

Advanced Surface Engineering Room 323 - Session SE-MoA

Hard Coatings: Preparation, Properties, Wear, and Nanotribology

Moderator: L. Hultman, Linköping University, Sweden

2:00pm SE-MoA1 High-resolution TEM Study the Microstructure of W-Si-C Films in the Vicinity of the Crystalline-Amorphous Transition, *J.E. Krzanowski, J. Wormwood*, University of New Hampshire

The addition of silicon to transition metal nitride and carbide thin films has generated considerable interest due to reports of greatly enhanced mechanical properties. It has been proposed that the effect of adding Si is to gradually reduce the crystallite size while introducing a thin amorphous interlayer between crystallites, ultimately resulting in an amorphous structure. In our work, we have examined a series of WC/SiC thin films over a composition range where the crystalline to amorphous transition occurs. By using high-resolution transmission electron microscopy, we have obtained a detailed picture of the mechanisms of this transformation in the W-Si-C system. These experiments have led to observations of novel microstructures not previously reported for Si-containing carbide/nitride thin films. A series of WC-SiC thin films has been deposited by RF magnetron co-sputtering, with compositions ranging from 15 to 38% SiC. X-ray diffraction analysis of these films confirmed the crystalline-to-amorphous transition in this compositional range. HRTEM observations revealed the following microstructural changes as the Si content increases: first, we observed fully crystalline nano-crystallites embedded in an amorphous matrix. Next, we observed the formation of larger (~50 nm) domains within which a novel droplet-like morphology of an amorphous phase is found. As Si is further increased, the droplets adopt a morphology where they appear to be strung together as the matrix phase becomes increasingly disordered. Finally, at yet higher Si contents, a spinodal-like two-phase structure is observed where one phase is amorphous and the second is best described as highly disordered. Despite the presence of these extensive microstructural changes, the hardness of the films within this compositional range was essentially constant.

2:20pm SE-MoA2 Metrology of 1-10 nm Thick CNx Films: Thickness, Density and Surface Roughness Measurements, *D.J. Li*, Northwestern University, Tianjin Normal University; *Y. Chen, Y.W. Chung*, Northwestern University

Ultrathin nitrogenated carbon (CNx) films were synthesized using pulsed dc magnetron sputtering. The influence of substrate tilt angle and rotation speed on surface roughness was explored. Atomic force microscopy studies showed that the smoothest films were obtained at substrate tilt of 45°, and rotation speed 20-25 rpm, corresponding to 2-3 rotations per deposited atomic layer. The root-mean-square surface roughness under these optimum conditions is ~0.3 nm when sampled over 20i, 20 i-m2 areas, increasing to ~0.4 nm when sampled over ~0.05i, 3 cm2 using x-ray reflectivity measurements. In addition, x-ray reflectivity measurements showed that the mass density of these CNx films is ~2.0 gm/cc, independent of film thickness from ~1 to 10 nm, consistent with ion beam analysis.

2:40pm SE-MoA3 Reactive Magnetron Sputtering of Hard Si-C-N and Si-B-C-N Films and Their Properties, *J. Vlcek, J. Cizek, S. Potocky, M. Kormunda, J. Houska, P. Zeman, Z. Soukup*, University of West Bohemia, Czech Republic

INVITED

Based on the results obtained for C-N films a systematic investigation of reactive magnetron sputtering of hard ternary Si-C-N and quaternary Si-B-C-N materials has been carried out. The Si-C-N and Si-B-C-N films were deposited on Si(100) substrates by dc magnetron co-sputtering of silicon and carbon (Si-C-N films) and silicon, boron and carbon (Si-B-C-N films) in nitrogen-argon gas mixtures using a composed C-Si and C-Si-B (at a fixed 20% boron fraction in the erosion track area) target, respectively, with variable Si/C area ratios. Elemental compositions of the films (determined by RBS and ERD), their bonding structure, and mechanical (hardness and friction coefficient) and optical (refractive index and extinction coefficient) properties were controlled by the Si fraction (5-80%) in the magnetron erosion track area, by the Ar concentration (0-75%) in the gas mixture, by the rf induced negative substrate bias voltage (from a floating potential to -500V) and by the substrate temperature (135-800°C). The total pressure and the discharge current on the magnetron target were held constant at 0.5Pa and 1A, respectively. The energy and flux of ions bombarding the

target and the growing films were estimated on the basis of the discharge characteristics measured for both the dc magnetron discharge and the rf discharge dominating in a deposition zone. Mass spectroscopy was used to explain differences between sputtering of carbon, boron and silicon from the composed targets in nitrogen-argon discharges. The films, typically 1-2µm thick, were found to be amorphous with a very smooth surface (R@sub a@ less than 1nm) and good adhesion to substrates at a compressive stress less than 1.2GPa. They exhibited hardness up to 35GPa (Si-C-N films) and 50GPa (Si-B-C-N films), enhanced high-temperature oxidation resistance and very high optical transparency (at a high Si content), and promising tribological properties (at a high C content).

3:20pm SE-MoA5 Using NMR to Probe the Bonding in Amorphous Carbon Nitride Thin Films, *W.J. Gammon*, College of William & Mary; *O. Kraft*, Inst. für Materialforschung II, Germany; *G.L. Hoatson, A.C. Reilly, B.C. Holloway*, College of William & Mary

In this study the chemical bonding in hard and elastic amorphous carbon nitride (a-CNx) films is investigated with 15N, 13C, and 1H nuclear magnetic resonance (NMR) spectroscopy. Nanoindentation yields an elastic recovery of 80%, a hardness of 5 GPa, and an elastic modulus of 47 GPa. Our 13C NMR study demonstrates the lack of sp3 bonded carbon in this material. Furthermore, the 13C and 15N NMR data imply a film-bonding model that has an aromatic carbon structure with sp2 hybridized nitrogen incorporated in heterocyclic rings and in pentagons; a suggestion that is supported by our preliminary total energy calculations of graphite defect structures. Results from 15N and 13C cross polarization (CP) and 1H magic angle spinning (MAS) NMR experiments also suggest that the nitrogen bonding sites are susceptible to protonation. The most likely source of protons is from water absorbed during sample preparation for the NMR experiments. The sensitivity of the surface of a-CNx to water absorption may impact tribological applications for this material.

3:40pm SE-MoA6 DLC and CNx Coatings Produced by Pulsed Laser and Filtered Vacuum Arc Techniques, *A.A. Voevodin, J.G. Jones, T.C. Back, J.S. Zabinski*, Air Force Research Laboratory; *V.E. Strelitzki, I.I. Aksenov*, Kharkov Physical Technical Institute, Ukraine

Unhydrogenated amorphous diamond-like carbon (DLC) and fullerene-like carbon nitride (CNx, N/C ratio ~ 0.2) are rival surface protection coatings with exceptional mechanical and tribological properties. A comparative study was performed on their benefits for sliding wear protection. The coatings were grown in the same deposition system, using similar substrates, surface preparation procedures, functionally graded interlayers (Ti-TiC-C), and top layer thicknesses. They were produced using pulsed laser deposition (PLD) and filtered cathodic arc deposition (FAD). Samples of laser-DLC, laser-CNx, arc-DLC, and arc-CNx coatings were prepared. Comparisons of coating chemistry, structure, hardness, elastic modulus, internal stress, coefficient of friction (c.o.f.) against steel and SiC balls, wear rate, and wear mechanism in humid and dry environments were performed. PLD and FAD provided very similar coating chemistry, structure and properties. Independent of the growth technique, DLC coatings had hardnesses within 52-57 GPa and elastic moduli within 490-560 GPa. The CNx coatings offered a reasonably high hardness of 28-30 GPa, while their elastic modulus was as low as 160 GPa. There was a clear difference in tribological behavior of DLC and CNx, which depends on the environment humidity. In humid air, DLC coatings had a c.o.f. of 0.1, a very low wear rate, and formed a graphitic transfer film in friction contact. In the same tests, CNx coatings had a c.o.f. of 0.3-0.4, a higher than DLC wear rate, and did not form a transfer film. In this environment, wear tracks on CNx coatings were polished by abrasion wear. In dry nitrogen, DLC coatings had a c.o.f. of about 0.15 and a higher wear rate, while CNx coatings had a c.o.f. 0.03-0.04 and a lower wear rate with formation of a graphitic-like transfer film. The observed difference in mechanical response and tribological performance can be used to optimize selection between DLC and CNx, depending on application requirements.

4:00pm SE-MoA7 Fabrication and Properties of Ultra-nano, Nano, and Polycrystalline Diamond Membranes and Sheets, *D.K. Reinhard*, Michigan State University and Fraunhofer Center for Coating and Laser Applications; *M. Becker*, Fraunhofer Center for Coating and Laser Applications; *R.A. Booth*, Michigan State University and Fraunhofer Center for Coating and Laser Applications; *T.P. Hoepfner*, Michigan State University; *T.A. Grotjohn, J. Asmussen*, Michigan State University and Fraunhofer Center for Coating and Laser Applications

Thin diamond membranes and free-standing sheets are of interest for a variety of potential applications. One such application is the motivation of this research, i.e. achieving diamond electron-stripping foils for use in

Monday Afternoon, November 3, 2003

heavy ion (1 - 11 MeV total energy) accelerators. The objective of this research is to produce large area free-standing foils/membranes of diamond. Stripping foils have areas of approximately 1 cm by 1 cm and thickness of approximately 1 μm . They must be positioned and mounted to a metal frame, supported on three sides. This paper describes the film nucleation, synthesis, and subsequent fabrication steps required to make large area free-standing diamond foils. Films are deposited on silicon wafers as ultra-nano (10 nm or less grain size), nanocrystalline (100 nm grain size), and as polycrystalline (micrometer grain size) diamond by varying gas composition, nucleation, power, substrate temperature, growth rate, and pressure. Large area foils are fabricated from each of these film types. Subsequently the diamond is separated from the substrate and mounted as a supported foil. Mechanical properties of the foils before and after mounting are described as a function of film morphology and thickness (0.5 μm to 5 μm). Examples of stripping foils and associated frames are presented. C. J. Liaw, Y. Y. Lee, and J. Tuozzolo, "Lifetime of Carbon Stripping Foils for the Spallation Neutron Source, Proceedings of the 2001 Particle Accelerator Conference, Chicago, (2001), 1538.

4:20pm **SE-MoA8 Nanotribological Properties of Nanocomposite and Amorphous CrBN Thin Films**, *D.M. Mihut, J. Turner, T.P. Butler*, University of Nebraska, Lincoln; *S.M. Aouadi*, Southern Illinois University; *S.L. Rohde*, University of Nebraska, Lincoln

Thin films with nanocomposite and/or amorphous CrBN structures can be successfully used for applications where high hardness, good wear resistance, low roughness and good corrosion resistance are required. CrBN films were deposited on to silicon substrates using reactive unbalanced magnetron sputtering. The deposition was monitored in-situ using spectroscopic ellipsometry. Films were characterized using X-Ray diffraction (XRD), atomic force microscopy (AFM), Auger electron spectroscopy (AES) and X-Ray photoelectron spectroscopy (XPS). Nanotribological behavior of CrBN thin films with differing composition were studied using a Hysitron Triboscope in conjunction with an AFM. Microscratch measurements were carried out in both constant and ramped load modes, after which the wear tracks were imaged and measured using AFM. The failure modes were also investigated using scanning electron microscopy (SEM). The measured friction coefficient, residual wear depth, and percent elastic recovery were compared for CrBN films of differing deposition conditions to begin to develop an understanding of process-property relationships in these new materials.

Author Index

Bold page numbers indicate presenter

— A —

Aksenov, I.I.: SE-MoA6, 1
Aouadi, S.M.: SE-MoA8, 2
Asmussen, J.: SE-MoA7, 1

— B —

Back, T.C.: SE-MoA6, 1
Becker, M.: SE-MoA7, 1
Booth, R.A.: SE-MoA7, 1
Butler, T.P.: SE-MoA8, 2

— C —

Chen, Y.: SE-MoA2, 1
Chung, Y.W.: SE-MoA2, 1
Cizek, J.: SE-MoA3, 1

— G —

Gammon, W.J.: SE-MoA5, 1
Grotjohn, T.A.: SE-MoA7, 1

— H —

Hoatson, G.L.: SE-MoA5, 1
Hoepfner, T.P.: SE-MoA7, 1
Holloway, B.C.: SE-MoA5, 1
Houska, J.: SE-MoA3, 1

— J —

Jones, J.G.: SE-MoA6, 1

— K —

Kormunda, M.: SE-MoA3, 1
Kraft, O.: SE-MoA5, 1
Krzanowski, J.E.: SE-MoA1, 1

— L —

Li, D.J.: SE-MoA2, 1

— M —

Mihut, D.M.: SE-MoA8, 2

— P —

Potocky, S.: SE-MoA3, 1

— R —

Reilly, A.C.: SE-MoA5, 1
Reinhard, D.K.: SE-MoA7, 1
Rohde, S.L.: SE-MoA8, 2

— S —

Soukup, Z.: SE-MoA3, 1
Strelnitzki, V.E.: SE-MoA6, 1

— T —

Turner, J.: SE-MoA8, 2

— V —

Vlcek, J.: SE-MoA3, 1
Voevodin, A.A.: SE-MoA6, 1

— W —

Wormwood, J.: SE-MoA1, 1

— Z —

Zabinski, J.S.: SE-MoA6, 1
Zeman, P.: SE-MoA3, 1