Monday Afternoon, November 4, 2002

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

Nanoparticle and Nanofiber Surface Technologies
Moderator: A.A. Voevodin, Air Force Research Laboratory

2:00pm **SE+NS-MoA1 Investigation of Erbium Dispersion in Electrospun Nanofiber Matrices**, *W. Kataphinan, **R.D. Ramsier**, E.A. Evans, D.H. Reneker*, University of Akron

Thermally stable nanofibers can be doped with molecular and atomic species. As an example, electrospun nanofibers made from polydiphenoxyphosphazene (PDPP) have been doped with erbium (Er) using Er(III) nitrate hydrate dissolved in ethanol. The Er/PDPP matrices are thermally stable up to 150 C in air for extended periods of time. Nanofibers electrospun from ceramic precursors are stable up to much higher temperatures. Infrared spectroscopy, electron microscopy and other techniques are used to quantify the influence of the electrospinning parameters (voltage, solvent, concentration, etc.) on the structural and spectral properties of the nanofibers and the dispersion of the Er-based dopants. Differences between methods for doping the fibers will be described based on these results. These results expand the useful operating temperature range of polymer nanofiber systems as well as the use of nanofiber matrices as a support for the dispersion of molecular and atomic scale dopants.

2:20pm **SE+NS-MoA2 Grafting of Poly (N-isopropylacrylamide) in Surfactant Templated Mesoporous Silica Films and Particles**, *Q. Fu, **G.V. Rama Rao**, J. Huang, G.P. Lopez*, The University of New Mexico

Surface-initiated atom transfer radical polymerization (ATRP) is an effective and versatile method used to generate grafted polymers on surfaces. We report grafting of a poly (N-isopropylacrylamide) (PNIPAAM), a thermally responsive polymer, into a mesoporous silica matrix using the ATRP technique. PNIPAAM exhibits a lower critical solution temperature (LCST) at 32°C in water, below which it is in an expanded conformation and soluble in water. Above the LCST, PNIPAAM is in compacted state and insoluble in water. Synthesis of mesoporous films and monodisperse microparticles was carried out through an acid catalyzed sol-gel process using a surfactant template approach. We used a non-ionic surfactant (Pluronic-P123) and a cationic surfactant (cetyltrimethyl ammonium bromide) for the present study. The LCST of the hybrid films was established by static contact angle measurements. These hybrid materials exhibited thermo responsive behavior by changing from hydrophilic to hydrophobic state with change in temperature. X- ray diffraction and transmission electron microscopic studies on the films and particles confirmed the presence of an ordered porous structure before and after ATRP. The grafting of the polymer onto the pore surface was confirmed by drastic decrease in pore volume of the particles after ATRP. Pore opening and closing due to contraction and expansion of PNIPAAM was studied by fluorescent dye uptake behavior of particles by monitoring the fluorescence intensity in flow cytometry experiments. It was found that the uptake of the dye into the pores was obstructed below LCST, and above LCST, the polymer was collapsed and facilitated the passage of dye into the mesopores. The dye in the pores was entrapped by cooling the particles to below LCST and subsequently the dye was released by washing with water above LCST. These materials have potential application in controlled release, chemical separation and control of fluidic transport.

2:40pm **SE+NS-MoA3 Structural, Optical and Photocatalytic Properties of Nd^{3+} Doped TiO_2 Nanoparticles**, ***W. Li**, S.I. Shah, C.-P. Huang*, University of Delaware, *O. Jung*, Chosun University, Korea

TiO_2 nanoparticles, with Nd^{3+} dopant concentration ranging from 0 to 1.5 at.%, were synthesized using metallorganic chemical vapor deposition. The dopant concentration and TiO_2 stoichiometry were verified by x-ray photoelectron spectroscopy and energy dispersive x-ray spectroscopy. Particle size and crystal structure were obtained by x-ray diffraction and high-resolution transmission electron microscopy which showed the nanoparticles are polycrystalline anatase with 22 nm average particle size. Red shifts of TiO_2 absorption edge with the increase of Nd^{3+} concentration were observed by spectrophotometery. 1.5 at.% Nd^{3+} shows ~0.15 eV red shift. The photoreactivities of Nd^{3+} doped and undoped TiO_2 were measured by studying the degradation of 2-chlorophenol solutions under ultra violet radiation. Nd^{3+} position in TiO_2 lattice critically affects the photocatalytic activity of TiO_2 nanoparticles. Nd^{3+} position in TiO_2 lattice was studied by using XRD peak shifts. The results of these studies will be presented.

3:00pm **SE+NS-MoA4 Computational Studies of Gas-Phase Growth of Soot Nanoparticles Using Fully-Integrated Integrated Molecular Dynamics and Kinetic Monte Carlo Methods**, ***A. Kubota**, W.J. Pitz, C.K. Westbrook*, Lawrence Livermore National Laboratory

Combustion under fuel-rich gas conditions leads to the formation of soot nanoparticles. We study this process of carbon nanoparticle formation through the use of fully-integrated kinetic Monte Carlo and molecular dynamics methods. Rule-based polymerizatio n and gas-surface kinetics are used in the chemical kinetic mechanism. This mechanism includes competitive H-abstraction and H-addition, as well as carbon-species addition, termination and cyclodehydrogenation and ring-closure reactions. We demonstrate that nanoparticle structure, morphology and rates are strongly coupled to the chemical kinetics as well as the gas-phase conditions. We compare modeling results with available experimental measurements.

3:20pm **SE+NS-MoA5 Enhancement of High Temperature Oxidation Resistance of Fe-Cr-Ni Alloys Using Nanocrystalline CeO2 Coating Synthesized by Microemulsion Technique**, ***S. Seal**, S. Patil, S. Kuiry*, University of Central Florida

Fe-Cr-Ni alloys are usually subjected to high temperature oxidation during their various processing stages like rolling, forging and heat treatment. Extensive scaling losses are found to occur in these components in such aggressive environments at elevated temperatures. Therefore, development of coating that imparts oxidation resistance to Fe-Cr-Ni alloys is important not only for applications of these alloys at elevated temperatures but also to protect the oxidation losses during high temperature processing. The present study investigates the effectiveness of nano-sized CeO2 coating to enhance high temperature oxidation resistance of Fe-Cr-Ni alloys. Nanocrystalline CeO2 particles were synthesized with micro-emulsion technique using AOT [sodium bis(2-ethylhexyl) sulphosuccinate] as a surfactant. Kinetics of high temperature oxidation was studied on both bare and coated rectangular specimens in dry air. The scale cross section and surface morphology were characterized by using SEM, EDS, XPS and HRTEM studies.

4:00pm **SE+NS-MoA7 Formation and Optical Properties of Peridically Arranged Silver Nanoparticles by Irradiation with Linear Polarized Ultrashort Laser Pulses**, *A. Heilmann, A. Kiesow, **D. Katzer**, Fraunhofer-Institute for Mechanics of Materials Halle, Germany, A. Podlipensky, G. Seifert, H. Graener*, Martin-Luther-University Halle, Germany

We report on a new and simple method to generate periodically ordered metallic, wire-like structures in an organic polymer-like matrix by irradiating thin films with series of ultrashort laser pulses. The films, which were deposited by alternating plasma polymerization and metal evaporation, are characterized by a two-dimensional particle size and shape distribution, i.e. all silver particles are arranged on one plane within the plasma polymer matrix. After laser irradiation with linearly polarized ultrashort (pulse duration < 150 fs), the nanostructure of the film changes from a relatively uniform particle distribution to a formation of an ensemble with metal particle nanowires. This was demonstrated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Material ablation during laser irradiation was not observed. The individual nanowires are between 100 to 250 nm wide with equal line space ratio. The obtainable structure size is not a function of the focusability of the laser and is significantly smaller than the laser wavelength used. The orientation of these wire-like structures is correlated to the linear polarization of the laser pulses, and is independent on the write direction of the laser beam. This dependence on laser polarization results in anisotropic optical properties. The optical extinction spectra were measured by locally resolved optical spectroscopy and by using linearly polarized light. The shift of the extinction peak depending on different steps of nanowire formation was analyzed. The optical spectra were correlated with the different nano-structures and various models were discussed to explain the material transport in the film.

Tuesday Morning, November 5, 2002

Nanometer Structures
Room: C-207 - Session NS+SE+SS+MM-TuM

Nanotribology
Moderator: K.J. Wahl, Naval Research Laboratory

8:20am **NS+SE+SS+MM-TuM1 Ultralow Friction Coatings and Surfaces**, ***J.M. Martin***, Ecole Centrale de Lyon, France **INVITED**

From a technological point of view, very low friction in solid lubrication may be interesting in micromechanisms requiring neither friction noise nor instabilities, together with low power consumption. Theoretical approaches at the atomic scale coupled with experimental approaches using proximal probe techniques have been developed to study atomic scale friction behaviors and energy dissipation modes. The two limiting factors for friction reduction at the macro-scale are S0 (shear strength of the interface film) and a (pressure coefficient).[1] Approaching very low friction requires the reduction of both S0 and a below the MPa range. Thus lowering to zero friction would require the vanishing of both the adhesive and the external pressure. However these conditions are unlikely to be perfectly achieved in practice. Thus zero friction may not be possible. However, friction values in the 10-3 range or even less (near-frictionless sliding) have been experimentally reached in some practical situations. Here we examine ultralow friction by using a macro-scale sphere/plane contact configuration (maximum pressure of 1 GPa). Friction in the 0.001 range is associated with a shear strength of 1 MPa. We report experimental evidence of superlow friction with different coatings: pure molybdenum disulfide MoS2,[2] molybdenum dithiophosphate (Modtp) tribofilms and hydrogenated diamondlike carbon a-CH.[3]

[1] I. Singer, J. Vac. Sci. Technol., A12(5), (1994) 2605.
[2] J.M. Martin, C. Donnet, Th Le Mogne and Th Epicier, Physical Review B 48, No 14, (1993) 10583.
[3] C. Donnet et al, Surface and Coating Technology, 94, (1997) 456.

9:00am **NS+SE+SS+MM-TuM3 Frictional Properties of Small Model Lubricant Molecules Adsorbed on VC(100)**, ***L.C. Fernandez-Torres***, *S.S. Perry*, University of Houston, *B.-I. Kim*, Sandia National Laboratories

The frictional modification of the non polar (100) of vanadium carbide (VC) surface through small molecule adsorption at room temperature has been investigated from a fundamental perspective. These molecules represent the functionalities incorporated into lubricants and used to appropriately tailor the lubricant's properties and enhance its performance. Ultrahigh vacuum atomic force microscopy (AFM) has been employed to determine the changes in frictional response and interfacial adhesion. Scanning tunneling microscopy (STM) has been used to elucidate surface morphology. X-ray photoelectron spectroscopy (XPS) has been utilized to determine the composition of the species formed by the interaction of these adsorbates with the VC surface. This successful methodology has been developed during a recent investigation of ethanol, and in this study has been extended to other low molecular weight alcohols as well as an ester. The results will be rationalized in terms of chemical reactivity, adsorbate layer composition, extent of coverage, and changes in the interfacial shear strength and discussed in terms possible lubrication schemes.

9:20am **NS+SE+SS+MM-TuM4 Adhesion and Deformation in Nanoscale Contacts between W(110) and Au(110) in Ultra High Vacuum**, ***S.A. Smallwood***, *R.J. Lad, W.N. Unertl*, University of Maine

Tribological phenomena change as the contact area decreases from macroscopic to atomic dimensions, but these changes are not well understood. We report studies of the force versus deformation behavior of contacts with diameters up to about 50 nm using well-characterized metal surfaces in ultra-high vacuum. These contact sizes are intermediate between those previously studied. The contacting bodies were a Au(110) single crystal and sharp tips of W wires. The W probes were cleaned by field evaporation and their atomic structure determined using field ion microscopy (FIM). All were terminated by (110) planes and radii varied between 12 nm and 24 nm. The probes were mounted in double cross-hair force sensors. After cleaning by sputtering and annealing cycles, the Au was transferred to a piezoelectric tube scanner and moved into tunneling contact with the probe. Deflection of the force sensor and electrical current were measured as the Au crystal was brought into mechanical contact to a predetermined maximum displacement and then withdrawn. Prior to the first yielding event, the data is well described by elastic contact mechanics theory. The reduced modulus of 61 Â± 26 GPa agrees with the value calculated assuming bulk properties. The work of adhesion has an upper bound of about 0.3 J/m2. The first observable yielding events occur at a mean normal stress of 12 Â± 2 GPa, comparable to the values reported for larger probes, but half that reported for smaller contacts on Au(111). Hardness is about 6 GPa near the surface and decreases by about fifty percent at 8 nm indentation depth. Prior to first yield, contact conductance remains far below one quantum. Deformation is confined to the Au. FIM demonstrates that the W probe is not deformed for penetrations as deep as its radius. Scanning tunneling microscopy shows that the indentation holes are asymmetric and that pile-up extends about one indentation diameter beyond the indent.

9:40am **NS+SE+SS+MM-TuM5 Chemical Force Microscopy of Aluminium Oxide Surfaces**, ***T.T. Foster***, *M.R. Alexander*, UMIST, UK, *E. McAlpine*, Alcan International, UK, *G.J. Leggett*, University of Sheffield, UK

The combination of wettability, chemical force microscopy (CFM) and friction force microscopy (FFM) has been used to analyse changes at the oxide-covered surface of aluminium after magnetron sputter deposition. A model self-assembled monolayer (SAM) system was first developed to enable comparisons to be made with the more complex aluminium system. The monolayers were produced by self-assembly on Au (111) and Ag (111) substrates. The gold-coated AFM tips were modified with SAMs of alkanethiols terminated in a methyl or carboxylic acid group. Friction coefficients were measured for SAMs varying in chain length and terminal group chemistry. Using carboxylic acid modified tips; measurements were performed on the surface of aluminium. Adhesion forces were found to decrease with storage time in a desiccated environment, attributed to the adsorption of contaminant molecules from the atmosphere. In contrast the friction coefficient showed no significant change with storage time, presumably because the sliding tip, under loading, is able to displace contaminant molecules. Contact angle goniometry was used to study changes in surface wettability on the aluminium surface. The water contact angle increased linearly with the log of storage time, supporting the hypothesis that adsorption of hydrophobic contaminants modifies the aluminium surface. Contact mode characterisation of the aluminium oxide surface provided clear images of the oxide surface. A nitric acid-based cleaning procedure was developed that was capable of removing adventitious contamination and returning the aluminium oxide surface to condition that appears similar to the freshly deposited surface. This study clearly demonstrates the capability of CFM for characterising complex aluminium surfaces and studying changes in surface chemistry.

10:00am **NS+SE+SS+MM-TuM6 Nanotribology and Related Structural Changes During Wear of Diamond-like Carbon Films**, ***J. Goldsmith***, *E.A. Sutter, J. Moore, B Mishra*, Colorado School of Mines, *M. Crowder*, Maxtor Corporation

Diamond-like carbon (DLC) thin films are used for wear and corrosion protection of magnetic disks, micro-electro-mechanical systems (MEMS), and tool bits. Magnetic information storage density increases when the read-write head gets closer to the disk. The magnetic layers degrade very quickly without a good protective interface. The use of DLC thin films becomes increasingly popular as they can provide a protective surface due to their excellent tribological properties as low friction and high hardness. In both magnetic disks and MEMS applications, the DLC films are in the thickness range of 2 - 5 nm and in most cases are amorphous in structure. Characterizing the tribological and structural properties and identifying the wear mechanisms of DLC films on the nanoscale is a challenge. Here we present results on the nanotribology of the DLC films performed using both an atomic force microscope and a nanoindenter. We investigate the wear behavior of the DLC films and the role of transfer film. We find that the formation of transfer film plays an important role in providing low-friction. The nanotribological investigations are correlated with the structural changes that occur in the DLC film as well as in the transfer film detected using Raman spectroscopy and cross-sectional transmission electron microscopy.

10:20am **NS+SE+SS+MM-TuM7 Tribology and Surface Forces in MEMS**, ***J.S. Zabinski***, Air Force Research Laboratory, *S.T. Patton, K.C. Eapen*, UDRI, *S.A. Smallwood*, Systran, Inc. **INVITED**

Microelectromechanical systems (MEMS) offer the potential to provide new capabilities and products for commercial and military applications. Simple devices are already common in the marketplace, but friction, stiction, and wear prevent reliable operation of more sophisticated types of MEMS devices that have contacting surfaces in relative motion. These tribological problems are fundamentally difficult to solve and are magnified because MEMS are expected to operate in very harsh environments, such as at elevated temperature and in space. The performance and reliability of MEMS are strongly dependent on the environment in which they operate.

For example, moisture can cause device failure by stiction or it can provide excellent lubrication, depending on the device and the relative concentration of water vapor (i.e., relative humidity). Operation in vacuum is particularly severe and the wear mechanisms are different than in dry or moist environments. Methods to control system tribology include lubricant coatings, monolayers, and new materials. The tribological mechanisms operating in moist air through vacuum will be discussed along with strategies to control friction, stiction, and wear that have significantly improved MEMS reliability. In addition, the effects of storage on device performance will be presented.

11:00am **NS+SE+SS+MM-TuM9 Tribological Measurement on MEMS Platforms**[1], ***M.T. Dugger***, *S.V. Prasad*, Sandia National Laboratories **INVITED**

Microelectromechanical systems (MEMS) fabricated using surface micromachining (SMM) and other lithographic techniques such as LIGA have resulted in actuators, counter-meshing gears and other moving mechanisms having complex tribological interfaces that are rough on the nanometer scale and have unusual surface morphologies. Meaningful friction and wear measurements of microsystems must be made at loads and speeds relevant to MEMS operation. Since friction and wear are properties of systems, measurements must also involve interactions of surfaces having the morphology and chemistry present in real devices. Experimental techniques for acquiring friction data during sub-micron displacement and under nanoNewton forces are critical for the fundamental understanding of energy dissipation and wear mechanisms in MEMS. However, experimental investigation of surface interactions in MEMS under relevant contact conditions requires techniques beyond those that are currently available. MEMS friction measurement platforms which bring real MEMS surfaces into contact are needed to define the design space, to investigate aging and failure mechanisms, and to validate models of friction and wear derived from fundamental studies. We have therefore developed both SMM and LIGA devices containing isolated tribological contacts from which quantitative friction forces can be extracted. These structures are used to investigate interface performance, degradation and failure mechanisms. Methods of quantifying static and dynamic friction in SMM and LIGA micromachined contacts will be presented. Examples will be shown of how these structures are being used to investigate degradation of monolayer lubricants and hard coatings for SMM devices, as well as the tribological behavior of metallic contacts in LIGA.

[1]Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

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°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.

Tuesday Afternoon, November 5, 2002

Surface Engineering
Room: C-111 - Session SE+TF-TuA

Systems Design of Functional Coatings
Moderator: A.A. Voevodin, Air Force Research Laboratory

2:00pm **SE+TF-TuA1 Mechanical Design of Coated Systems Based on Elastic Surface Contacts**, ***T. Chudoba***, Federal Institute of Materials Research and Testing, Germany, *N. Schwarzer, I. Hermann, F. Richter*, TU Chemnitz, Germany **INVITED**

Problems in contact mechanics can be solved very conveniently using analytical solutions, even for layered systems and non-axissymmetric systems involving friction. The calculation time is much lower than for finite element calculations, especially for non-axissymmetric problems, and allows an optimization in a large parameter field, which is difficult to achieve with other methods. In many cases, with a foreknowledge of the type of failure to be avoided, the elastic stress fields computed permit critical values of stress to be avoided by a change in input parameters. One of the key requirements of an analytical solution to a contact problem is the availability of accurate and representative values of material properties. Such properties are not generally available for thin film systems where mechanical properties may not be the same as the bulk properties. The present work shows how elastic modulus and yield stress can be obtained experimentally using nanoindentation techniques for films down to a thickness of some nanometres. Results are given for several film substrate combinations. The parameters can be used for a mechanical modelling to optimize film thickness or to find the required mechanical properties of an intermediate layer to withstand a Hertzian contact at the surface. This is demonstrated by some calculations. In another example ternary (B,C,N) films on Si and fused silica produced by magnetron sputtering with a modulus range of 130 GPa to 300 GPa are used. The mechanical properties so obtained are then used as inputs in an analytical model to determine the optimum thickness and properties of an interlayer for a particular loading configuration, that of contact with a spherical indenter. The work extends the analytical treatment to nearly any cases of indenter shape by showing how the results of individual elastic analytical solutions can be assembled and solved using boundary element methods.

2:40pm **SE+TF-TuA3 A Combinatorial Sputtering Approach to Properties Modification in Polaron Conducting Films**, ***R.R. Owings***, *P.H. Holloway*, University of Florida, *C.F. Windisch, Jr., G.J. Exarhos*, Pacific Northwest National Laboratory

The influence of sputtering parameters and cation composition on measured resistivity and optical transparency of mixed transition metal spinel oxides (AB_2O_4) has been systematically studied. A two-cathode system was used to deposit films having continuously variable compositions onto glass, silicon, and sapphire substrates (25 mm in length) as a function of process gas composition and pressure, target to substrate distance, substrate temperature, sputtering power, and sputtering time. The intent was to correlate transparency and conductivity with composition, phase purity, grain size, film thickness, and cation oxidation state. Both mixed metal oxide and metal alloy targets (nickel, cobalt, rhodium, palladium) were used for sputter deposition with variable gas mixtures of argon and oxygen. Post deposition annealing of sputtered films was found to lower film resistivity but had little effect on optical transparency. Film resistivity returned to its original value upon standing in air for two weeks. However, partial substitution of lithium for cobalt was found to not only improve the conductivity and increase transparency but also to significantly reduce property variations when subjected to post deposition annealing in air. Results suggest that the presence of lithium stabilizes higher oxidation states of the resident transition metal cations leading to lattice compression and diminished oxygen transport.

3:00pm **SE+TF-TuA4 Profile Coatings and Their Applications**, ***C. Liu***, *L. Assoufid, A. Macrander*, Argonne National Laboratory, *G. Ice, J. Tischler*, Oak Ridge National Laboratory, *K. Zhang*, Illinois Institute of Technology

We report a method of profile coating to achieve a certain pre-selected thickness profile of a thin film coating using dc magnetron sputtering. In profile coatings, the substrate is passed over a contoured mask at a constant speed to obtain a desired profile along the direction perpendicular to the substrate-moving direction. The shape of the contour depends on the desired profile and the thickness distribution directly above the gun at the substrate level. Four-inch-diameter Si wafers were coated through a 100 x 152 mm^2 aperture on the top of the shield can. The thickness distribution was then obtained using a spectroscopic ellipsometer with computer-controlled X-Y stages. A model has been developed to fit the measured thickness distribution. The relative thickness weightings are then digitized at every point 1 mm apart for the entire open area of the aperture. When the substrate is moving across the shield can during depositions, the film thickness is directly proportional to the length of the opening on the can along the moving direction. By equating the summation of relative weighting to the required relative thickness at the same position, the length of the opening at that position can be determined. By repeating the same process for the whole length of the required profile, a contour can be obtained for a desired thickness profile. The contoured mask is then placed very close (~1 mm) to the substrate level on the shield can opening. The number of passes and the moving speed of the substrate are determined according to the required thickness and the growth rate calibration. This method of profile coating has been applied to coat laterally graded W/C multilayers for tunable x-ray double-monochromator and x-ray fluorescence detection applications. It has also been applied to coat Au on a cylindrical mirror to obtain an elliptical mirror for x-ray focusing applications. Test results for these applications will be presented.

3:20pm **SE+TF-TuA5 Nano-Structure Substoichiometric Zirconium Nitride Coatings with Unique Metallic Colors and Superior Abrasion and Corrosion Resistance**, ***G. Chen***, Vapor Technologies, Inc., *J.S. Lipe, P.B. Jonte*, Delta Faucet Company, *S. Moysan*, Baldwin Hardware Company

Low temperature arc vapor deposition (LTAVD) is one of the widely applied techniques for industrial production of decorative and functional coatings. Nickel and stainless steel color protective coatings were deposited using substoichiometric nano-crystal size zirconium nitride and oxynitride. Generally the total amount of nitrogen and oxygen is between about 14 to about 50 atomic percent with a nitrogen content of at least about 6 atomic percent. The slightly nitrided or nitrided and oxidized color layer is mainly comprised of nano-phase to amorphous metallic refractory metal with textured metal nitride phase, as determined using x-ray diffraction. For example, zirconium nitride primarily oriented in (111) plane and smaller than 50 nm in grain size, or metallic zirconium primarily oriented in (112) plane and smaller than 80 nm, depending on the proportion of oxygen in total gas flow. Such types of structures are produced at relatively low processing pressures, ranging from 1 to 5 millitorr. These nano-phase coatings have superior abrasion resistance and corrosion resistance over the relative large crystal size coatings have the same atomic percent of nitrogen content.

3:40pm **SE+TF-TuA6 The Adhesion Behavior of Alumina-based Ceramic Nanocoatings and Nanostructures**, *M.V. Kireitseu, I.A. Nemerenco, L.V. Yerakhavets*, ***M. Istomin***, Institute of Machine Reliability, NAS, Belarus

The adhesion behavior of alumina-based ceramic coatings and alumina-based nanostructures involved CrC nanoparticles in contact with themselves, metals and polymer surfaces is strongly dependent upon the chemistry of the ceramic surface and that of the solids with which contact is made. With clean alumina-based ceramic coating surfaces in contact crystallographic orientation influences adhesion as determined by friction force measurements. Friction force measurements are especially effective in gaining quantitative information on interfacial bond strengths. Ceramics, just as has been observed with metals, exhibit the smallest adhesive bond forces and accordingly the lowest friction for the high atomic density low surface energy crystallographic planes. This has been observed with oxide ceramics such as aluminum oxide and nanocomposites based on alumina matrix and chrome carbide nanoparticles. For metals contacting alumina-based ceramic coatings again the chemical activity of the metal is important to adhesive behavior. With noble metals silver and gold interfacial adhesive bonds were sufficiently weak so as not to result in separation of damage to the surfaces of the contacting solids. With other metals that form stable oxides, the interfacial adhesive bonds were sufficiently strong so as to result in fracture of single crystal sapphire when cleavage planes were parallel to the contact interface. Metals undergo shear when the alumina-based ceramic coatings is poly-crystalline aluminum oxide matrix of alpha and gamma phases and attempts are made to, by tangential motion, to fracture the adhered interface. Adsorbates reduce singificantly adhesion and friction forces.

4:00pm **SE+TF-TuA7 Adhesion Fundamentals and Nanomechanics in Alumina-diamonds Nanocomposites**, ***M.V. Kireitseu***, *L.V. Yerakhavets, I.A. Nemerenco*, NAMATEX System Division, Institute of Machine Reliability, Russia

When alumina-based ceramic coatings are brought into contact with a ceramic, a polymer, or a metal, strong bond forces can develop between the materials. The bonding forces will depend upon the state of the surfaces, cleanliness and the fundamental properties of the two solids, both surface and substrate. Adhesion between alumina-based ceramic coatings and another solid are discussed from a theoretical consideration of the nature of the surfaces and experimentally by relating bond forces to the interface resulting from solid state contact. Surface properties of alumina-based ceramic composites correlated with adhesion include orientation, reconstruction, and diffusion as well as the chemistry of the surface specie. Where a ceramic is in contact with a metal their interactive chemistry and bond strength is considered. Substrate properties examined include elastic and plastic behavior in the surficial regions, cohesive binding energies, crystal structures, and crystallographic orientation. Materials examined with respect to interfacial adhesive interactions include alumina composite hardened by chrome carbide nanoparticles and diamonds nanoparticles and aluminum oxide. The surfaces of the contacting solids are studied both in the atomic or molecularly clean state and in the presence of selected surface contaminants.

4:20pm **SE+TF-TuA8 Nanoindentation of Alumina - Chrome Carbide and Alumina - Ultra Dispersed Diamonds nanoComposites**, ***L.V. Yerakhavets***, *M.V. Kireitseu, I.A. Nemerenco*, NAMATEX System Division, Institute of Machine Reliability, Russia

Nanoindentation experiments have been done on alumina-chrome carbide and alumina-ultra dispersed diamonds nanocomposite coating on different substrates like steel, aluminum and corundum. Films with thicknesses between 60 and 300 ?m prepared at various current intensities were indented with spherical indenters with nominal radii of 10, 50, and 150 ?m. The influence of deposition current and drying conditions were investigated using SEM. The suitability of this technique to determine morphology and the use of small spherical-tipped indenters to evaluate the mechanical properties of powder compacts was established. The revealed results may be summarized as follows: (1) The structure, grain size and morphology strongly depend on deposition current although the film density does not. At low current intensity, the grain size is found to be close to the initial particle size, whereas at higher current intensity an apparent coarser grain size occurs that, however, also contains pores and internal voids. (2) it is expected that the higher over potential results in the coarser grain size and formation of pores at higher current intensity that caused the onset of electrolysis of the aqueous medium. The localized electrolysis and oxygen evolution near the anode, resulting in a localized change in pH of the aqueous suspension, produced particle agglomeration as well as bubble formation. (3) Spherical indentation technique is found to be effectively measured contact pressure and effective elastic modulus as a function of penetration depth. The difference in contact pressure and elastic modulus vs. the indenter depth could be adjusted by the modulus vs. the ratio of the contact radius to the film thickness. The errors in the data could be also associated with radial cracks within the contact area. (4) Evidence of residual tensile stresses within the film manifested itself in the form of radial cracks from pores. The thicker films showed a greater influence of the cracks.

none

4:40pm **SE+TF-TuA9 Rheological Behaviour of Alumina-Diamonds-Polymer NanoComposite Structure**, ***I.A. Nemerenco***, *M.V. Kireitseu, L.V. Yerakhavets*, NAMATEX System Division, Institute of Machine Reliability, Russia

To predict strength and deformation of the alumina-diamonds-polymer nanocomposition under Hertzian indentation the rheological model has been developed. The model is based on combined simple rheological elements that in general gives accurate results in comparison with one obtained in Hertzian indentation technique. Based upon the investigations we have suggested the following requirements to be used in rheological model of the nanocomposite structure: 1. Since the composite include hard alumina layer and steel substrate that exhibit plasticity, the irreversible deformations has to be considered as plastic in nature. Deformations develop only after excess of some critical yield strength for the particular layer of the composite. 2. if the deformations are smaller then yield strength, the deformations at constant stress have to grow up step-by-step to final value; 3. Cyclic loading increases summarized plastic deformation of the composite; 4. Curve of deformation vs. time at constant load exhibits a linear dependence in one of plotted region. 5. At unloading the retardation of deformations (elastic return) has to be observed; 6. Stress at constant deformations is relaxed. The selection of model that adequate to the studied composite material is determined by comparison of developed models and experimental results. The composite of hard alumina-diamonds-aluminum can be presented as elastic-tenacious-plastic rheological model of the composite. The mechanical prototype of the model is described in a book. Structural equations of the integral model of the composite looks like (H || N || St-V) - (H-N || H). In general, the kind of the rheological equation depends on a level and form of stress applied on model. The polymer layer can be presented as the rheological model consisting from two elastic elements and one tenacious element. As a prototype of the model, we can consider connection of the Maxwells' model and elastic element. The composite exhibits linear relation of stress curve, whereas unloaded composite shows retardation of deformations (elastic return) shown as downfall segment of the curve. The plotted relations of experimental data and calculated data have revealed very close agreement of developed rheological model and real mechanical behavior of the composite. The above stated conditions are found to be used in investigations of mechanical and rheological properties of the alumina-aluminum-polymer-steel composite systems. The rheological properties and perspectives to be considered in development of such nanocomposite structure have been discussed.

5:00pm **SE+TF-TuA10 Adhesion of Alumina-based Nanocomposites to Polymer Substrate**, ***A.G. Fedaravichus***, *M.V. Kireitseu, I.A. Nemerenco*, NAMATEX System Division, Institute of Machine Reliability, Russia

Adhesion bonding of alumina-based nanostructures to several polyimides has been studied as a function of technological parameters of the layers deposition and polymer surface modification by ion beam and chemical pretreatment. The effects of the alumina-based layer deposition method and parameters have also been examined. The materials of interest include a low thermal expansion polyimide derived from 3,3,4,4-biphenyl tetracarboxylic acid dianhydride-p-phenylene diamine (BPDA-PDA) polyamic acid, and pyromellitic dianhydride-4,4-oxydianiline (PMDA-ODA) polyimide, formed from polyamic acid or polyamide ethyl ester precursors. The alumina/polyimide adhesive strength was determined by the scratch peel test, while the interfacial regions were examined using x-ray photoelectron spectroscopy and ellipsometry. It is found that for PMDA-ODA systems, exposure to low energy Ar + and/or O2+ ions improves adhesion of the alumina-based nanooverlayer, while for BPDA-PDA polyimide, the role of O2+ is more significant. The fracture location is found to lie 20-300 A within the polymer, depending upon the ion beam dose and the specific polyimide employed.

Surface Engineering
Room: Exhibit Hall B2 - Session SE-TuP

Poster Session

SE-TuP2 Optimum Combination of Surface Roughness for Materials with Smooth Sliding in a Vacuum, ***A. Kasahara***, *M. Goto*, *T. Oishi*, *M. Tosa*, Nanomaterial Laboratory, Japan

We used a probe of stainless steel sphere with surface roughness of 60nm, and we measured friction of stainless steel substrate which with surface roughness prepared on a submicron scale. As a result, the materials with about 100nm surface roughness showed same friction force in a vacuum as the force out as atmospheric pressure. However, frictional force is generated by relative movement between materials. Therefor we studied a difference of surface roughness of probe and form of surface roughness of a sample in order to obtain the most optimum combination condition for smooth sliding in a vacuum.We measured frictional force of stainless steel sheet surface roughness of 110nm by probes with diameter of 3.18mm and with surface roughness of 60nm,100nm and 200nm. we also used titanium and copper sheets with surface roughness polished on a submicron scall and studied relation between a direction of sliding and generated friction force. The results showed decrease in friction force under optimum combination conditions that surface roughness of substrate was smaller than that of probe with surface roughness of about 100nm and that surface grove line patterns of sliding probe and substrate cross each other at right angles.

SE-TuP3 Three-dimensional Surface Structures Created by PVD Method, ***I.G. Levchenko***, *M. Romanov*, Kharkov Aerospace University, Ukraine

We describe a new class of the plasma coatings namely the three-dimensional surface structures, as well as the technique of deposition and methods for calculating the main process parameters. These special films were produced with a view to increase a coating service life under the hard loading conditions, especially when fatigue endurance and wear resistance are the most critical factors. We created the real three-dimensional surface structures of a faceted multi-layer hard-ceramic film consisting of facets separated with the pure metal. As the hard-ceramic film, the titanium nitride and zirconium nitride composition was used. The mask technology was used for production of these structures. According to the concept proposed, the pure metal separator is used as a solid-state lubricant. Besides, the use of isolated hard-ceramic facets provides increased adhesion strength and adhesion fatigue limit; this enables deposition of relatively thick films (up to 40 micrometers) without loss of the adhesion stiffness, and prolongs the film service life before delamination. For deposition of these films, we used the molybdenum masks with various transparency factors and various facet shapes. The films were deposited using vacuum-arc deposition equipment that provides generation of the filtered ion flow free of droplets. The wear tests showed considerable increase in the wear-resistance and decrease in friction coefficient when the steel was used as the rider. For cylindrical sliding couple, the fatigue test was performed that had proved the efficiency and utility of this kind of technology.

SE-TuP4 Electron Transport Characteristics of Ultrathin Cu Films Analyzed by In-situ ac Impedance Spectroscopy, ***S.Y. Park***, *Y.H. Hyun*, Hanyang University, Korea, *J.Y. Rhee*, Hoseo University, Korea, *Y.P. Lee*, Hanyang University, Korea

The impedance and resistance are measured simultaneously by using in-situ impedance spectroscopy and I-V source during the deposition of Cu films with a thickness of 1 to 7 nm onto a glass substrate. The growth stages of films, such as the discontinuous, semicontinuous, and continuous regimes, are determined by analyzing the AC impedance spectra in addition to the rather traditional DC method. We also observed that the percolation threshold thickness is 2.5 nm by either method and that the boundary for continuous stage is 3.3 nm. The complex dielectric moduli of films thinner and thicker than 2.5 nm could be described with a parallel R-C and a series R-L equivalent circuit, respectively. It is found that the relaxation time and the inductance for the semicontinuous and continuous films are increased with increasing the film thickness, and that the changes are discussed by considering the roughness and grain-boundary scattering effects. The mechanism of growth for a variety of ultrathin films could be elucidated by applying in-situ impedance spectroscopy.

SE-TuP6 Copper Seeding on the Tantalum-insulated Silicon Oxide Film by Ion Beam Assisted Deposition for the Growth of Electroless Copper, *S. Han*, National Taichung Institute of Technology, Taiwan, R.O.C., *C.J. Yang*, National Chung Hsing University, Taiwan, R.O.C., *J.H. Lin*, National Tsing Hua University, Taiwan, R.O.C., *Z.C. Chang*, *C.H. Hsieh*, National Chin-Yi Institute of Technology, Taiwan, R.O.C., ***H.C. Shih***, National Tsing Hua University, Taiwan, R.O.C.

The major aim of this study is to combine the techniques of using ion beam assisted deposition (IBAD) and electroless plating to deposit Cu onto a Ta diffusion barrier layer in order to accomplish the ULSI interconnection metallization. Distribution and depth of the implanted Cu was measured by secondary ion mass spectroscopy (SIMS) profiling. The crystallinity of the electroless plated Cu was analyzed by x-ray diffraction (XRD). Cross-sectional transmission electron microscopy (XTEM) and field emission scanning electron microscopy (FESEM) were used to elucidate the growth mechanism of the electroless deposited Cu film on the Cu-seeded layer by IBAD. The surface morphology of the films was observed by atomic force microscopy (AFM). This study successfully combines the techniques of IBAD and electroless plating for Cu to provide an appropriate quality for the gap-filling submicron trenches and vias with excellent step coverage.

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