Surface Engineering
Room: C-111 - Session SE+NS-TuM

Nanocomposite and Nanolayered Coatings
Moderator: Y.-W. Chung, Northwestern University

8:20am **SE+NS-TuM1 The Effect of Columnar Growth in the Hardness of TiN/NbN Superlattices**, ***J.M. Molina-Aldareguia***, *T. Joelsson*, *M. Oden*, Linkoping University, Sweden, *W.J. Clegg*, Cambridge University, UK, *L. Hultman*, Linkoping University, Sweden

Nitride superlattices can be much harder than the individual component materials of which they are made, for a comparable defect and residual stress state. However, there appears to be considerable variation in the observed magnitude of this effect. The aim of this work was to investigate the origin of this variation by comparing two series of epitaxial TiN/NbN superlattices grown by reactive magnetron sputtering on MgO(001) single crystals: one that displayed superlattice hardening and another that did not. According to X-Ray Diffraction and X-Ray Reflectivity studies, the composition modulation was strong and the composition change at the interfaces abrupt in both series, indicating that the hardening is strongly influenced by some other microstructural parameter besides the layering. To investigate this, the deformation mechanisms were studied using a focused ion beam workstation to prepare cross-sectional transmission electron microscopy specimens under nanoindentations. These studies show that the superlattices with no hardening possess a columnar structure with voided boundaries, which act as preferential sites for shear to take place. This implies that the incorporation of porosity at the columnar boundaries, which is dependent on the growth conditions, is responsible for the variation observed in the magnitude of the hardening effect in TiN/NbN superlattices.

8:40am **SE+NS-TuM2 Optical Behavior of Zirconia-Titania Nanolaminate Films**, ***C.R. Aita***, University of Wisconsin-Milwaukee, *J.D. DeLoach*, Texas Instruments

Nanolaminate films of wide band gap semiconductors have bilayer periodicity much less than the wavelength of optical photons. These films are excellent candidates for high refractive index coatings througout the visible spectrum, coupled with optical band gap tailorability in the near-ultraviolet region. Here, we demonstrate this concept using ZrO_2-TiO_2 nanolaminates. Multilayer films were grown at room temperature by sequential reactive sputter deposition from metal targets using O_2-bearing discharges. Bilayer periodicity ranged from several to tens of nanometers. Total film thickness was in the 200 to 500 nm range. Optical transmission and reflection measurements were carried out in the 190 to 1100 nm wavelength range. Optical parameters were determined from these measurements. The results show that the refractive index throughout the region of high transmission was constant, equal to 2.2, and independent of nanolaminate architecture. On the other hand, the onset of fundamental optical absorption was strongly dependent upon bilayer architecture. A blue shift of the optical absorption edge was observed as the bilayer ZrO_2 increased. Optical band gap values spanned a range of 2 eV, from appproximately 3 eV for TiO_2 to 5 eV for ZrO_2, giving the system tailorability. The results are discussed in terms of the primacy of the coordination of a central cation (Zr or Ti) with its nearest neignbor O atoms in determining the features of the fundamental optical absorption edge. We show that the model developed to explain the results for the ZrO_2-TiO_2 system can be applied to other nanolaminates or nanocomposites in which the spatial extent of the wavefunctions describing near edge optical transitions is comparable to the short-range order in the film.

9:00am **SE+NS-TuM3 Nanocomposite and Nanolayered Hard Coatings**, ***J. Patscheider***, *T. Zehnder*, *J.C. Cancio*, EMPA, Switzerland **INVITED**

Nanostructuring of hard coatings, which is achieved by combining two phases with atomically sharp interfaces, opens up new possibilities to improve conventional coatings with respect to their hardness, limited temperature stability and their frictional behavior. The best known combinations of well-separated phases for increased hardness are multilayered superlattices as well as nanocomposite coatings. Nanocomposite coatings proved successful in promoting hardness, oxidation resistance, improved wear behavior and other properties relevant for protective coatings. Such coatings are composed of nano-crystalline grains of transition metal nitrides or carbides, which are surrounded by amorphous hard matrices. Most nanocomposite hard coatings show typically a maximum of the hardness, which can range from 30 GPa to reported values above 60 GPa, as the composition is changed from the pure crystalline phase (no amorphous component) to compositions dominated by the amorphous phase. At the hardness maximum the domain size of the nanocrystalline phase is below 10 nm and the amorphous layer separating the nanocrystals, is only a few atomic bond lengths thin. A comparison to hadness-enhanced superlattices show that the critical dimensions necessary to obtain this effect are of the same order, i.e. the domain size in hard nanocomposites and the single layer thickness in superlattices are both below 10 nm. Due to the absence of dislocation activity, deformation of nanocomposites will be only due to grain boundary sliding. This process requires more energy than deformation by dislocation movement, which is synonymous to increased hardness. In some cases the amorphous phase can act as a solid lubricant (a-C or a-C:H) or as diffusion barriers (Si_3N_4) for improved thermal stability. The amorphous phases in nanocomposites thus cause, apart from the enhanced hardness, additional effects that are beneficial for the performance of these new wear-protective coatings.

9:40am **SE+NS-TuM5 Characterization of TiCrN Nanocomposite Protective Coatings for Biomedical Applications**, ***S.M. Aouadi***, Southern Illinois University, *K.-C. Wong*, *K.A.R. Mitchell*, University of British Columbia, Canada, *F. Namavar*, *E. Tobin*, Spire Corp., *D.M. Mihut*, *S.L. Rohde*, University of Nebraska, Lincoln

The structural, chemical, optical, and mechanical properties of TiCrN nanocrystalline multiphase films deposited by ion beam assisted deposition (IBAD) were studied by means of X-ray diffraction (XRD), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), spectroscopic ellipsometry (SE), and nanoindentation. The primary phases in the films, their volume fractions, and the elemental compositions were determined from XRD and XPS measurements. The TiCrN films consisted of two phases, namely Ti-N and Cr, for nitrogen concentrations lower than titanium concentrations. For larger nitrogen concentrations, an additional phase (Cr2N) was identified. The topography of the various films was measured using AFM. The optical constants were measured using spectroscopic ellipsometry. A correlation between the elemental/phase composition and optical constants was established. The usefulness and limitations of effective medium theories (EMA) to model the optical constants of these nanocrystalline composite materials will be discussed. The mechanical properties of the coatings were evaluated using nanohardness testing. The hardness and elastic modulii were found to depend on the constituting phases and were measured to be 22-32 GPa and 180-260 GPa, respectively.

10:00am **SE+NS-TuM6 Preparation and Characterization of Chemically Bonded Si_3N_4 and TiN Nanocomposites Prepared by Mechanical Alloying and Sintering**, ***S.W. Deore***, *M. Kesmez*, *M.A. Hossain*, Lamar University, *J.R. Parga*, Instituto Technologico de Saltillo, Mexico, *D.L. Cocke*, Lamar University

Mechanical alloying using high-energy ball milling is a promising materials processing technique to synthesize nanocomposites for superior mechanical and chemical properties. However, the need to sinter, the application of heat to a powder or a powder body, to increase interparticle bonding, and usually density, tends to result in the destruction of the nanosized components. We have been examining the use of chemical binders that can be pyrolyzed to ceramic binding components at lower temperatures. The heating regime for the sintering process has been determined from the DSC analysis of the binders. Silicon nitride and titanium nitride nanocomposite powders have been prepared using high energy SPEX milling in a nitrogen atmosphere. The composites have been characterized using XRD, XPS, FTIR and SEM. Although both solid phase and liquid phase binders have been examined for their binding properties and hence, the properties of the obtained nanocomposites. The preferred characteristics of the binder precursors will be discussed and a major problem of wetting of the binder to the nanoparticles encountered will be delineated.

10:20am **SE+NS-TuM7 Comparison Studies of Titanium Silicon Carbide Hard Coatings Deposited by Pulsed Laser Deposition and Magentron Sputtering Assisted Pulsed Laser Deposition**, ***A.R.P. Ayalasomayajula***, *J.E.R. Krzanowski*, University of New Hampshire

Titanium silicon carbide films have been grown by Pulsed Laser Deposition (PLD) as well as Magnetron Sputtering Assisted Pulsed Laser Deposition (MSAPLD) on Si (111) and 440C steel substrates at different substrate temperatures and at different substrate bias at 400^{o}C. Experiments are also conducted with different laser powers for C ablation and sputtering powers for $TiSi_2$ content in the deposited films to investigate the effect of C and $TiSi_2$ mechanical and tribological properties. X-ray Diffraction has been employed to find the crystal structure and orientation of the deposited films. Film morphology and roughness are measured by Scanning Electron

Microscopy (SEM) and Atomic Force Microscopy (AFM) techniques, respectively. The film hardness was measured by nano-indentation, while x-ray photoelectron spectroscopy (XPS) was used to estimate the film composition using depth profiling. The residual stress of the deposited was measured by 2D-area General Area Detector Diffraction System. TiSiC films deposited by PLD have shown reasonably high hardness values (37GPa) compared to $TiSi_2C$ films by MSAPLD which have shown hardness values 30GPa at 400°C. The hardness is correlated with residual stress of the deposited films, where we have observed high tensile stress for MSAPLD films leading to decrease in hardness values. Tribological studies have also been conducted to evaluate the friction and wear properties of these films. The mechanisms of hardness enhancement and its relation to tribological properties has also been explained.

10:40am **SE+NS-TuM8 Response of Nanocrystalline Materials to Ion and Neutron Irradiation**, *A. Kubota,* ***M.-J. Caturla****, T. Diaz de la Rubia, B.D. Wirth,* Lawrence Livermore National Laboratory

Plasma-facing materials are generally exposed to a harsh radiation environment. Radio-frequency excited plasmas under biased conditions produce energetic ion radiation which can lead to material damage and erosion at the surface. In fusion plasma applicat ions however, materials face significant bulk defect production and damage due to deeply penetrating 14 MeV neutrons and Helium nuclear reaction products, leading to embrittlement and void swelling. We discuss results of computational simulations to asses s the feasibility of high grain-boundary-density nanocrystalline materials in fusion environments. The performance of the nanocrystalline metals is discussed in terms of defect migration to and annihilation at the grain boundaries, as well as Helium migration along the grain boundary network.

11:00am **SE+NS-TuM9 Novel Properties and Potential Applications of CrBN Films Produced via Unbalanced Magnetron Sputtering**, ***D.M. Mihut****, T.Z. Gorishnyy, D.M. Schultze,* University of Nebraska, *S.M. Aouadi,* Southern Illinois University, *S.L. Rohde*, University of Nebraska

CrBN nanocrystalline and amorphous materials produced using ion-assisted unbalanced magnetron sputtering were deposited on to a variety of substrates, to investigate the potential of these coating in several applications ranging from coatings on AFM tips to very smooth films for tribological coatings. Coatings were deposited over a range of temperatures from ambient (<200°C) to nearly 900°C, and their thermal stability investigated. Selected films were studied both in-situ and ex-situ using spectroscopic ellipsometry to determine their optical properties and provide correlation between the optical properties and chemical/structural changes in the films, providing a valuable resource for work in these new, but complex multi-phase materials. In addition, these films were characterized post-deposition using X-ray diffraction (XRD), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), infrared spectroscopic ellipsometry (IR-SE), transmission electron microscopy (TEM), nanoindentation, and microwear. XPS, AES, and IR-SE were used in tandem to reveal the crystal structure of the BN phase in these ternary compounds. The amorphous to nanocrystalline nature of the coatings were deduced using AFM and TEM. The mechanical properties (wear rate, hardness, elastic modulii) of the coatings were evaluated using a nanohardness/microwear analyses. Several interesting applications, are currently under investigation as CrBN films have been found to provide a unique combination of very low roughness (rms < 0.2 nm) and high surface hardness (> 22 GPa) under certain growth conditions.

11:20am **SE+NS-TuM10 Preparation, Structure, and Properties of Composite Fullerene-Like CNx Films Produced by Pulsed Laser Ablation**, ***A.A. Voevodin****, J.G. Jones, J.S. Zabinski,* Air Force Research Laboratory, *Zs. Czigany, L. Hultman*, Linkoping University, Sweden

Production of composite CNx films made of fullerene-like structures in an amorphous matrix using laser ablation of graphite in nitrogen is reported. Deposition was optimized based on investigations of chemistry, excitation stage, kinetic energy, temperature, and spatial distributions of molecular (CN and C2) and atomic (C and N) species, using element specific imaging, time-of-flight experiments, fluorescence spectroscopy, and molecular vibration sequence analyses. Studies showed the importance of plume / substrate interaction in generating excited CN and C2 molecules with high vibrational energy at the condenasation surface for low deposition pressures. Films were characterized with x-ray photoelectron spectroscopy, Raman spectroscopy, high-resolution transmission electron microscopy, nanoindentation, and stress analyses. Nitrogen content directly depended on the concentration of CN radicals at the condensation surface. Formation of fullerene-like structures required a high vibrational temperature of these radicals, which was maximized at about 4 eV for depositions at 10 mTorr N2 and laser fluences of ~7 J/cm2. The presence of C2 had only a minor effect on film composition and structure. Optimization of plasma characteristics and a substrate temperature of 300 C helped to produce about 1000 nm thick solid films of CNx (N/C ratio 0.2 - 0.3) and pure carbon consisting of fullerene-like fragments and packages. Films exhibited elastic recovery of about 80%, elastic modulus of 160-250 GPa and hardness of up to 30 GPa, which was twice that of fullerene-like carbon films. The unusual combination of high elasticity and hardness was explained by cross-linking of fullerene fragments induced by the incorporated nitrogen. Correlations between plasma composition, film structure and properties are established. Results of film mechanical testing demonstrate benefits of the film application as a hard protective coating to resist brittle fracture at high contact loads.

11:40am **SE+NS-TuM11 Tribological Analysis of Nano-composite Diamond-like Carbon Films Deposited by Unbalanced Magnetron Sputtering**, ***D.-Y. Wang***, Mingdao University, Taiwan, *Y.-Y. Chang*, National Chung-Hsing University, Taiwan

Ti contained nano-composite DLC coatings have been developed with improved tribological characteristics. These coatings were synthesized using an unbalanced magnetron sputtering (UBMS) process with a combination of graphite and metal targets. A 100 kHz pulsed d.c. power supply was applied to the substrates to control the substrate arcing and radical excitation during the DLC formation. The microstructure of the nano-composite DLC film was investigated by using cross-section TEM/SAD, x-ray diffraction, Raman and XPS. Tribological properties such as wear mechanism, transfer phenomenon, friction coefficient, and wear life were evaluated and compared with commercial Ti-C:H DLC coatings by using pin-on-disk wear test analyses. The optimized Ti/C multi-layered DLC coatings give satisfied friction performance in the pin-on-disk test with lower wear rate of 1-3 x 10^{-17} m^3/Nm and lower friction coefficient of 0.09-0.1 sliding against 100Cr6 and WC materials. The easily transferred oxide- free graphite-like sp^2 phases form a lubricious layer, which posses low shear strengths under applied stresses. The low friction coefficients and wear rates during the tribological action are anticipated.

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