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 ^{o}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 as-deposited films were annealed at 900 ^{o}C and 1100 ^{o}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 Al_2O_3, TiO_2, and SiO_2 or others at high temperature. Cr, Al, and Si would diffusion outward to form the oxidative layers of Al_2O_3, Cr_2O_3, and SiO_2 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 high-angle configurations for phase identification. The microstructure was investigated by field emission gun high resolution transmission electron microscopy (FEG-HRTEM, FEI Tecnai G^2 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

$Ti_{1-x}Si_xN_y$ ($0 \le x \le 0.22$) 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 NaCl-structure 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. As-deposited 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 $0.05 \le x \le 0.10$, 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 arc 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 ~ 18 GPa, H3/Er2 ~ 0.1 GPa, and We ~ 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_2 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_2 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).

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/N_2 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 SiN_x 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 scratch-resistant 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 ºC. 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/C_2H_2 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 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.

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