O. Auciello*, Argonne National Laboratory, *R.J. Cannara*, IBM Zürich, Switzerland, *T.A. Friedmann*, Sandia National Laboratories, *W.G. Sawyer*, University of Florida, *J.A. Carlisle*, Advanced Diamond Technologies **INVITED** 

Nanostructured carbon-based materials, such as nanocrystalline diamond and atomically smooth, nanometer-thick diamondlike carbon films, have outstanding and in many cases unrivalled tribo-mechanical properties. The atomic structure of the surfaces, verified by detailed surface spectroscopy, critically affects nano-scale friction and adhesion. We will specifically discuss how hydrogen termination, sp2-content, and crystal orientation affect adhesion and friction at the nanoscale. Next, we discuss how surface spectroscopy and imaging can be simultaneously applied to study wear of carbon films using photoelectron emission microscopy (PEEM)/X-ray absorption near edge structure (XANES). From these studies we test the hypotheses of ultralow friction in these materials, specifically, the extent to which chemical passivation of dangling bonds and convertion to graphitically bonded carbon occur. Finally, we will discuss taking advantage of this knowledge for nanoelectromechanical systems and advanced nanoprobe applications.

9:20am **TR4+SE-FrM5 Wear in MEMS-Based Microball Bearings**, *B. Hanrahan*, *M. McCarthy*, University of Maryland, *C. Zorman*, Case Western Reserve University, *A.V. Sumant*, Argonne National Laboratory, *R. Ghodssi*, University of Maryland

PowerMEMS devices supported on microball bearings have been successfully demonstrated at low operating speeds. Continued research on the tribological properties of these support structures is necessary for the realization of robust high-speed devices. Critical dimensions need to be maintained within tight tolerances when operating high speed micromachines. The wear between stationary and moving elements must, therefore, be minimized to reduce the change in critical dimensions over the lifetime of the device. Accordingly, the mechanism of wear between silicon and hardened steel microballs is the focus of this work. Silicon test structures, 23 mm in length, were fabricated with 300 µm wide deep-etched rectangular trenches acting as housings for the microballs. The 285 µm steel balls were sandwiched between two test structures under an applied normal loading. Oscillatory motion is generated between the two structures using an externally controlled stepper motor at 400 rpm and a traveling distance of 4mm. At periodic time intervals, the test device is disassembled and inspected using an optical profilometer to determine changes in the surface topography. To the best of our knowledge, this is the first investigation of wear in MEMS-fabricated ball bearings. Initial results show both deposition and removal of material within the microfabricated trenches. At 50,000 cycles, equivalent to 200 meters of travel, an increase in average surface roughness from 7.5 nm to 30.2 nm is observed. These results suggest the adhesion and subsequent shearing of contacting materials, increasing the overall roughness. The properties of the mating materials play a critical role in determining the wear mechanism. To expand the scope of the study, solid thin film lubrication has been explored. Silicon carbide and ultrananocrystalline diamond are ideal candidates for wear resistant films because of their high hardness, low interfacial energy, and compatibility with MEMS fabrication processes. In our analysis we will present a detailed investigation of the wear mechanisms of steel balls on silicon with and without solid lubrication.

9:40am TR4+SE-FrM6 Microstructure and Tribological Behavior of W-DLC Coated Rubbers, Y.T. Pei, X.L. Bui, University of Groningen, the Netherlands, X.B. Zhou, SKF Research and Development B.V., the Netherlands, J.T.M. De Hosson, University of Groningen, the Netherlands W-DLC coatings have been deposited on FKM, ACM and HNBR rubbers via unbalanced magnetron reactive sputtering from a W target in C2H2/Ar plasma. The surface morphology and fracture cross sections of uncoated and coated rubbers are characterized with high resolution SEM. The tribological behaviors of uncoated and coated rubbers have been investigated with ball-on-disc tribotest under dry sliding against 100Cr6 ball. The coefficients of friction (CoF) of uncoated rubbers are very high (µ > 1). Relatively high CoF of W-DLC coated FKM (about 0.6) is observed due to the gradual fracture and delamination of the coatings. In contrary, W DLC coated HNBR rubbers exhibit superior tribological performance with a very low CoF of 0.2-0.25 (comparable to that of Me-DLC coatings deposited on steel substrates). After 10000 sliding laps, almost no damage of the coatings is observed on the wear tracks. The micro-crack networks as deposited facilitate the flexibility of the coatings. The different surface

roughness and mechanical properties of the rubber substrates explain the differences in the tribological performances of the coated rubbers. For soft and flexible substrates such as rubbers, metallic interlayer does not enhance the interfacial adhesion but negative effects are observed.

# 10:00am TR4+SE-FrM7 Adaptive Tribological Nanocomposite Coatings, C. Muratore, J.J. Hu, A.A. Voevodin, Air Force Research Laboratory INVITED

Plasma processing allows precise control of the composition, microstructure and architecture of nanocomposite coating materials, enabling the design of materials that automatically adapt to variable aerospace environments, including humid and dry ambient air, space, and high temperature oxidizing conditions. Self-adaptive materials are of particular interest in tribological applications because most solid lubricants are effective in only a narrow range of ambient conditions. Thoughtful selection of multiple solid lubricant phases and the development of novel lubricant delivery mechanisms such as controlled diffusion, catalysis and chemical reactions with the surrounding atmosphere enhanced by contact between moving surfaces have recently been realized to achieve adaptation in diverse environments. For example, nanocomposite yttria-stabilized zirconia (YSZ) coatings containing Ag, Mo and other nanosized inclusions depend on temperature-activated adaptations to yield low friction (<0.2) from 25-700 °C in air. For YSZ-Ag-Mo nanocomposites, lubrication below 500 °C results from diffusion and coalescence of silver at the surface. Above 500 °C, the silver is pushed out of the wear contact, exposing a limited quantity of molybdenum in the coating to air, and initiating the controlled formation of MoO<sub>3</sub> and other compounds exhibiting low shear strength and thus easy sliding at high temperatures. While these adaptations at the surface reduce friction, irreversible compositional and structural changes resulting from the migration of film components can compromise the mechanical properties of the coating, thus reducing its utility over long periods at high temperature or through multiple thermal cycles. Moreover, some lubrication mechanisms occur over the entire coating surface in addition to the area experiencing wear, thus wasting the limited quantity of lubricious material stored in the coating. Coating architectures that control adaptation rates or selectively inhibit adaptation on coating surfaces unaffected by wear have been developed to increase the lifetime of adaptive tribological materials. Additionally, smart coatings with wear sensing capability have been developed to facilitate coating development and to improve reliability in critical applications.

#### 10:40am TR4+SE-FrM9 Hard Nanostructured Sulfur-Doped CHx-TiB2 Coatings for Improved Friction and Mechanical Performance, B. Zhao, Y.W. Chung, Northwestern University

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

#### 11:00am TR4+SE-FrM10 The Relation of Hydrogen to Superlubricity

of DLC Films, O.L. Eryilmaz, A. Erdemir, Argonne National Laboratory In this study, we investigated the critical role of hydrogen in friction and wear mechanisms of hydrogen-free and -poor films in dry nitrogen and high-vacuum environments. Using TOF-SIMS and XPS, we found a very important relationship between friction coefficient and the degree of hydrogenation in these films. Specifically, friction and wear test results showed that the films grown in hydrogen-free or -poor plasmas, the friction coefficients were very high (more than 0.5)and un-steady; and these films wore of very quickly during the sliding tests. However, when these films were subjected to very short-duration (a few minutes) post-hydrogen plasma treatment, their friction coefficients became very low (i.e., less than 0.1) and they were able to last very long during sliding tests. Surface analytical characterizations of the films and sliding contact surfaces were done using XPS and TOF-SIMS as well as Raman Spectroscopy and the chemical and structural findings were correlated with the tribological performance of the films. In particular, TOF-SIMS results revealed very close relationship between surface chemistry and tribological performance of DLC films.

11:20am **TR4+SE-FrM11** Friction and Wear Properties of Nanocrystalline Diamond Coatings, *C.C. Baker*, *N.D. Theodore*, Naval Research Laboratory, *T. Feygelson*, GeoCenters Incorporated, *J.E. Butler*, *K.J. Wahl*, Naval Research Laboratory

The tribological behavior of nanocrystalline diamond (NCD) coatings was studied under both unidirectional and reciprocating sliding conditions. Coatings were deposited by microwave plasma chemical vapor deposition onto Si substrates under varying growth conditions to thicknesses between 1-2 microns. Friction behavior was investigated using pin-on-flat geometry with sapphire counterfaces at average contact pressures of 0.43-0.74 GPa. Wear volumes of the ball counterface and coating wear tracks were determined with optical interferometry. Coating microstructure, chemistry, and surface morphology were examined using X-ray diffraction (XRD), micro-Raman spectroscopy, and atomic force microscopy (AFM). We have found that friction coefficients for the sapphire-NCD sliding interface are low, ranging from 0.03 to 0.1. However, there were large differences in friction run-in, with run-in from high to low friction taking between 50 to as many as 10000 cycles over a wide range of NCD deposition conditions. The role of coating microstructure, bonding chemistry, wear, and roughness of worn and unworn surfaces on run-in friction behavior of NCD will be discussed.

11:40am TR4+SE-FrM12 Effects of Annealing on Anti-Wear and Anti-Bacteria Behaviors of TaN-Cu Thin Films, J.H. Hsieh, M.K. Cheng, Y.K. Chang, Mingchi University of Technology, Taiwan, S.H. Chen, National Chiayi University, Taiwan, P.C. Liu, Mingchi University of Technology, Taiwan

TaN-Cu nanocomposite films were deposited by reactive co-sputtering on Si and tool steel substrates. The films were then annealed using RTA (Rapid Thermal Annealing) at 400 °C for 2, 4, 8 minutes respectively to induce the nucleation and growth of Cu particles in TaN matrix and on film surface. C-AFM (Conductive Atomic Force Microscopy) and FESEM (Field Emission Scanning Electron Microscopy) were used to confirm the emergence of Cu nano-particles on the surface of TaN-Cu thin films. The effects of annealing on anti-wear and anti-bacteria properties of these films were studied. The results reveal that annealing by RTA can cause Cu nano-particles with various dimensions to emerge on the TaN surface. Accordingly, hardness and friction coefficients will change, as well as the anti-bacterial behavior.

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