SYMPOSIUM P

Advances in Surface Engineering–Fundamentals and Applications

November 26 – 29, 2001

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SESSION P1: MECHANICAL AND TRIBOLOGICAL PROPERTIES OF NANOSTRUCTURES
Chairs: Stan Veprek and Wen Jin Meng
Monday Morning, November 26, 2001
Room 311 (Hynes)

8:30 AM *P1.1
NANO- AND MICRO-SCALE CONTACT AT SURFACES: EXPERIMENT, SIMULATION AND APPLICATIONS. Subra Suresh, Massachusetts Institute of Technology, Dept of Materials Science and Engineering, Cambridge, MA.

This presentation will provide an overview of recent work on nano- and micro-scale contact at surfaces, with applications in nanotribology, micro- and nanoelectromechanical systems, nanoindentation and atomic force microscopy. First, experimental simulations of atomic level contact, along with detailed continuum as well as crystalline inelasticity and molecular dynamics computations, will be described for the purpose of establishing the validity of different scales of modeling tribological contact at surfaces. Particular attention will be directed at elucidating the effects of atomic and microscopic roughness of surfaces on the nucleation of defects at surfaces during contact. Specific experimental data will be presented to highlight micro- and nano-scale contact at surfaces in thin films and coatings. Next, a series of systematic experiments will be described to illustrate the possibility of damage and crack suppression at surfaces during normal and sliding contact by recourse to continuous or step-wise gradients in composition and microstructure. The presentation will conclude with a summary of key issues pertaining to engineering of surfaces to resist tribological damage and failure in a variety of structural and functional applications.

9:00 AM P1.2
HOW CAN WE UNDERSTAND THE UNUSUAL MECHANICAL PROPERTIES OF THE SUPERHARD NANOCOMPOSITE COATINGS? Ali S. Argon, Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MS; Stan Veprek, Institute for Chemistry of Inorganic Materials, Technical University Munich, Garching, Munich, GERMANY.

The superhard nanocomposite coatings prepared according to the generic design principle [1] which results in a self-organization of a stable nanostructure show an unusual combination of mechanical properties, such as high hardness of 40 to $\geq$100 GPa, high elastic modulus measured by the load-depth sensing indentation technique, high elastic recovery up to 94% and high resistance against crack formation even under a strain of $\geq$10%. In contrast, conventionalhard materials are brittle and undergo fracture at a strain of the order of 0.1%. We shall show that the unusual properties of the superhard nanocomposites can be understood in a logical way by scaling the fracture physics and mechanics to the crystallite size of 3-5 nm. In such nanocomposites which have a strong interface between the nanocrystals, the stress concentration factor is estimated to be of about 2-4, i.e. orders of magnitude smaller than in conventional microcrystalline materials. The high elastic recovery and high elastic energy stored in the nanocomposite coatings under the indentation can be explained by reversible flexing. The surprisingly high resistance against crack formation is due to the high stress needed for the initiation and propagation of nanocracks. It is not necessary to evoke any enhancement of the fracture toughness for which there is no rational physical justification. The very high values of elastic modulus are probably due to a high pressure under the indenter. [1] S. Veprek and S. Reiprich, Thin Solid Films 268 (1996) 64.

9:15 AM P1.3
MECHANICAL AND TRIBOLOGICAL PROPERTIES OF CERAMIC NANOCOMPOSITE COATINGS. B. Feng, D.M. Cao, W.J. Meng, Mechanical Engineering Department, Louisiana State University, Baton Rouge, LA; L.E. Rehn, P.M. Baldo, Materials Science Division, Argonne National Laboratory, Argonne, IL.

Ceramic nanocomposite coatings have been intensely researched in recent years. In selected coating systems, such as metal-containing amorphous hydrocarbon (Me-C:H) and metal-containing amorphous silicon nitride (Me-Si:N), elastic modulus and hardness values exceeding the linear rule of mixtures have been reported. We report recent experiments on these coating systems aimed at probing the existence or absence of these mechanical property enhancements. Coating tribological characteristics will also be reported.

9:30 AM P1.4
DETERMINING THE LIMIT OF HARDNESS IN TERNARY CARBIDE THIN FILMS. James E. Krzanowski, Jose L. Endrino, Sirma H. Koutzaki, Mechanical Engineering Dept., University of New Hampshire, Durham, NH.

The ultimate strength level of hard coating materials is a subject of considerable scientific interest as well as commercial importance. While traditional hard coating materials, such as nitrides, borides, and carbides, have inherently high hardness, significantly higher hardness levels, even exceeding that of diamond, have been reported in microstructurally modified nitride thin films. However, others report maximum hardness levels only in the range of 40-50 GPa despite the presence of nano-scale grain structures or multilayers. In the present study, we have examined hardness levels in a number of ternary carbide systems, such as Ti-Si-C, Ti-W-C, Ti-Mo-C and Ti-Hf-C. We have attempted to manipulate the microstructure via the extent of alloying, as well as by controlling deposition parameters such as temperature and substrate bias. In all cases, we have only obtained maximum hardness levels of about 40 GPa, despite obtaining nano-scale microstructures in numerous coatings. The effect of substrate bias was to first increase hardness, reaching a maximum of about 40 GPa, but with further increases in bias the hardness declined due to a high defect content and amorphization of the structure. While the substrate bias level at which the hardness maximum was achieved depended on alloy content, the maximum hardness did not. Both transmission electron microscopy (TEM) studies of micro-structure and measurements of residual stresses in these coatings have been applied to help understand the effect of microstructure, film density and residual stress on the measured hardness.

9:45 AM P1.5
NANO INDENTATION STUDIES OF TiN/ TiN/(Ti,Al)N MULTILAYERS COMBINED WITH CROSS-SECTIONAL ELECTRON MICROSCOPY OBSERVATIONS. N.J.M. Carvalho, J.Th.M. De Hosson, Department of Applied Physics, Materials Science Center and Netherlands Institute of Metals Research, University of Groningen, Groningen, THE NETHERLANDS.

This investigation is aimed at examining the mechanical performance and mechanism of delamination of multi-layer systems by nano-indentation and cross-sectional electron microscopy. Both titanium nitride (TiN) and titanium nitride/titanium-aluminum nitride (TiN/(Ti,Al)N) multilayers deposited by physical vapor deposition onto steel substrates were subjected to ultra-low load indentations. The homogeneous coating was deposited using a triode evaporation ion plating process, whereas the multilayers were deposited using a reactive hybrid deposition process consisting of a combination of electron beam evaporation of Ti and d.c. magnetron sputtering of Ti-Al alloy. The mechanical properties e.g. hardness and effective Young's modulus - were measured by nano-indentation tests using the continuous stiffness techniques. The information from load-displacement curves were critically analyzed and the cracking mechanisms were characterized using a new technique for cross-sectional electron microscopy of the nano-indentations. The information retrieved with this technique eliminates problems inherent in assessing, at this small contact scales, whether delamination of the coating occurs along the substrate or by interfacial failure inside the multilayer.

10:30 AM *P1.6
INSTABILITIES AND FAILURE PHENOMENA IN COMPRESSED THIN FILMS. Anthony Evans, Princeton University, Princeton Materials Institute, Princeton, NJ.

Compressed thin films are inherently unsatable against out-of-plane displacements, which reduce the stresss and the associated energy density. The specific response is governed by the properties of the adjoining materials, the magnitude of the stress and the film thickness. The presence of imperfections and their morphology are also crucial. Two categories of response are presented. The first consists of diamond like carbon (DLC) films on a range of different substrates, which fail by buckle delamination. One example in this category comprises DLC on steel substreates wirh a Cr adhesion layer useed for enhancing the fatigue life of gears and bearings. Another refers to DLC on glass substrates used for optical purposes. The second category relates to thermally grown oxides (TGO). The example chosen relates to an alumina TGO that forms on a Ni(Al) alloy within a thermal barrier systems used in gas turbines. In this case, the film has materials on both sides: a superalloy on one side and a stablized ziconia thermal barrier on the other. Failure occurs through a displacement instability that vectors into the alloy, as the system thermally cycles, resulting in delamination of the ziconia.The failure mechanisms and discussed, emphasising their dependence on the properties of the constituents and the interfaces and the essentila role of imperfections. Simulations are presented that animate the basic concepts.

11:00 AM P1.7
MECHANICAL CHARACTERIZATION OF FUNCTIONALLY GRADED MATERIALS WITH A YIELD STRENGTH GRADIENT. Ali Nayebi, Gérard Mauvoisin, Olivier Bartier, Rochdi El Abdi, Rennes 1 University, Larmaur, Rennes, FRANCE.

An elastic-plastic spherical micro-indentation study of functionally graded materials (FGMs) with gradient in yield strength, such as steels having undergone thermal hardening (nitriding), is made by experimental and finite element methods. Indentation simulations are done with diameter sphere of 1.5875 mm. Various surface-substrate yield stress ration β ($1< \beta <6$) and strain hardening exponent n ($0.0< n< 0.3$) of studied materials are considered in modeling. The thin film thicknesses vary from 50 to 300 μm.
The analysis of the normalized mean contact pressure by the representative equivalent flow stress corresponding to Tabor plastic strain, as a function of a dimensionless strain parameter for graded materials, shows that the mean contact pressure presents the same tendency as that of equivalent homogenous materials. For the fully plastic case, the maximum mean contact pressure approaches 2.8 times of equivalent stress which is in good agreement with the empirical value for homogenous materials. Then, a simple model for the average plastic zone radius evolution of FGMs during spherical indentation is given. Plastic zone radius evolutions of FGMs during spherical indentation is given. Plastic zone radius evolutions of FGMs and of equivalent homogenous materials are very similar, which confirms the definition of equivalent yield stress for FGMs.
Based on finite element results, a functional equation is developed to predict the hardness variation as a function of indentation depth, which depends on mechanical and geometrical properties of studied materials. Lastly, a theory based on effective hardness evolution is proposed to determine the yield stress evolution and hardness profile for materials with a decreasing yield stress with depth.
Results for carbo-nitriding steels obtained by the standard Vikers micro hardness techniques are compared with those obtained by the proposed method.

11:15 AM P1.8
DIFFERENT MECHANISMS OF ACHIEVING SUPEHARDNESS IN COATINGS: STABLE NANOCOMPOSITES VS. HIGH COMPRESSIVE BIAXIAL STRESS. S. Veprek, P. Karvankova, J. Prochazka, H. Männling, Institute for Chemistry of Inorganic Materials, Technical University Munich, Garching, GERMANY; M. Jilek, SHM Ltd., Novy Malin, CZECH REPUBLIC.

A strong enhancement of the hardness above 40 GPa in coatings can be achieved by the formation of a stable nanocomposite or by large biaxial compressive stress of $\geq$5 GPa. The latter can be an artefact of the load-depth sensing technique caused by pile-up in ductile materials. A hardness of 70-100 GPa was reported e.g. for HfB_2 [1], TiN, (TiAlV)N [2] when the stress achieved 5-7 GPa (bulk hardness 16-25 GPa). We have compared, for a number of different nanocomposites which did not show pile-up and had either a high or low ($\leq$1Gpa) stress, the hardness values from the load-depth sensing technique with Vickers hardness calculated from the projected area of the plastic deformation and found a good agreement. Thus, the only reliable way how to distinguish between these different mechanisms of hardening is isochronal annealing. Superhard, stable nanocomposites (nc-TiN/a-Si_3N_4, nc-(TiAl)N/a-Si_3N_4 and others) retain their room-T hardness after annealing to 1000-1100°C. In contrast, coatings of CrN/Ni and ZrN/Ni [3] show a strong decrease of the hardness to the bulk values already after annealing to 400-500°C due to the relaxation of the compressive stress, in agreement with the behavior of ordinary hard coatings [1]. This shows that the superhardness of stable nanocomposites originates from their nanostructure whereas that of CrN/Ni, ZrN/Ni and similar [3] is due to the high compressive stress. No contribution to the enhancement of the hardness due to "nanocomposite effect" in these coatings could be identified. [1] W. Herr, E. Broszeit, Surf. Coat. Technol. 97 (1997) 335 [2] J. Musil et al., Thin Solid Films 167 (1988) 107 [3] J. Musil, Surf. Coat. Technol. 125 (2000) 322

11:30 AM *P1.9
MECHANISMS OF PLASTIC DEFORMATION IN NANO-STRUCTURED CERAMIC THIN FILM MATERIALS. Lars Hultman, Thin Film Physics Division, Department of Physics, IFM, Linkoping University, SWEDEN.

Nanostructured ceramic thin films are attractive in that they can exhibit high mechanical strength. The materials comprise nanolaminates - s.c. superlattices - and nanocomposites of, e.g., amorphous and nanocrystalline phases. Hardness enhancements in such materials can exceed 300% of the bulk phases. The detailed mechanisms of plastic deformation and fracture are poorly understood, however, interactions of dislocations between the phases, block-slip, grain rotation, and fracture are identified as strength-limiting factors. Nanoindentation in combination with atomic force microscopy and electron microscopy provides important information on dislocation generation and glide as well as fracture mechanisms. Examples are given from nitride superlattice films (TiN/NbN) that stay relatively intact during mechanical deformation, whereas TiN itself exhibit persistent slip bands [1]. Glide within layers of these superlattices is the dominating deformation mechanism in support of present models for superhardening. The corresponding theory presumes dislocation plasticity with dislocation hindering at interfaces between phases with different shear modulus. A study of oxide superlattices Y_2O_3/ZrO_2, however, revealed no significant hardness enhancement compared to rule-of mixture, possibly due to micro fracture. Both of the above phenomena are present for multilayers composed of hard and soft materials. For example, in TiN/Cu superlattice films, hardness is limited by fracture in the high-elastic modulus ceramic layers because of poor load-bearing properties of the low-modulus metal layers. It is concluded that future design of nanostructured materials requires reliable data for elastic constants of the constituents as well as an understanding of the role of intrinsic residual stress. Finally, this presentation will discuss the mechanical behavior for the class of nanocomposites, e.g., Si_3N_4-TiN, however, the observations on the nanometer level of deformation phenomena becomes progressively cumbersome with the increased dimensionality of the system. [1] L. Hultman, Z. Metallk. 90 (1999) 803. [2] P. Yashar, S.A. Barnett, L. Hultman, W.D. Sproul, J. Mater. Res. 14 (1999) 3614.

SESSION P2: MACRO-, MICRO-, AND NANO-TRIBOLOLOGY I
Chairs: Yang Tse Cheng and James B. Adams
Monday Afternoon, November 26, 2001
Room 311 (Hynes)

1:30 PM *P2.1
RESEARCH CHALLENGES AND OPPORTUNITIES IN SURFACE ENGINEERING AT THE NANO-SCALE. Jorn Larsen-Basse, National Science Foundation, Surface Engineering and Materials Design Program, Arlington, VA.

Developments in the many different aspects of surface engineering have been very rapid during the past decade. As a result the surface of an object is moving towards having a clearly defined functional role rather than as just being the border with the outside. This new two-dimensional world has been proclaimed a part of "neo-technology" which fits over the old, three-dimensional world of "paleo-technology", becoming its skin. Much research is in progress in this area but much more is needed to take advantage of its promises. In this brief overview I present a personal view of some of the current research opportunities and needs and I try to extrapolate to some of the exciting research challenges of the near future in this dynamic field. Topics vary from the somewhat mundane development of design data, metrology and testing techniques, standards and process control, to advanced modeling, development of multi-layered and multi-structured coating systems with nano-scale features and sculpting, low-friction MEMS surfaces, and superhard coatings, and even further on to smart or intelligent surfaces, self-healing coatings, etc. Further into the future we may see even more exciting developments if, as expected, there will be a scramble for whole new ways of dealing with and manipulating information as well as to incorporate nanostructures into surface layers and MEMS and microfluidic devices into coatings. Finally, in order for the currently evolving nano-technology to become reality there will need to be many advances made in materials and surface engineering and some of those are outlined as well.

2:00 PM P2.2
MD SIMULATIONS OF HIGH SPEED NANOINDENTATION AND PLOWING ON Al SURFACE. Hualiang Yu, Arizona State Univ, Science and Engineering of Materials Program, Tempe, AZ; James Adams, Arizona State Univ, Dept of chemical and Materials Engineering, Tempe, AZ; Yang-Tse Cheng, Louis Hector Jr. General Motor R&D Center, Warren, MI.

Recently, molecular dynamics simulations are used to study the micro properties of materials surface. A series of molecular dynamics simulations has been performed in order to study the nanoindentation and plowing of a hard tip into an Al (100) surface. Different geometries of indenters were used in the simulations. The effects of many other process variables are investigated, including temperature, tip-substrate bonding, indentation force, and plowing speed. We also studied the alloy effects of the substrate. The indentation loading and unloading curves and plowing curves are generated. Also, we discuss the hardness of materials and the nucleation and propagation of dislocation during the indentation and plowing.

2:15 PM P2.3
FRICTION ANISOTROPY AT Ni(100)/(100) INTERFACE. Yue Qi, Tahir Cagin, William A. Goddard III, Material & Processing Simulation Center, Caltech, Pasadena, CA; Yang-Tse Cheng, GM R&D Center, Warren, MI.

Analytic theories indicated that there is no static friction on clean incommensurate interfaces, while a recent experiment revealed that the static friction coefficient was anisotropic with respect to the lattice orientation, but did not vanish on two clean Ni(100) mis-orientated surfaces. To understand this friction anisotropy and the difference between theory and experiment, we carried out a series of Non Equilibrium Molecular Dynamics (NEMD) simulations for sliding of Ni(100)/Ni(100) interfaces under a constant force. We found that the clean, flat, and incommensurate interface indeed has a very small static friction coefficient. However, surface roughness can increase the static friction on the incommensurate interfaces dramatically and increase the friction on the commensurate interfaces to a lesser extend. Thus, the rough surfaces show similar anisotropy behavior as experimental results. The effects from temperature, roughness, disordering and defects on interface are discussed as well.

2:30 PM P2.4
CHANGES IN SURFACE MECHANICAL PROPERTIES THROUGH ELECTROCHEMICAL MODIFICATIONS.
Martha M. McCann, Sean G. Corcoran, Virginia Tech, Dept Materials Science and Engineering, Blacksburg, VA.

The mechanical response of materials can be dramatically altered by the presence of absorbed species on the surface. An electrochemical environment enables discrete control of the surface, keeping it clean (as compared to ultra-high vacuum) and inducing stable stress states. Applying a potential to the surface can lead to charge accumulation, which changes the surface free energy. Oxides are easily added or removed. Utilizing the phenomenon of underpotential deposition (upd), discreet monolayers of metal can be added to a surface. The degree of lattice mismatch between the metal and its adlayer will also control the degree of surface stress. The changes in the mechanical properties of these highly controlled surfaces are measured by in-situ nanoindentation at various potentials. Nanoindentation of single crystals with very low dislocation densities allows for careful observation of dislocation behavior with applied load. This enables the identification of mechanisms by quantifying the changes in mechanical properties under specific environments. Au has been extensively studied in electrochemistry literature; it is well behaved and well characterized. It is a model system that has demonstrated variation in mechanical properties in different electrochemical states. Lessons learned on Gold have also been applied to Zn and Ni systems.

2:45 PM P2.5
KINETIC MONTE CARLO STUDY OF DISLOCATION ETCH PITS. Daniel Bentz, Kenneth Jackson, University of Arizona, Dept of Materials Science and Engineering, Tucson, AZ.

Chemical mechanical polishing and stress corrosion cracking result from chemical attack at stressed regions. To better understand the mechanisms involved, a kinetic Monte Carlo (kMC) study of the formation of dislocation etch pits is being pursued. Atoms from a diamond cubic lattice are irreversibly removed with a probability which depends on an atom's number of nearest neighbors as well the local stress developed from its physical location with respect to the dislocation in the lattice. In accordance with experimental observations, both faceted and non-faceted dislocation etch-pits have been observed. Simulations have been performed for various values of the strength to the etchant attack and the magnitude of the stress generated by the dislocation. By using kMC in conjunction with molecular dynamics and quantum calculations we are able to increase the length and time scales of both these methods to make direct comparisons to experimentally observed phenomena.

3:30 PM *P2.6
DIRECTIONS FOR TRIBOLOGICAL COATING DEVELOPMENT.
Allan Matthews, Adrian Leyland, Research Centre in Surface Engineering, University of Hull, Hull, UNITED KINGDOM.

With the availability of advanced (mostly plasma-based) coating and treatment methods, coating process developers can now acheive surface properties which fully meet the requirements of all kinds of tribological contacts. This paper discusses how these requirements differ for different contact types (e.g. sliding, abrasion, impact, etc). The need to consider the requirements of the substrate and the coating together is emphasised, and the way in which this influences the likely direction for the future development of tribological coatings is discussed. It involves, for example, the development of duplex and hybrid processes which can provide a more effective load-bearing support capability beneath and within coatings. Such processes include the prior plasma-treatment of a substrate, followed by a PVD coating. It can also involve the development of nanocomposite coatings which acheive a suitable combination of high hardness (H) with a relatively low elastic modulus (E), to provide enhanced ability to absorb impact and deflect with the substrate when under contact loads. These new developments will include new multilayer coatings which can also accomodate substrate deformations without cracking or debonding. Various examples of the above approaches to coating development are described, together with wear test results and practical applications.

4:00 PM P2.7
TRIBO-CONTACTS WITH MICRO SLIP IN COATED SOLIDS.
Lanshi Zheng, Seagate, Minneapolis, MN; and S. Ramalingam, University of Minnesota, Minneapolis, MN.

In a frictional contact, both stick and slip zones exist between two contacting bodies. It leads to changes in frictional stresses at the contact interface. A theoretical solution for the frictional contact on a layered solid involving stick-slip zones is obtained using Chebychev polynomial. Contact forces and stresses in the film-substrate field are calculated. Indentation problem involving mixed boundary conditions is formulated based on the displacement method. Solutions of contact normal pressure for frictionless contact are first obtained. Solutions of Fourier series and Chebychev polynomial are evaluated. Cases involving indentations by a cylinder and flat-ended stamp are examined.

4:15 PM P2.8
TRIBOLOGICAL AND MECHANICAL CHARACTERIZATION OF BORON CARBIDE NANO-COMPOSITE COATINGS. Srikant Nekkanty, Mark Walter, The Ohio State University, Department of Mechanical Engineering, Columbus, OH; Gary Doll, Case Western Reserve University, Dept of Chemical Engineering, Cleveland, OH.

Boron carbide (BC) is well known as a bulk ceramic and a coating material that is important for a wide range of technological applications. The applicability of boron carbide stems from the fact that it is a very hard material with high lubricity, high elastic modulus, low specific gravity, and good chemical stability. Disadvantages, however, include extreme brittleness and sometimes poor adhesion. Recently, a reactive sputtering involving boron carbide targets and hydrocarbon gases has been used to produce novel nano-composite boron carbide thin films comprised of BC nano-crystals embedded in a matrix of hydrogenated amorphous carbon (DLC). The microstructure of these thin films is similar to that of other metal carbide/DLC nano-composite films. This paper presents results of the characterization of the mechanical and tribological properties of boron carbide nano-composite thin films that have been sputter deposited onto both silicon and 52100 steel disks. Tribological properties are investigated with pin-on-disk tests and scratch tests. Mechanical properties are determined by indentation experiments at meso and nano-scales. Prior to and following all experiments, microstructural characterization through electron microscopy, scanning Auger microscopy, and scanning probe microscopy are performed. Linkages between the processing conditions and the microstructure are established, and are correlated with the tribological and mechanical properties. In addition, from the meso-indentation experiments, information regarding cohesive and interfacial strengths is inferred. Ultimately, the results of the characterization will lead to microstructural models that advance the scientific understanding of boron carbide nano-composite coatings.

4:30 PM P2.9
NANOINDENTATION AND WEAR BEHAVIOR OF TITANIUM-NICKEL ALLOYS. Wangyang Ni, Michigan State University, Dept of Materials Science and Mechanics, East Lansing, MI; Yang-Tse Cheng, General Motors Research and Development Center, Materials and Process Laboratory, Warren, MI; David S. Grummon, Michigan State University, Dept of Materials Science and Mechanics, East Lansing, MI.

The unusual constitutive behavior of NiTi alloys that display shape memory and transformational superelasticity may impart useful tribological properties. This paper presents some preliminary results on nanoindentation and pin-on-disk wear experiments that are suggestive of tribological applications of NiTi alloys. It is shown that high levels of spring-back reversibility together with high hardness, as measured by nanoindentation experiments, correlate with improved wear resistance in both bulk nitinol and NiTi thin films. Amorphous thin films of equiatomic NiTi are readily produced by physical vapor deposition and are found to be especially hard and wear resistant. Finally, stress induced B2-B19 transformation is shown to occur during wear-loading of martensitic NiTi, indicating that wear processes are capable of inducing superelastic effects in B2 NiTi alloys.

4:45 PM P2.10
WETTING AND FRETTING ON QUASICRYSTALS. J.M. Dubois, P. Brunet, G. Bonhomme, V. Demange and M.C. de Weerd, Ecole des Mines, Nancy, FRANCE; E. Belin-Ferré LCPMR, Universite P. et M. Curie, Paris, FRANCE; A. Merstallinger, Austrian Research Centers, Seibersdorf, AUSTRIA; D.J. Sordelet, M. Besser, Dept of Materials Science, ISU and Ames Laboratory, Ames, IA; J. Anderegg, C. Jenks, V. Fournée, P.A. Thiel, Dept of Chemistry, ISU and Ames Laboratory, Ames, IA.

Wetting and fretting are two essential surface properties that to a large extent -and as yet for quasicrystals - embody their technological potential when employed in the form of coatings. By quasicrystals, one considers here the whole family of complex intermetallics based on aluminum, which comprises true quasicrystals, their approximants and some crystalline materials of related composition. Experimentally, wetting of these surfaces by water is largely reduced in comparison to conventional metal surfaces. A clear correlation is observed between the reversible adhesion energy of water on the one hand and the density of states at the Fermi energy on the other. Such surfaces are necessarily oxidized and it turns out from results of our new experiments that the oxide layer plays an essential role in explaining the observed behavior. Our conclusions go beyond the unique wetting behavior of quasicrystals and challenge the admitted theory of wetting on metals. Similarly, friction and fretting are reduced on quasicrystals, with a sharp minimum observed at the position of the genuine quasicrystal in the phase diagram. In high vacuum, the characteristic values measured in contact with diamond or tungsten carbide riders are smaller than in ambient atmosphere, thus indicating that the oxide layer is involved to some extent in determining the tribological mechanisms. Nevertheless, reduction of friction is far more important on the true quasicrystal than on its neighboring crystals. Our data show that the specific crystallographic structure of quasicrystals is responsible for this effect. Hence, the paper will focus at a summary of these findings and of their actual technological relevance. The present work was supported by CNRS-NSF International Co-operative Program PICS 545.

SESSION P3: INDUSTRIAL APPLICATIONS OF SURFACE ENGINEERING I

Chairs: Clark VanTine Cooper and Wen Jin Meng
Tuesday Morning, November 27, 2001
Room 311 (Hynes)

8:30 AM *P3.1
CHARACTERIZATION OF ANTIWEAR FILMS USING MICRO-FOCUS XANES AND IFM. P.R. Norton, Than Do, M. Nicholls, M. Kasrai, T. Woo, N. Mosey, G.M. Bancroft, Dept of Chemistry, University of Western Ontario, London, Ontario, CANADA.

The characterization of anti-wear films for tribological applications is one of the most challenging problems faced by many industries including the automotive industry in the development of lightweight engines to meet more demanding fuel economy and emission standards. We are carrying out an experimental and theoretical study of tribology of wear films, covering length scales from nm to many micrometers. An understanding of wear films requires the use of modern surface techniques and modelling, and is highly interdisciplinary in that it also requires the systematic study of a wide range of mateirals subjected to realistic sliding/wear conditions. In this presentation, the mechanical properties of the tribo-films, such as elastic modulus and hardness, are determined by nano- and micro-indentation using interfacial force microscopy (IFM) and the Hysitron nanoindenter. The chemical nature (composition and changes) of the same tribo-films are examined using X-ray absorption near edge structure (XANES) and XANES spectromicroscopy techniques. In parallel with these studies, modern modelling techniques are being applied to determine the origins of the beneficial properties of the antiwear films. Materials include cast iron, thermal spray and high silicon aluminum alloys. This presentation will illustrate how the structure of antiwear films, formed under lubricated conditions influence the friction properties based on both mechanical and chemical studies. These data provide new fundamental insights into the mechanisms of the lubricated wear, which can be used to design better engineered surfaces for automotive applications.

9:00 AM P3.2
CHEMICAL AND MECHANICAL POLISHING BETWEEN STEEL AND CARBON-CONTAINING CERAMIC COATINGS.
Stephen J. Harris, Chemistry Dept., Ford Scientific Research Lab, Dearborn, MI.

Thin ceramic coatings can significantly increase the fatigue lifetime of bearings and gears, in part by polishing their counterparts, reducing stresses from asperities. Thus, a coating's ability to polish or abrade without damaging the counterpart may determine its usefulness. Yet there has been little work examining factors which control polishing by such coatings. We have analyzed the abrasiveness of diamondlike carbon and boron carbide coatings for this study. We find an extremely steep dependence of abrasiveness on hardness. We show that nanometer-scale features on the coating surface are strongly correlated with abrasiveness, while micron-scale features are not. The nano-scale–but not the micro-scale–structure on the ceramic coating is quickly polished by sliding against steel, explaining the drastic reduction in the abrasiveness of the coating that we observe. It is remarkable how quickly the nano-scale surface features of a ceramic coating are altered by steel, which is several times softer than the coating. We derive quantitative scaling relationships that show how the time dependence of the abrasion rate varies with important parameters of sliding wear, and we use these relationships to predict abrasion kinetics for new experiments. Detailed contact mechanics modeling has been correlated with AFM images to explain the evolution of the steel surface in terms of mechanical wear. In contrast, we show that changes on the surface of the ceramic coating are chemical in nature. These results have important consequences for the design of coatings to improve fatigue resistance.

9:15 AM P3.3
BORON NITRIDE PROTECTIVE COATING FOR HIGH TEMPERATURE APPLICATIONS. Ravi Bathe, R.D. Vispute, Ichiro Takeuchi, R.P. Sharma, and T. Venkatesan, CSR, Dept of Physics, Univ of Maryland, College Park, MD.

Protective coatings of ceramic materials are of great interest for high temperature applications. Boron nitride is an ideal candidate for protective coating applications for high temperature elements and components due to its structural and chemical stability at very high temperatures (> 2000°C), high thermal conductivity, and high chemical inertness to corrosive gases and oxidizing atmospheres. In this paper, we report on fabrication, characterization, and processing of boron nitride films on metallic components of high temperature wafer heaters. The hexagonal BN films have been fabricated by pulsed laser deposition and spray techniques. The deposited films were characterized by x-ray diffraction, FTIR, Rutherford backscattering spectrometry, scanning electron microscopy, atomic force microscopy, and electrical resistivity. The as deposited BN films have been found to be poorly crystalline, however, the films annealed at 900°C have been found to be polycrystalline. The as-deposited films were annealed at various temperatures ranging from 500°C to 1200°C in order to densify the films. Adhesion of the films with the heater components was also greatly improved for the high temperature annealed samples due to a good interfacial bonding with the substrate material. The performance of the BN coating was tested up to a temperature of 1000°C in vacuum, air, oxygen, nitrogen, and argon atmosphere. The results on the properties of BN films with the emphasis on microstructural characterization and processing will be presented, and its implication for high temperature applications will be discussed. Funding support from Maryland Industry Partnerships (MIPS, Grant #2-92419) and Blue Wave Semiconductors, Inc. is acknowledged.

9:30 AM P3.4
SLIDING WEAR OF PLASMA TRANSFER WIRE ARC THERMAL SPRAYED LOW CARBON STEEL COATINGS. T. Perry, Y.-T. Cheng, General Motors Research and Development Center, Warren, MI; A. Edrisy, A.T. Alpas, Department of Mechanical, Automotive and Materials Engineering, University of Windsor, Windsor, Ontario, CANADA.

Low carbon steel coatings were applied on 319 Al alloy substrates using a plasma transfer wire arc (PTWA) type thermal spraying process. A pin on disc type wear tester placed in an environmental test chamber was used for the wear tests. Tests were performed in an atmosphere with various humidity levels in the range of 10-99% RH. It was shown that the wear rates of the coatings were a strong function of the testing environment in addition to the applied load and test speed. The wear is dominated by the formation of iron oxides. The mechanism for the wear process depends on the composition of the oxides formed; at low sliding velocity the oxides degrade and dominate the material removal from the surface. At high velocity more robust oxides are formed that coat the surface and act as a tribolayer that reduces the wear rate. The addition of moisture to the test atmosphere alters the ratio of the various iron oxides formed, strongly favoring Fe_2O_3. As the atmospheric humidity increased, a tribo-polishing process became active, and the wear rates decreased with increasing humidity. Automotive applications of thermal spayed coatings will also be discussed.

9:45 AM P3.5
NITRIDING OF TOOL STEELS USING ELECTRON-BEAM-EXCITED PLASMA DEVICE. Hiroaki Shoyama, Toshihiro Kobayashi, Hideki Sato, Yoshiki Tsunekawa, Tamio Hara, Toyota Technological Institute, Nagoya, JAPAN; Petros Abraha, Faculty of Science and Technology, Meijyo Univ., Nagoya, JAPAN; Kazunari Taniguchi, Department of Physics, Kyoto Univ. of Education, Kyoto, JAPAN; Manabu Hamagaki, The Institute of Physical and Chemical Research (RIKEN), Saitama, JAPAN.

It is well known that atomic nitrogen plays a key role in the synthesis of nitride films or the nitriding of material surfaces. Glow discharge plasmas and their outgrowths have been generally applied to the surface nitriding of structural materials. However, in the conventional plasma sources, there are only few electrons with energy enough to break the molecular bond, because the electron energy distribution is generally Maxwellian where the electron temperature is several eV. Therefore, it has been reported that the degree of dissociation of nitrogen was below the limit of the experimental detection. In contrast to this, the electron-beam-excited plasma (EBEP) device used in this experiment has an electron beam energy of 50-150 eV that is selected to coincide the energy range in which the cross section of nitrogen dissociation is maximum. At the beam current of 3.4 A and beam voltage of 140 V, the dissociation of nitrogen was measured to be 0.16 at processing volume of 6 liter. In addition to the high performance of nitrogen dissociation, EBEP device has an advantage that the surfaces to be treated need not be applied a voltage for plasma production. Therefore, it is expected that the applicability to complex shapes is high. The EBEP was applied to the nitriding of tool steel. It was investigated the efficiency of nitriding for narrow gap. Two disks, which were 20 mm in diameter and 2 mm in thickness, were prepared and piled together with spacer. In a slit between the disks, it was found that the modified region extended to 5 mm in the radial direction from the edge when the width of slit was 0.4 mm where the treatment time was 1.5 hour. This results indicates high potential of EBEP device for the nitriding of objects that have complex shape.

10:30 AM *P3.6
THE MICROSTRUCTURE AND WEAR BEHAVIOR OF Cr- AND W-DLC COATINGS SPUTTER-DEPOSITED ONTO AISI 52100 SUBSTRATES AS ELUCIDATED USING FOCUSED-ION-BEAM SEM. C.V. Cooper, United Technologies Research Center, East Hartford, CT; R. Wang, A.G. Evans, Princeton University, Princeton, NJ; H.K. Yoon, M.A. Taher, Caterpillar, Inc., Peoria, IL.

Magnetron sputtering has been used to deposit metal-containing, diamond-like-carbon (Me-DLC) coatings onto substrates composed of AISI 52100 steel in quenched-and-tempered condition. Coatings of two distinctly different compositions, one containing W as the metallic constituent and the second containing Cr, have been deposited in a plasma containing Ar and C_2H_2. Interrupted, unidirectional sliding experiments of the block-on-ring type have been conducted in a poly-alpha-olefin (PAO) lubricant at a load of 667 N for discrete numbers of cycles, N, of between 10 and 1000. Focused-ion-beam, scanning electron microscopy (FIB/SEM) has been applied to characterize the morphology of as-deposited and worn Me-DLC coatings. This technique has resulted in the determination that the Cr-DLC coating, deposited using the investigated processing parameters, fractures in a brittle manner through the formation and propagation of "channel cracks," which unzip in a direction parallel to the grinding direction outside of the region of contact. Conversely, the application of specific processing parameters to deposit W-DLC produces a coating that wears by gradual recession, consistent with polishing wear. Distinctive characteristics of the FIB/SEM technique and its efficacy and value in observing the coating and substrate subsurface will be highlighted as a means to investigate coating/substrate interfaces and to establish wear mechanisms.

11:00 AM P3.7
LOW FRICTION W-C:H COATINGS FOR WEAR RESISTANCE IN ROLLER BEARINGS AND GEAR WHEELS. Thorsten Kacsich, Metaplas Ionon GmbH, Bergisch Gladbach, GERMANY; Peter Werner Gold, Jörg Loos, Institute for Machine Elements and Machine Design, RWTH Aachen, GERMANY.

Life time limiting effects in roller bearings and gear wheel applications are wear, sizing and fatigue damages like micro pitting. These mechanisms are related to a number of parameters: lubrication conditions, surface roughness, and the hardness of the bulk material, for example. Nowadays, Me-DLC coatings like MAXIT^{TM} W-C:H offer surface protection under dry, mixed, and hydrodynamic friction conditions. This allows the increase of load capacities, respectively the decrease of gearing size. Moreover, the reduction of toxic lubrication additives can be achieved. The performance of the Me-DLC coatings in roller bearings was investigated on the FE8 test rig under mixed friction conditions. MAXIT^{TM} W-C:H was depositied via the PVD technique of magnetron sputtering onto case hardened steel bulk material. The deposition temperature was 180°C. The coating thickness was varied from 1.5 to 6μ with respect to optimized wear resistance. The wear of roll bodies and disks was drastically reduced by powers of ten as compared to uncoated roller bearings. Additionally, results on FZG gear wheel tests, as well as examples of the successful application of MAXIT^{TM} W-C:H in motor power engineering and hydraulic technique are presented.

11:15 AM P3.8
PITTING FATIGUE IN AUTOMOTIVE PLANETARY GEAR SETS. Leonid C. Lev, Neil Anderson, Gregory Mordukhovich, GM R&D, Warren, MI.

Operating conditions in typical automotive planetary gearsets lead to harsh tribological conditions. Relatively low operating speeds and low viscosity lubricants limit the formation of protective oil films. As power density demands increase, these conditions become more severe and pitting fatigue resistance becomes more important. In this study, typical gear contacts are characterized with two and three dimensional surface finish methods. The results are compared to film thickness predictions made with traditional EHD methods adapted to helical gear geometry and also with a 3D contact analysis programs to establish the operating regimes. SEM and digital micrographs are used to illustrate the condition of the surfaces at several stages of testing.

11:30 AM P3.9
THE EFFECT OF DEPOSITION CONDITIONS ON THE PROPERTIES OF W-DLC COATINGS. Christian Strondl, Hauzer Techno Coating, Venlo, THE NETHERLANDS; Ton Hurkmans, Hauzer Techno Coating, Conover, NC; Ron Dielis, Gerrit Jan van der Kolk, Hauzer Techno Coating, Venlo, THE NETHERLANDS.

Among the metal containing diamond like carbon coatings (Me-DLC) the W-DLC is most widely used in practice. The deposition conditions of these coatings control the film properties and the resulting mechanical and tribological properties. The coatings are all deposited at 160 degrees C by unbalanced magnetron sputtering from WC targets in an argon/acetelyne atmosphere. At this low temperature it is possible to coat low carbon steel types without changing their properties. The paper reports on the effect of substrate motion and strength of magnetic fields on coating properties like hardness and E-modulus and wear and fatigue resistance.

11:45 AM P3.10
PROCESS-PROPERTY RELATIONSHIPS OF ULTRA-THIN BORON CARBIDE FILMS. J.D. Kiely, Mei-Ling Wu, Timothy Klemmer, Yiao-Tee Hsia, Kent Howard, Seagate Research, Pittsburgh, PA.

Boron carbide (B_4C) is the third hardest material at room temperature. It has wide range of applications on coatings and cutting tools development. However, there are very limited studies of this material at ultra-thin regime (less than 10nm thick). In this paper, we characterize the properties of B_4C films with thicknesses less than 10 nm. We focus on nanotribological and mechanical properties of thin B_4C films deposited by magnetron and ionized magnetron sputtering techniques and compare the performance with those of diamond like carbon (DLC) films. Using atomic force microscopy (AFM), we have investigated the surface morphology of B_4C thin films deposited on Si substrates and have found that ultra smooth surfaces of B_4C thin films can be achieved. We find surface RMS roughness as low as 0.13 nm can be attained by applying appropriate substrate bias to enhance the ion bombardment during film growth. We have evaluated the mechanical properties using AFM nanoscratch techniques and find that these films have scratch resistances superior to that of DLC films. We have surveyed variations in mechanical properties as a function of deposition parameters, including sputtering pressure, RF ionized power, and target power, and correlate scratch resistance with other film properties such as composition and stress. Finally, we comment on the use of these films as protective overcoats for hard-disk recording media.

SESSION P4: DEPOSITION, CHARACTERIZATION, AND PROPERTIES OF FILMS AND COATINGS

Chairs: James E. Krzanowski and Gary L. Doll
Tuesday Afternoon, November 27, 2001
Room 311 (Hynes)

1:30 PM *P4.1
IN-SITU STRESS CLINIC FOR SURFACE ENGINEERS. Roy Clarke, University of Michigan Applied Physics Program, Darryl Barlett and Charles Taylor III, k-Space Associates Inc., Ann Arbor, MI.

The applications of thin-film coatings to satisfy a wide variety of technological needs, from machine tools to magnetic media and MEMS devices, have expanded enormously in recent years. These developments are made possible by increasingly powerful thin film deposition techniques whereby novel electronic, optical and mechanical properties can be achieved by structuring the coatings at the nanoscale level. The purpose of this presentation is to emphasize that the sophistication of methods to characterize these thin films and coatings, especially during their deposition, must keep pace with the extreme demands that particular applications place on their production. In this presentation we will describe in-situ, real-time, probes of thin film structure, morphology,and stress, showing how the information gained can be used to improve the quality and reproducibility of the coating process by closed loop feedback. We will focus on optical reflective methods which are very versatile and can be used in a wide variety of deposition situations. We will also demonstrate how real-time, in-situ probes have led to useful insights into the mechanism of thin film growth and stress remediation in ultrahard coatings such as cubic boron nitride. We also indicate some future opportunities for in-situ monitoring and control which hold promise for dramatic improvements in the capabilities and performance of thin-film coatings.

2:00 PM P4.2
CHARACTERIZATION OF THE DEGRADED MICRO-STRUCTURES OF A PLATINUM ALUMINIDE COATING.
Hyungjun Kim and Mark Walter, The Ohio State University, Department of Mechanical Engineering Columbus, OH.

Thermal barrier coatings (TBCs) are typically composed of a ceramic top coat, a thermally grown oxide, and an aluminide bond coat. Although bond coats almost universally contain aluminides, their composition and processing vary greatly. Recently developed models of TBC failure indicate that bond coat properties have a deterministic effect on the ultimate TBC failure. Given the need to understand the rate controlling mechanisms of TBC failure and the desire to design TBCs as integrated systems, study of the deformation of aluminide coatings is warranted. This paper concerns itself with an inward diffusing, unactivated pack cementation platinum aluminide (PtAl) bond coat system that is studied under isothermal exposure and thermal cycling up to 1100 degrees C. The highly non-homogeneous microstructure is presented for the various thermal exposures and the changes in elemental gradients are given. The PtAl coating is seen to interact strongly with the substrate. In order to characterize coating properties, spherical indentation experiments have been undertaken. Thermally grown oxide is removed after each thermal exposure. The indentation modulus for isothermally and thermo-cyclically exposed specimens gradually decreases over time. The modulus of the cyclically exposed specimen is higher than that of the isothermal specimen. Numerical simulations of the indentation experiments were undertaken. The simulations account for the elastic and plastic material properties of the dominant phases. Simulations are compared to the experimentally measured force and displacement curves as well as the residual area of the indent and the pile-up surrounding indent.

2:15 PM P4.3
FUNCTIONALLY GRADED MATERIALS PRODUCED WITH HIGH POWER LASERS.
Jeff Th. De Hosson, Department of Applied Physics, Netherlands Institute of Metals Research, Univ of Groningen, Groningen, THE NETHERLANDS.

In this work we explored a new method of producing functionally graded materials by laser-melt injecting ceramic particles in a metallic substrate. The laser melt injection (LMI) method is aimed at producing a metal matrix composite (MMC) layer on top of a substrate1. Unlike laser cladding, the contact between laser beam and added material in LMI is limited to a level that is just necessary to form a strong bonding interface between the ceramic particles and the metallic matrix in the final MMC layer. In this paper the method of laser melt injection of carbide particles into an Al or Ti-base substrate is investigated both experimentally and theoretically. An extremely small operational parameter window was found for successful injection processing of Sic in Al-alloys. It is shown that the final injection depth of the particles is mainly controlled by the temperature of the melt pool rather than by the particle velocity. A theoretical model that takes into account the wetting behavior and the particle penetration processes is developed on the base of the observed particle velocity, the thickness and the area fraction of the oxide skin that partially covers the surface of heated Al melt pool. The model reveals the role of the oxide skin in such a way that it is relatively strong at low temperature and acts as a severe barrier for the injection process. The mechanical and tribological properties of the coatings are tested and analysed using the Digital Image Correlation technique. 1 J. Th.M. De Hosson, in: Intermetallic and Ceramic Coatings, Marcel Dekker, N.Y., Edited by N.B. Dahotre, T.S. Sudarshan, p. 307-441, 1999.

2:30 PM P4.4
IN-PLANE CRACKING BEHAVIOR OF THERMALLY AGED AND CYCLED THERMAL BARRIER COATINGS.
Zhehua Zhang, Jun Kameda[a], Arne. H. Swanson, Iowa State University, Ames Laboratory, Ames, IA. [a]Office of Naval Research International Field Office, Tokyo, JAPAN; Shigeo Sakurai, Hitachi Ltd., Mechanical Engineering Research Laboratory, Hitachi, JAPAN; Minoro Sato, Tohoku Electric Power Co. Ltd., Sendai, JAPAN.

In-plane cracking behavior near and away from the interface of thermal barrier coatings (TBC) and thermally grown oxides (TGO) formed while in-service have been recently characterized in terms of the critical local tensile stress (σ*) using a protruded TBC bend testing technique together with a finite element stress analysis. It was shown that in-plane TBC cracking near the interface occurred more easily than that near the TBC midst. Near- and away-from-interfacial TBC cracking were shown to have opposite effects of the substrate thickness. The characteristics of in-plane TBC cracking are related to the formation of TGO and residual stresses induced by thermal cycling due to the thermal expansion mismatch. In order to examine how the two factors control in-plane TBC cracking, thermal ageing and cycling at 950°C in air were carried out in 8% Y_2O_3 stabilized ZrO_2 TBC/BC thermally sprayed over a Ni base superalloy substrate. Thermal ageing, giving rise to layered formation of TGO but no residual stresses, resulted in a slight increase in σ* for the near- and away-from-interfacial TBC cracking due to the sintering effect. In addition, in-plane TBC cracks near and away from the interface were initiated at the same σ*, respectively, in both the unaged and thermally aged specimens tested. These results indicate that the TGO formation itself does not cause the mechanical degradation of TBC near the interface. The effect of thermal cycling on the in-plane TBC cracking is examined to clarify the role of residual stresses in the in-plane cracking behavior. This study was carried out as Work for Other program approved by the USDOE, Office of Basic Energy Sciences, Division of Materials Sciences.

2:45 PM P4.5
AN INVESTIGATION INTO THE COATING/SUBSTRATE BOND IN THE HIGH VELOCITY PARTICLE CONSOLIDATION PROCESS.
S.C. Johnson, T.J. Eden, and M.F. Amateau, The Applied Research Laboratory, The Pennsylvania State University, State College, PA.

High Velocity Particle Consolidation (HVPC, also known as the cold gas dynamic spray technique) is a relatively new, low temperature, thermal spray competitive process used for applying wear resistant, corrosion resistant, and other coatings to a variety of substrates. The process generally involves using a converging-diverging nozzle to accelerating a high pressure gas with entrained powder particles to supersonic velocity and impinging the subsonic velocity powder particles onto a substrate. The mechanism by which the powder particles initially bond to the substrate and subsequently bond to previously deposited powder particles is not well understood. It has been proposed that the coating/substrate bonding mechanism is similar to cold welding processes. The bond between coating and substrate materials has been investigated for three different metallic materials; Al, Cu, and 316L stainless steel. These materials have been applied as similar coating/substrate combinations (i.e.; Al on Al) and as dissimilar coating/substrate combinations (i.e.; Al on 316L stainless steel). The interface between the as-deposited coating splats and the substrate has been characterized using optical metallography, SEM, and SEM-EDS. Results will be presented in an attempt to more quantitatively explain the mechanical and/or chemical nature of the bond between the coating and the substrate.

3:30 PM *P4.6
NANOSTRUCTURED THIN FILMS AND COMPOSITES.
Jagdish Narayan, Dept of MS&E, North Carolina State University, Raleigh, NC.

We review our research on the formation and properties of "artifact-free" nanocrystalline metallic and ceramic films and composites using controlled physical vapor deposition (PVD) such as pulsed laser deposition. Using relatively insoluble elements such as W and Ta in Cu and Zn, and NiAl in WC, we can modify interfacial energy and control the nucleation process which can be used to tune the grain (nanocrystallite) size. Using this approach, we were able to vary nanocrystallite size of zinc from 7nm to 100nm. Pulsed laser deposition lends itself to this novel approach where a monolayer of W or Ta is added after a certain thickness of Cu or Zn. The grain size is determined by the thickness as well as on other deposition parameters. Using this technique, we can form, for the first time, nanocrystalline materials with uniform grain size and controlled microstructure without porosity. It should be mentioned that by controlling the amount of W, Ta or NiAl, we can systematically vary the grain boundary properties and stabilize the nanostructures against recrystallization. We have shown that hardness increases with decreasing grain size (H $\propto$ d-) following the Hall-Petch relationship. However, the slope decreases with decreasing grain size and turns negative below a critical size (11nm for NC Zinc). This was considered to be the first definitive evidence for negative Hall-Petch behavior in nanocrystalline materials. We can control mechanical properties precisely by controlling grain size and boundary structure. By ranging the grain size as a function of distance from the interface, we can produce functionally gradient materials. As an example, softer more pliable material near the surface, which can improve adhesion and enhance wear properties of thin film coatings. Thus, an accurate control over the grain size and boundary structure/chemistry can be result in functionality by design.

4:00 PM P4.7
SPECTROSCOPIC ELLIPSOMETRY AS A POTENTIAL IN-LINE

METROLOGY TOOL FOR POROSITY MEASUREMENTS OF LOW-K DIELECTRIC FILMS. N.V. Edwards, J. Vella, Q. Xie, S. Zollner, I. Adihetty, Motorola Materials and Structures Laboratories, Mesa, AZ; J. Vires and K.H. Junker, Motorola Materials and Structures Laboratories, Austin TX.

The International Technology Roadmap for Semiconductors predicts that the progressive downward scaling of device dimensions required for the 100nm technology node will require materials with dramatically lower static dielectric constants, achieved without sacrificing robust mechanical properties. One strategy for achieving these ultra-low-k materials is to incorporate porosity into otherwise dense dielectrics, yet there is no definitive in-line metrology solution that yields porosity and mechanical property information. Our results obtained on OSG (organosilicate glass) suggest that optical techniques might provide a crucial first step toward such a solution: mechanical hardness can be correlated with ellipsometrically-obtained porosities. Spectroscopic ellipsometry (SE) was performed from 0.7 to 6.5 eV on a series of low k OSG films with a Woollam VASE ellipsometer. While preliminary TEM and XPS measurements yielded no observable differences in the films, SE results yielded: (1) Samples with dramatically higher hardness had higher indices of refraction (RI) and thus lower porosities than films with lower hardnesses. The reverse was true for films with low hardnesses. (2) The films did not have the same optical properties as porous SiO_2 across the spectral range measured. The change in structure introduced by the interstitially located methyl groups in the OSG film manifests itself in the optical data in a way that is very different from merely triggering an increase in the porosity of the SiO_2 film. In order to understand the unusual absorption behavior of the films and its correlation to film mechanical properties, the ellipsometry measurements were extended into the Vacuum Ultraviolet (to 8.7 eV) with a J.A. Woollam VUV Ellipsometer and the absorption edge of these materials was observed for the first time. These results will be explained in the context of Electron Energy Loss and X-Ray Reflectivity spectra, which in turn yield additional information about nanoporosity and film density, respectively.

4:15 PM P4.8
ALUMINOSILICATE ENVIRONMENTAL BARRIER COATINGS FOR SiC CERAMICS. Ramanathan Krishnamurthy, Brian W. Sheldon, Division of Engineering, Brown University, Providence, RI; J. Allen Haynes, Oak Ridge National Laboratories, Oak Ridge, TN.

It is now well established that SiC ceramics suffer from severe oxidation problems in high-temperature environments that contain water vapor. Aluminosilicates have a lower silica activity than the native silica layer and are thus being considered as possible protective coating materials. In this investigation, we examine the stability of these coatings in typical operating environments. Most of this work emphasizes mullite as a model material, however, more complex materials such as Barium aluminosilicates will also be discussed. Mullite is a non-stoichiometric oxide that can tolerate a significant range of O, Si, and Al compositions. A multi-species diffusion formalism for ionic species is adopted for the purpose of our study. Onsager reciprocity is assumed for the mobility coefficients and a resulting moving boundary problem is solved numerically. These model calculations are also compared with experimental results, and then used to design optimal coatings and to predict life.

4:30 PM *P4.9
NOVEL PREPARATION METHOD OF THIN FILMS BY ABLATION PLASMA PRODUCED BY INTENSE PULSED ION BEAM. Kiyoshi Yatsui, Hisayuki Suematsu, Weihua Jiang, Tsuneo Suzuki, Sung-Chae Yang, Yoshiaki Kinemuchi, and Makoto Hirai, Extreme-Energy Density Inst., Nagaoka Univ. of Technology, Nagaoka, Niigata, JAPAN.

If an intense pulsed ion beam is irradiated on solid target, high-density ablation plasma is produced because the energy density will be high due to short range in the target. In 1988, the author proposed and demonstrated quick preparation of thin films of ZnS by the ablation plasma, named intense pulsed ion beam evaporation (IBE). The preparation has been carried out without substrate heating or post-annealing, in a vacuum, with the instantaneous deposition rate on the order of cm/s. Good stoichiometry has been kept between the target and the films. Since basic principle has been published elsewhere, new results on the preparation of crystallized B_4C films are discussed here since we believe this is the first time in the world. As well known, B_4C is a hard material after diamond. It is wear resistant as well. The melting point is 2,450°C, and it is very stable even at high temperatures. Furthermore, it is a good thermoelectromotive material, where Seebeck coefficient is considerably high. Nobody has succeeded in the preparation of the crystallized films. The experimental results, together with various characterizations by XRD, FT-IR, EELS, FE-SEM, high resolution TEM, and hardness tester, revealed that the crystallized B_4C films have been successfully prepared by IBE. Vickers hardness of 2,300 has been obtained by the films. Similar results of the preparation of many kinds of films will be presented on, for example $(Ba,Sr)TiO_3$, YBaCuO, ITO, $SrAl_2O_4$:Eu,Dy and polycrystalline Si. Furthermore, such a high-density plasma provides to synthesize ultrafine nanosize powders, typically characterized as 5 - 20 nm in diameter, by rapid cooling with the ambient gas. By various combinations of the target and the gas, we have succeeded in the synthesis of powders of Al_2O_3, AlN, TiO_2, and TiN. Fruitful applications seem to be available by the high-density ablation plasma produced by pulsed ion beam.

SESSION P5: POSTER SESSION
SYNTHESIS AND CHARACTERIZATION
Chairs: Wen Jin Meng, Ashok Kumar, Yip-Wah Chung, Gary L. Doll, Yang Tse Cheng and Stan Veprek
Tuesday Evening, November 27, 2001
8:00 PM
Exhibition Hall D (Hynes)

P5.1
ADVANCES IN CATHODIC ELECTRODEPOSITION OF ORGANOCERAMIC FILMS. Igor Zhitomirsky, A. Petric, Dept. of Materials Science and Engineering, McMaster University, Hamilton, Ontario, CANADA.

The rapidly increasing scientific interest in electrodeposition of organoceramic materials has opened new opportunities in development of advanced thin films for novel applications. Electrodeposition offers important advantages such as rigid control of surface uniformity and deposition rate as well as the possibility of formation of multilayer deposits of controlled thickness on substrates of complex shape and on selected areas of the substrates. Organoceramic films based on oxides or hydroxides of Zr,Ce,Gd,Fe,Ni,Cr,Y,Cu,Co,La and cationic polyelectrolytes, such as poly(diallyldimethylammonium chloride), polyethylenimine, poly(allylamine hydrochloride) were prepared. The deposition method is based on electrolytic (ELD) or electrophoretic (EPD) deposition of inorganic phases and EPD of polymers. Cathodic electrodeposition of polyvinyl alcohol (PVA) involves a pH increase and electrochemical crosslinking of PVA molecules near the cathode surface. EPD and ELD were used for intercalation of ceramic particles into growing polymer films. By varying the current density and concentration of polymer, ceramic and electrolyte, the amount of the deposited material and its composition could be controlled. Deposition rate was evaluated at different experimental conditions. Films in the range of thickness up to 10 microns were prepared as monolayers or laminates of different materials. Possible applications of the prepared materials are discussed.

P5.2
IN-SITU MONITORING OF NUCLEATION STAGE DURING ALUMINUM-CVD FOR NANO-STRUCTURE CONTROL. Tomohisa Iino, Masakazu Sugiyama, and Yukihiro Shimogaki, Univ. of Tokyo, School of Engineering, Tokyo, JAPAN.

The ever growing integration of ULSI devices reduces the device feature size. The sub-micron devices require continuous and smooth film with thickness of several nano-meter. These technical trend arouse the interest and importance of initial nucleation during film growth by chemical vapor deposition (CVD). We have examined the kinetics of aluminum CVD using dimethylaluminumhydride (DMAH) as the source precursor, and established elementally reaction mechanism of this CVD process. We could succeed in improving surface morphologies by the aid of this chemical perspectives. The only thing that remained as a black box is the initial nucleation issues. We have employed in-situ monitoring of surface morphologies by laser-light reflection. This method enabled us to monitor the incubation time before the nucleation of CVD-Al. We investigated the change of incubation time by the change of DMAH concentration and the substrate temperature. The higher concentration of DMAH provides shorter incubation time and higher reflectivity in laser light reflection. These nucleation behavior of Al-CVD will be discussed in conjunction with the elementary surface reaction mechanism.

P5.3
FABRICATION OF CaO INSULATOR COATINGS BY MOCVD FOR APPLICATION IN FUSION REACTOR BLANKETS. Zuotao Zeng, Ken Natesan, Argonne National Laboratory, Energy Technology Division, Argonne, IL.

The liquid lithium blanket for fusion reactors requires an electrically insulating coating on the duct to minimize the magnetohydrodynamic pressure drop that occurs during the flow of liquid metal in a magnetic field. Calcium oxide (CaO) is a good candidate for the coating material because it is an excellent electrical insulator and also

because it is stable in a liquid lithium environment. In this paper, details are presented on the metalorganic chemical-vapor deposition method that was used to fabricate the CaO Coating. A 20-μm thick CaO coating was successfully obtained by this method. Composition and phase analyses of the coating were performed by energy dispersive X-ray analysis and X-ray diffraction. Scanning electron microscopy images show that the coating did not crack after several thermal cycles from room temperature to 715°C. The resistance of the coating is high enough for an insulating coating on the liquid lithium blanket of fusion reactors.
Work supported by U.S. Department of Energy, Office of Fusion Science, under Contract W-31-109-Eng-38.

P5.4
MEASUREMENT OF MECHANICAL PROPERTIES OF SINGLE AND MULTI-LAYERED NITRIDE THIN FILMS PREPARED BY CATHODIC ARC DEPOSITION. A.K. Sikder[a], I.M. Irfan[a], Ashok Kumar[a], Robert Durvin[b] and M.D. Smith[b]; [a]Center for Microelectronics Research, College of Engineering, University of South Florida, Tampa, FL; [b]BryCoat Inc., Safety Harbor, FL.

Mechanical properties of thin films differ significantly from those of bulk materials due to the effects of interfaces, microstructure and thick underlying substrates. In this study we will present the results of nanoindentation tests to evaluate mechanical properties of nitride (TiN, CrN, TiCN and TiAlN) single and multi-layered thin films. Films were coated on steel substrates using cathodic arc deposition technique. We have extended the measurement to the multilayer coating with indenter displacements increasing to different layer thicknesses. Nanoindentation was performed by MTS NanoIndenter XP with a Berkovich indenter. Indentation mark and defects created by nanoindentation was investigated using scanning electron microscopy (SEM). Surface morphology of the samples was studied using SEM and atomic force microscopy. Also using SEM/AFM we have observed elastic/plastic deformation, cracking, phase transformation etc.

P5.5
CaO ELECTRICAL INSULATOR COATING ON V-4%Cr-4%Ti: FUNDAMENTALS AND APPLICATIONS. J.-H. Park, K. Natesan and D.L. Smith, Energy Technology Division and Technology Development Division, Argonne National Laboratory, Argonne, IL.

The objective of this study is to assess our basic understanding of the thermodynamic and kinetic aspects of fabricating and/or self-healing of defects of electrically insulating CaO coatings for use in vanadium/lithium magnetic fusion reactor blankets. To form CaO film at the interface of V-Ti-Cr-alloys and the liquid lithium, it needs precharged-O from the V-Ti-Cr-alloys, and Ca in the liquid lithium. To understand O-incorporation in the alloys, we used the binding and/or formation energies between the metal elements and O. Additionally, we conducted several experiments on in-situ fabrication of CaO film ($\sim$10 μm thickness) on the V-Cr-Ti-alloys. *Work supported by the U.S. Department of Energy, Office of Fusion Science, under Contract W-31-109-Eng-38.

P5.6
SPUTTER-DEPOSITED BCC TANTALUM ON STEEL WITH AN INTERFACIAL TANTALUM NITRIDE LAYER. Anamika Patel, Marek Sosnowski, Leszek Gladczuk, New Jersey Institute of Technology, Dept of Electrical Engineering, Newark, NJ.

Tantalum has mainly two phases: alpha phase (bcc structure) and beta phase (tetragonal structure). The meta-stable beta phase is usually obtained in sputtered films. Alpha phase is preferred over the beta for some applications as beta phase is very brittle. One of such application is to protect steel from the erosive and the corrosive wear. It was found that with the intermediate layer of tantalum nitride the preferred alpha phase was grown on steel by DC magnetron sputtering technique. Electrical and structural properties of these films were studied by four-point probe measurment and x-ray diffraction (XRD). Stociometery of interfacial tantalum nitride layer was investigate by rutherford backscattering (RBS). Influence of the interfacial film thickness and the flow ratio of argon and nitrogen gas during reactive deposition of tantalum nitride on the tantalum phase was investigated. This work also reports on the dependence of tantalum phase on the sputtering gas (Ar, Kr) and on the substrate temperature (100-400°C) during deposition.

P5.7
A NOVEL SILICON-CARBON PRECURSOR FOR OLIGOMER CHEMICAL VAPOR DEPOSITION OF SILICON CARBIDE FOR HARSH ENVIRONMENTAL APPLICATIONS. Ulrike Futschik, Harry Efstathiadis, James Castracane, Alain E. Kaloyeros, UAlbany Institute for Materials and School of Nanosciences and Materials, The University at Albany-SUNY, Albany, NY; Leo Macdonald, Susan Hayes, and Walter Sherwood, Starfire Systems Inc, Watervliet, NY; and Costas Fountzoulas, Army Research Laboratory, Weapons Material Directorate, Aberdeen Proving Ground, MD.

Silicon carbide (SiC) films have been successfully deposited on various substrates by low pressure oligomer chemical vapor deposition (OCVD) from a novel, halogen free, oligomer precursor, hydridopolycarbosilane (HPCS). The high quality films were grown at substrate temperature in the range of 600C to 1200C and at process pressure in the range of 1 15 Torr. HPCS is a silicon carbide precursor composed of an alternating silicon and carbon backbone with hydrogen side groups. Depositions on silicon and graphite substrates yielded stoichiometric SiC films with thickness in the range 0.3 to 50 microns. Structural and chemical characterizations were performed by Auger electron spectroscopy (AES), x-ray diffraction (XRD), electron microprobe, Fourier transform infrared spectroscopy (FTIR), and optical and scanning electron microscopy (SEM). Environmental reliability studies were carried out by exposing the films to oxidizing flame jets and to acid/alkali baths for extended duration. The film nanohardness, modulus of elasticity, and ball-on-disk friction coefficient properties were measured using a nanoindenter, a Knoops hardness tester, and a ball-on-disk tribometer tester. The SiC coatings deposited at substrate temperatures below 1100C were found to be amorphous. Ex-situ post deposition annealing in inert gas above 1100C converted the SiC films to a polycrystalline phase. The OCVD SiC coatings are being examined for applications such as rocket nozzles, furnace hardware and other high temperature and corrosive uses. The films are also being investigated for use in Nano/Micro Fluidic structures for custom designed components such as valves, pumps and channels in corrosive or high temperature environments.

P5.8
CVD DIAMOND SYNTHESIS ON WC-Co CUTTING TOOL VIA ELECTROPHORETIC SEEDING PROCESS. Toshiki Tsubota, Masanori Nagata, Kumamoto Industrial Research Institute, Material Development Dept., JAPAN; Naoki Okada, Shintaro Ida, Yasumichi Matsumoto, Kumamoto University, Faculty of Engineering, JAPAN; Nobumitsu Yatsushiro, Kumabou Metal, Kumamoto, JAPAN.

Using ECR-MPCVD (electrocyclotron resonance microwave plasma checmical vapor deposition) apparatus, CVD, diamond film synthesis was attempted on WC-Co cutting tools. Electrophoretic deposition was utilized as a seeding process for the synthesis of CVD diamond films. A commercial diamond powder (grain size: 250 nm) was employed in this study. The diamond powder was suspended in acetone at the concentration of 0.1 g L-1, and was electrophoretically deposited on substrates. Si(100) plate or commercial WC cutting tool was used as an anode, and Pt plate was used as a cathode for electrophoretic deposition. The diamond particle density of Si(100) substrate depended on the electrophoretic condition. After electrophoretic pretreatment, CVD diamond was deposited on the WC substrate using ECR-MPCVD appartus. Electrophoretic deposition was effective for the synthesis of CVD diamond film on WC cutting tool without removing the cobalt on the surface, although the adhesion force between the CVD diamond and the WC substrate was insufficient for the application to a cutting tool. Heat treatment after electrophoretic deposition improved the adhesion force of CVD diamond. The strength of this adhesion force for the sample given the electrophoresis-heat pretreatment was as same as that for the sample given scratch pre-treatment, which is a popular pretreatment.

P5.9
NEW DEVELOPMENTS IN ELECTRODEPOSITION OF THIN FILMS FOR FUEL CELL APPLICATIONS. Igor Zhitomirsky, A. Petric, McMaster Univ., Hamilton, Ontario, CANADA.

Two processes were used to prepare ceramic coatings by cathodic electrodeposition: electrophoretic deposition (EPD) and electrolytic deposition (ELD). It was demonstrated that the ethyl alcohol-phosphate ester-polyvinyl butyral system is an effective solvent-dispersant-binder system for EPD of advanced materials for solid oxide fuel cells, including electrolytes, electrodes and barrier layers. EPD was used to produce single layers as well as consequtive layers of different materials. ELD has been utilized for deposition of thin electrolyte layers or intermediate layers preventing electrode/electrolyte degradation and protection of interconnects. A technique for electrodeposition of dense ceramic layers on porous electrode materials was developed. Organoceramic or polymer layers were utilized as intermediate layers to prevent penetration of ceramic particles (EPD) or ions (ELD) into porous electrodes. The techniques used for deposition of polymers and organoceramic materials include EPD, ELD and electrochemical crosslinking. In the case of organoceramic deposits, a two fold beneficial effect is expected: the possibility of deposition of dense electrolyte layers on porous electrodes and formation of barrier ceramic layers in the sintered product. Application of electrodeposition in various fuel cell technology configurations is discussed.

P5.10
CHEMICAL VAPOR DEPOSITION OF TUNGSTEN NITRIDE AS COPPER DIFFUSION BARRIER. Yang-Ming Sun, Ward Engbrecht, Tibor Bolom, Jang H. Sim, Cris Cilino, John M. White, and John G. Ekerdt, Texas Materials Institute, The University of Texas at Austin, Austin, TX; Steven Smith, Klaus Pfeifer Sematech International, Austin, TX.

Chemical vapor deposition of tungsten nitride using $W(CO)_6$ and NH_3 was studied by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and electron microscopy. At the temperature range from 250°C to 475°C, the tungsten to nitrogen ratio varied with NH_3 to $W(CO)_6$ flow ratio and the electrical resistivity increased with the increase of nitrogen content. The tungsten and nitrogen chemical states were identified by XPS as tungsten nitride. However, absence of sharp diffraction peaks in XRD spectra indicated that nitride films were grown with an amorphous or nano-crystalline structure. This was further proved by cross section transmission electron microscopy. 5 to 8 nm thick nitride films were tested for copper diffusion barrier resistance. After annealing a Cu/W2N/SiO2 stack at 360°C for 8 hrs, secondary ion mass spectroscopy (SIMS) depth profile revealed that copper was still constrained in the barrier. The film roughness increased at the lower growth temperature range 270 to 290°C. The increase of roughness was attributed to the face that the preferential growth on the nucleation sites might be enhanced. This was because of the increased difference of surface reactivity towards precursor decomposition at nucleation sites and bare substrate at low growth temperature. A thin seed layer of tungsten pre-deposited by plasma enhanced CVD significant changed the growth mode and improved the film roughness at low growth temperature. The interfacial interaction between tungsten nitride and several low dielectric materials was also investigated by in-situ XPS study.

P5.11
HYDROGEN FREE, HIGH SP^3 CoONTENT DLC FILMS PRODUCED BY PULSED LASER ABLATION OF AMORPHOUS GRAPHITE. J. Haverkamp, R.M. Mayo, Department of Nuclear Engineering, North Carolina State University, Raleigh, NC; J. Narayan, T.K. Nath, C. Jin, Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC.

Pulsed laser ablation is a unique technique for the deposition of a wide variety of thin films. These films include magnetic and optical films, novel semiconductors, high temperature superconductors, and diamond-like carbon films. Amorphous Carbon material is evaporated from a solid target and ionized by a high-energy KrF laser and ejected as a plasma plume. The plume expands outwards and deposits the target material on a silicon substrate. Plasma and flow parameters in this plume determine the quality of the thin film deposited on the substrate. In these experiments, a triple Langmuir probe is used to determine various plasma properties in the plume as a function of laser energy density on target, laser spot size on the target and probe position from target. These properties include electron temperature, ion flow speed, ion kinetic energy, plume peaking parameter, and ion density. Collisionality of the plume is inferred from plasma parameters. Plume energy balance shows that as much as 90% of the incident laser energy is converted directly to ion and neutral carbon atom kinetic energy. The bulk of the remainder is in thermal energy, with some small fraction going to conduction within the target and radiation. Film analysis was conducted by electron energy loss spectroscopy (EELS) indicating that DLC films have been sucessfully deposited with an sp^3 concentration as high as 72%.

P5.12
REAL-TIME UV-EXTENDED SPECTROSCOPIC ELLIPSOMETRY FOR CHARACTERIZATION OF CUBIC BORON NITRIDE. J.A. Zapien, R.W. Collins and R. Messier, Materials Research Laboratory, The Pennsylvania State University, University Park, PA.

The demand for real-time characterization techniques in thin film science and technology is motivated by the need to engineer complex graded deposition sequences that yield improved film characteristics. Optical characterization techniques, in particular real-time spectroscopic ellipsometry (RTSE), are well suited for measurement, monitoring, and control of such deposition sequences. Recently, we developed a uv-extended rotating polarizer multichannel ellipsometer with spectral capabilities covering the photon energy range from 1.5 to 6.5 eV (uv-RTSE). Given its minimum acquisition time of 24.5 ms while maintaining sub-monolayer sensitivity, the uv-RTSE is ideal for studying wide band gap thin film deposition in real time, including diamond, cubic boron nitride (cBN), and silicon oxy-nitrides (a-SiO_xN_y), among many other materials. cBN is a promising material for a number of applications ranging from hard protective coatings for cutting tools and optical elements to high temperature and high power electronic devices. To date, most of the research in cBN focuses in the study and control of cBN compressive stress and adhesion failure. Several techniques have been proposed to improve film adhesion and decrease film stress, and often these techniques involve the use of complex graded deposition sequences. The ability of uv-RTSE to resolve the phase evolution of BN films has been documented recently for cBN films grown using magnetron sputtering of BN and B_4C targets. In this contribution new findings on the effects of dynamic deposition conditions on the phase evolution of BN films grown by pulsed dc sputtering of a B_4C target and rf substrate biasing will be presented. In addition, improvements in data measurement and analysis resulting from the use of a new uv-RTSE design, the rotating compensator configuration, will be presented.

P5.13
COMPARISON OF MICROSTRUCTURES PRODUCED BY HIGH-KINETIC ENERGY PULSED INTENSE ION BEAMS WITH THOSE FROM MORE CONVENTIONAL TECHNIQUES. T.J. Renk, P.P. Provencio, S.V. Prasad, Sandia National Laboratories, Albuquerque, NM; J.R. Treglio, Cutting Edge Products, Poway, CA; M. Kawamura, Kitami Institute of Technology, Dept. of Materials Science, Kitami, JAPAN.

Intense pulsed beams of ions (700 keV, up to 400 A/cm^2, 150 ns, various species) can be used to modify the near-surface of materials through rapid heating, followed by rapid cooling into the substrate. This can produce grain refinement, mixing of species, and creation of metastable alloys that can demonstrate enhanced wear durability and corrosion resistance. At higher deposited energy, such beams can also produce thin-film layers by ablation and redeposition, in the same manner as pulsed laser deposition (PLD). As an example of the modification process, we have investigated the microstructure and wear durability of Pt-enriched Ti produced by two different techniques: 1a) high-dose ion implantation of Pt into a Ti substrate (70 keV, at 10^{17} cm^{-2}), and 1b) a 1 micron Pt/Ti sputtered layer mixed into a Ti substrate by a high-power ion beam. In the case of 1b), a metastable Pt/Ti phase was formed in the near-surface region. In both cases, cross-sectional transmission electron microscopy (XTEM) shows that microstructural changes were observed that extended well beyond the ion range and heat-affected zone, 1 micron in the implanted case, 150 microns in the ion beam case. Tribological wear tests are planned to correlate these microstructures with wear behavior. As an example of the ablation process, we have produced 1 micron Pt layers on Si (100) using both 2a) balanced magnetron sputtering, and 2b) high energy ion beam ablation. XTEM observations show that 2a) produces a polycrystalline micron-scale Pt layer, in contrast to the sub-micron grain size produced by 2b). Layers were produced both at room temperature, and at 350C. More XTEM is planned, and latest results will be presented.

P5.14
LASER WRITING OF NANOSTRUCTURES ON MAGNETIC FILM SURFACES WITH OPTICAL NEAR FIELD EFFECTS. S.M. Huang, M.H. Hong, D.M. Liu, W.D. Song and Y.F. Lu, Laser Microprocessing Laboratory, Data Storage Institute and Department of Electrical & Computer Engineering, National University of Singapore, SINGAPORE.

Laser directly writing of nanostrucrures on magnetic film surfaces with optical near field effects has been investigated. Spherical 0.5 micrometer silica particles were placed on Cr/CoCrPt multilayers. After laser illumination with a pulsed Ti:Sapphire laser, hillocks with size of about 350 nm were obtained at the original position of the particles. The mechanism of the formation of nanostructure pattern was investigated and found to be the near-field optical resonance effect induced by particles on the surface. A comparison with relative theoretical calculations of near-field light intensity distribution showed good agreement with the experiment results. The method of particle enhanced laser irradiation allows the study of field enhancement effects as well as its potential applications for nanolithography.

P5.15
CHARACTERISTICS OF POLYCRYSTALLINE SILICON THIN FILMS PREPARED BY PULSED ION-BEAM EVAPORATION. Sung-Chae Yang, Ali Fazlat, Hisayuki Suematsu, Weihua Jiang and Kiyoshi Yatsui, Extreme Energy-Density Research Institute, Nagaoka University of Technology, Nagaoka, Niigata, JAPAN.

The preparation of polycrystalline silicon (poly-Si) thin films has received much attention due to their wide application potential for a semiconductor in thin film transistors (TFTs), solar cells, peripheral circuits of liquid-crystal displays, and electrodes in Si-integrated circuits. Conventionally, poly-Si films were prepared by a plasma-enhanced chemical vapor deposition (PECVD) method with post annealing (~800°C) of a-Si:H films or substrate heating (200 - 400°C). This technique requires high processing temperatures and a long processing time. Since such a high temperature limits substrate materials or fabrication process. For practical engineering applications, furthermore, the very low deposition rate is a serious problem for achieving higher throughput of electronic devices, such as solar cells. If the pulsed proton beam irradiates solid targets, high-density ablation plasma can be produced due to short range of protons in targets. Using such the plasma, it has been found out to prepare thin films very efficiently, which was called as intense, pulsed, ion beam evaporation (IBE). After the first demonstration of the preparation of thin films of ZnS in 1988, various kinds of thin films have been successfully prepared by IBE, e.g., YBCO, ITO, $BaTiO_3$, BN, SiC, TiO_2, ZrO_2, and AlN. One of the aims of this study is to prepare poly-Si thin films without heating the substrate by IBE. By using IBE, we have succeeded in the preparation of polycrystalline silicon thin films without impurities on the substrate of silicon and quartz. High crystallinity and deposition rate (280 nm/shot) have been achieved. The crystallinity of poly-Si film has been improved with increasing the density of the ablation plasma. The crystallinity and the density of poly-Si thin films are increased by (-) bias voltage on the substrate. In this presentation, we will report the characteristics of poly-Si thin films prepared by using a high-density ablation plasma produced by IBE.

P5.16
ELECTROCHEMICAL SYNTHESIS OF CARBON DIAMONDLIKE COVERS ON METALLIC SUBSTRATES. Vladimir Novikov, Larisa Kuznetsova Institute of Solid State and Semiconductor Physics, Minsk, BELARUS; Patrice Aublanc LMGP ENSPG/CNRS, St Martin d'Héres; FRANCE; Michel Mermoux, LEPMI/ENSEEG/CNRS, St. Martin d'Héres, FRANCE.

Some attempts to synthesize diamond-like carbon coatings on metallic substrates using a new electrochemical technique are presented. The electrolyte was a molten mixture of potassium acetate, sodium formiate and sodium borohydride. Nickel, titanium, zirconium and stainless steel were used as electrode materials. The electrolysis was carried out in the 250 - 300°C temperature range. A shifted sinusoidal alternating voltage (50 Hz) of amplitude higher than 20V was applied to the electrochemical cell. The voltage shift was 5 - 10V, the current density was observed to vary from 0.5 to 0.5 A/cm^2. For each run, the electrolysis duration was about 30 min. Anodic oxidation of carboxilate ions leads to carbon deposition, while the presence of sodium borohydride in the electrolyte seems to provide some boron-doping of the carbon film. With the growth conditions described above, 2 μm thick, gray films were obtained on the substrate surfaces. These films have a strong adhesion to the substrate. For their analysis, they were subsequently removed from the metallic substrates using suitable acids. Then, the free standing films were cleaned in perchloric acid. Auger electron spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy, Raman and Infra Red spectroscopy were used as characterization methods. From SEM, these films appeared to be made of fine grains, with an average grain size of about 0.1 μm. Up to 1 at. % boron may be present in films. Raman spectra were similar to those usually reported for diamond-like materials and C-H bonds were observed from FTIR measurements.

P5.17
PREPARATION OF TiFe THIN FILMS BY PULSED ION BEAM EVAPORATION. H. Suematsu, T. Saikusa, T. Suzuki, W. Jiang and K. Yatsui Extreme Energy-Density Research Institute, Nagaoka University of Technology, Niigata, JAPAN.

TiFe is a hydrogen-storing alloy which can absorb hydrogen atoms as much as 1.8 wt% of the alloy. Because of the high reactivity of Ti with oxygen, thin films of crystallized TiFe have not been obtained. A novel thin film deposition method of pulsed ion-beam evaporation (IBE) enables us to prepare various crystallized thin films at room temperature. In the IBE method, a high density ablation plasma ($\sim 10^{19}$/cm^3) is formed. Thus, it was expected that the oxidation of the TiFe thin film may be prevented because the number of oxygen atoms in the vacuum chamber ($\sim 10^{15}$ particles) is too small to reacts with all the Ti and Fe atoms in the high density plasma. In the present work, preparation of TiFe thin films by IBE is performed. Thin films of TiFe were prepared in a pulsed ion beam generator ('ETIGO-II'). A pulsed ion beam of proton accelerated at 1 MV (peak) with a pulse width of 50 ns and a current of 70 kA was focused on a TiFe alloy target. Si single crystal and SiO_2 glass substrates were placed in front of the target. Phases in the thin films were identified by X-ray diffraction (XRD). XRD results revealed that the thin films deposited on the SiO_2 glass substrates consist of a TiFe phase. Although the films also contain a small amount of $TiFe_2$ as a second phase, there are no Ti-O or Fe-O phases in the films. Crystallized Ti-Fe thin films without oxides were successfully obtained. On the other hand, thin films deposited on the Si single crystal substrates consists of an amorphous Ti-Fe phase. The formation of amorphous phase on the Si was considered to be due to the fast quenching speed of the plasma on Si substrate, which has a higher thermal conductivity than that of SiO_2 glass.

P5.18
RAPID THERMAL PROCESSING OF POLYMER SURFACES. Michael J. Kelley, Thomas Jefferson, National Accelerator Facility, FEL Group, Newport News, VA and The College of William and Mary, Dept of Applied Science, Williamsburg, VA; Fredrick C. Zumsteg, E.I. DuPont Co. Inc., Central Research, Wilmington, DE.

Polymers offer a combination of low thermal conductivity, low heat capacity and strong absorption at selected wavelengths that makes them especially amenable to surface transformation by rapid thermal processing. Surface amorphization, micro-roughening or chemical transformation can be attained. We present experimental and computational results for PET polyester film using UV (excimer) and IR (FEL) laser irradiation.

P5.19
TIMING EFFECT OF SOLID SOURCE APPLICATIONS ON Si-C-N FILM DEPOSITION. Hui Lin Chang, Jing Hwa Lin, Cheng Tzu Kuo, Department of MS&E, National Chiao Tung University, Hsinchu, TAIWAN.

The Si-C-N films were synthesized on Si substrates by a MPCVD system using a mixture of CH_4 and N_2 as gas sources. The Si columns coated with Co film on one side were placed around the specimen to act as catalyst and additional Si source. The films were deposited by two conditions, i.e., applying both catalyst and additional Si source either: (1) before or (2) during film deposition. The preliminary results show that the timing of catalyst and Si source applications plays an important role. The films deposited by condition (1) show crystals with more re-nucleation phenomena, closer to T-Si_3N_4 crystal structure, less Si content, existence of Si(2p)-C bonding, lower nano-hardness and better field emission properties. In contrast, the films of condition (2) reveal the crystals with structure closer to α-Si_3N_4 and show an additional amorphous layer under the crystalline layer. The differences in structure and property between the films deposited by two conditions can be reasoned by the following facts. The condition (1) is close to the condition of carbon nitride deposition on $CoSi_x$ substrate, and gives more chance for C atoms to react with N atoms due to less Si source. The condition (2) supplies more Si source and greatly dilutes the catalytic effect of Co; therefore, more C sites are replaced by Si atoms, and results in no detectable Si(2p)-C bonding. The condition (2) also gives more chance for the substrate to react with gases to form an addition amorphous layer. The difference in nano-hardness between two conditions may relate to difference in crystal structure. The possible deposition mechanisms will be discussed.

P5.20
DURABLE OPTICAL FILM FORMATION WITH O_2 CLUSTER ION ASSISTED DEPOSITION. Noriaki Toyoda, Shinji Matsui, Laboratory of Advanced Science and Technology for Industry, Himeji Institute of Technology, Hyogo, JAPAN; Michitaka Terasawa, Dept of Engineering, Himeji Institute of Technology, Hyogo, JAPAN; Isao Yamada, Collaborative Research Center for Cluster Ion Beam Process Technology, Kyoto, JAPAN.

Formation of high-quality optical film is getting very important to fulfill the rapid progress of optical components. These films must be durable, dense and very flat. We have developed a noble film formation process by cluster ion beam assisted deposition. When cluster ions bombard a target, the bombarded area experienced high-temperature and high-pressure conditions transiently. It realizes enhancement of chemical reactions near the surface and formation of high-density films without a thermal treatment for the substrate. Also, we have shown that cluster ion beams have a surface smoothing effect that is important to fabricate a multi-layer structure. In this work, Ta_2O_5/SiO_2 multi-layer was fabricated with O_2 cluster ion assisted deposition. Ta_2O_5 and SiO_2 were supplied with an electron beam evaporator, and O_2 cluster ion bombards a target with energy of 3 to 9keV. The substrate was kept at room temperature. As an average O_2 cluster size was approximately 1000, the kinetic energy of each O_2 molecule was less than 10eV. After an environmental test, the Ta_2O_5/SiO_2 surface without O_2 ion irradiation was wrinkled, which was caused by a percolation of water due to a low-density of the film. However Ta_2O_5/SiO_2 with O_2 cluster ion irradiation showed a very flat surface with roughness below 1nm. The wavelength shift of a transmitted light after the environmental test was less than 1nm. It indicates a dense oxide film was formed with O_2 cluster assisted deposition. Besides durability, characterizations of oxide films were performed with a synchrotron radiation facility in Himeji institute of technology. *Work supported by NEDO.

P5.21
SURFACE MODIFICATION OF ULTRAFINE WC/Co BY ION IMPLANTATION. S.-C. Liao[a], L.D. Yu[b], G.W. Shuy[a], T. Vilaithong[c] and S.W. Hong[a], [a]Materials Research Lab., Industrial Technology Research Institute, Chutung, TAIWAN; [b]Institute for

Science and Technology Development, Chiang Mai University, Chiang Mai, THAILAND; [c]Fast Neutron Research Facility, Physics Dept., Chiang Mai University, Chiang Mai, THAILAND.

Surface properties of carbon ion implanted (at doses ranging from 10^{16} to 10^{17} ions/cm^2 and accelerating voltages from 120 to 140keV) WC/10Co composite (WC grain size $\approx$ 400 nm) have been studied. Through nanoindentation tests, it was found that surface hardness of the implanted (at the dose of 6×10^{17} ions/cm^2 and accelerating voltage of 120 keV) sample reached a maximum value of $\sim$25 GPa at the depth of $\sim$125 nm into surface, compared to $\sim$18GPa (HKN@500g) of the virgin material. Auger electron spectroscope (AES) analysis of the implanted sample indicated that a carbon rich layer ($\approx$ 120 nm thick) was formed in the subsurface. Glancing angle x-ray diffraction (GAXRD) analysis of the subsurface showed no evidence of the formation of new compounds and broadening of the peaks which is attributed mainly to the compressive stress (up to $\sim$4 GPa) induced by the implantation process. Average surface roughness measured by atomic force microscope (AFM) of the implanted sample is around 3.5 nm. Effect of implanted ion dose, energy, and species on surface hardness and roughness, friction coefficient, and wear resistance of ultrafine WC/10Co composite will be presented.

P5.22
HOMOEPITAXIAL GROWTH ON THE Ge(100) AND THE Sb-TERMINATED Ge(100) SURFACE. Min Li, Eric I. Altman, Yale University, Department of Chemical Engineering, New Haven, CT.

The growth of Ge on top of the Ge(100) and the Sb-terminated Ge(100) surfaces has been studied using scanning tunneling microscopy (STM) and other surface characterization techniques. When 0.12 ML of Ge was deposited on the bare Ge(100) surface at 315 K, $<130>$-oriented dimers dominated the surface with very few epitaxial dimer rows oriented across the substrate dimer row after deposition. The density of epitaxial dimer rows increased after 0.18 ML Ge deposition. At the same Ge coverage but at a higher growth temperature of 420 K, the $<130>$-oriented dimers disappeared and were replaced by larger Ge epitaxial islands with a structure similar to that of the substrate. The "smooth" Sb-terminated surface with about 0.1 ML Sb dimer clusters was prepared by flashing an Sb multi-layer to 620 K. After 0.18 ML Ge deposition at 310 K, epitaxial Ge clusters were randomly distributed on large Sb-terminated terraces. There was no appearance of $<130>$-oriented Ge dimers that were found on the bare Ge(100) surface. Some small epitaxial dimers ($\sim$0.06 ML) were observed as the topmost white features. The surface morphology remained the same on the Sb-terminated surface with either increased growth temperatures or Ge coverages. The morphology is basically dominated by Sb-Ge surface mixing. Based on our experimental results, the effect of Sb as a surfactant is discussed.

P5.23
ENGINEERING THE Si(111) 7x7 SURFACE ENERGY USING Ge. J.B. Maxson, B. Yang, A.R. Woll, and M.G. Lagally, University of Wisconsin-Madison, Madison, WI.

The importance of strain in modifying the free energy of 2D and 3D nanostructures and thus to affect structure, morphology, and structural phase transitions has recently been more widely recognized. Modifications in the stress state of a structure can be introduced by the deposition of a heteroepitaxial film even at the submonolayer level. For example, deposition of Ge onto Si(111) can increase the transition temperature between the 7x7 and disordered 1x1 phases relative to that of clean Si(111). We study this transition using Low-Energy Electron Microscopy (LEEM). Earlier work [1,2] neglected to consider Ge desorption at high temperature. We show that desorption significantly reduces the Ge surface concentration at high temperature. Tuning the temperature ramp rate and the initial Ge coverage and correcting for the loss of Ge allows us to achieve a transition temperature up to 960°C. Quantitative arguments are presented to show that Ge stabilizes Si(111) through modification of strain and bond energies. The surface energy is reduced by an additional 20 meV per 1x1 unit cell at a coverage of about $\theta_{Ge} = 0.75$ ML. [1] T. Ichikawa and I. Ino, Surf. Sci. 136, 267 (1984). [2] K. Kajiyama, Y. Tanishiro, and K. Takayanagi, Surf. Sci. 222, 38 (1989). Supported by ONR and NSF.

P5.24
PRECISE CONTROL OF CVD-ZrO_2 FILM PROPERTIES BASED ON KINETIC INFORMATION. Kawamoto Takashi and Yukihiro Shimogaki, Depertment of Materials Engineering, University of Tokyo, Tokyo, JAPAN.

The shrinkage of MOS (Metal-Oxide-Semiconductor) transistor enhances the performance of ULSI devices. Gate dielectric scaling will require new insulating materials with higher dielectric constants to provide increased capacitance without increasing the gate leakage current by direct tunneling. Various kinds of high-k materials have been studied to replace conventional thermal oxide or oxynitride. Among them, ZrO_2 have attracted a lot of attention recently. We have investigated ZrO_2-CVD reaction system, using Zirconium-tetra-tertiary-butoxide (ZTB) as a Zr source. We found that ZTB decomposes both on the growing surface and in the gas phase. The gas phase reaction produces intermediates species, that also contributes to film growth. The kinetic studies on gas phase and surface reactions provided the way to control the film precursors by changing residence time of the reactants in the reactor. We examined relationship with film properties and the growth species (ZTB and intermediates). Furthermore, we investigated the effect of thermal annealing on deposited ZrO_2 films for the further improvement of film characteristics. We also deposited ZrO_2 films using the other Zr source and compared the film properties.

P5.25
BIOCOMPATIBLE THIN FILMS ON RARE EARTH BASED PERMANENT MAGNETS. Ecaterina Vasilescu, Paula Drob, Romanian Academy, Institute of Physical Chemistry, Bucharest, ROMANIA; Doina Raducanu, Lucia Angelescu, Politehnical University of Bucharest, Bucharest, ROMANIA; Constantin Iliuc, The Institute of Solid Mechanics, Bucharest, ROMANIA.

The item of the paper is foccused on the biocompatible coatings for rare earth based permanent magnets which are used as dental materials for prosthetic deviced as retention unit. The studied alloys belong to Nd-Fe-B system with some Dy and Al content. The double layer coatings had different chemical compositions; first layer: 30Ag-70Cr, 30Co-70Cr, stainless steel and the second layer: titanium nitride. Data about wear behavior and corrosion resistance are presented. The corrosion resistance of these coatings was tested in artificial saliva using electrochemical potentiostatic, potentiodynamic and linear polarization techniques. The stability in the corrosion media, the localized corrosion susceptibility and the corrosion rates were determined. It resulted that the 30Nd-Dy-Fe-Al-B alloy with 30Ag-70Cr titanium nitride film is very stable in artificial saliva. The wear behavior of the coatings in different conditions of contact and loads was tested, also.

P5.26
SINGLE POLYCRYSTALLINE FERROELECTRIC SBN THIN FILMS OBTAINED FROM SYNTHESIS OPTIMIZATION ON OXIDE PRECURSOR METHOD. Eudes Borges Araújo, Universidade Estadual Paulista, Departamento de Física e Química, Ilha Solteira, SP, BRAZIL; Ricardo Gonçalves Mendes, José Antonio Eiras, Universidade Federal de São Carlos, Departamento de Física, São Carlos, SP, BRAZIL.

Ferroelectric materials are an important class of materials whose main characteristic is the presence of a spontaneous polarization that can be changed with an external electric field. An important representing of this family is the SBN ($Sr_xBa_{1-x}Nb_2O_6$), known by excellent pyroelectric and electro-optic properties. The recent development of integrated optical devices has stimulated the demand for thin films using attractive materials such as SBN. This material has been prepared as thin film by several techniques like Sol Gel processing, Metalorganic Chemical Vapor Deposition (MOCVD) and recently by Oxide Precursor method, based on a polymeric resin containing metallic ions. In this work, single polycrystalline tetragonal phase of $Sr_{0.75}Ba_{0.25}Nb_2O_6$ (SBN75) thin films were obtained by the cited oxide precursor method. The effects of the atmosphere on film crystallization were investigated to remove the undesired $SrNb_2O_6$ (SN) phase in SBN films. For this purpose, films were crystallized under air, oxygen and nitrogen atmosphere. Structure and microstructure of the films were studied by X-Ray diffraction and Atomic Force Microscopy at room temperature. Only films crystallized under oxygen and nitrogen presented a single SBN75 phase while film crystallized on air present both SBN75 and SN phases. The effect of SN on ferroelectric properties was also investigated. Films crystallized without SN presented a well defined hysteresis loops than films crystallized with SN. This effect is probably associated with increasing in conductivity due to presence of SN in grain boundaries, as observed by Atomic Force Microscopy.

P5.27
INVESTIGATION OF MAGNETRON SPUTTERING CHARACTERISTICS USING THREE DIMENSIONAL MONTE-CARLO SIMULATION METHOD. Jai Kwang Shin, Seong Gu Kim, Young Dong Lee, Jae Joon Oh, Ji Hyun Hur, Won Taek Park, Samsung Advanced Institute of Technology, Yongin, KOREA.

Using three dimensional magnetic field solver and Monte-Carlo simulator, We investigate the dynamics of secondary electrons that are created at the target in moving- type magnetron sputter system. Triangular and circular type magnetron cathodes using magnet materials of Nd-Fe-B and Sm-Co are studied. Target erosion profile, the uniformity of the deposited film thickness, the efficiency of electron confinement and step coverage are calculated and compared with the experimental data. The local curvature of magnetron cathode and the magnetic field strength are assumed to determine the dynamics of secondary electron. Compared to the small curvature magnetron, electrons easily escape from the large curvature magnetron. Therefore the large curvature magnetron is found to be less efficient in confining secondary electrons and thus is expected to have a higher minimum chamber pressure. Also the strength of magnetic field and the configuration of magnets play an important role in determining the target erosion profile, the chamber pressure, the uniformity of sputtered thin film and the step coverage. This type of simulation turn out to be a useful method in designing new magnetron cathode since it is capable to predict all the important characteristics of sputtering processes.

P5.28
Abstract Withdrawn.

P5.29
MOTION OF SAPPHIRE SURFACE STEPS. N. Ravishankar, C.B. Carter, Dept. of Chem. Engr. Materials Science, University of Minnesota, Minneapolis, MN.

Oxide ceramics are commonly used as substrates for the growth of technologically important materials such as GaN, YBCO, Si, and ferroelectrics. The quality of the deposited film depends on the quality of the surface of the substrate. The quality of the surface is itself determined by the character and the behavior of steps and step-kinks, and on the presence of impurities. Under conditions where the steps on the surface are mobile, several interesting interactions are possible. For example, steps can bunch and form new facets; this process can be influenced by the presence of foreign particles on the surface. In this paper, the behavior of steps on sapphire under conditions used to prepare the substrate and for subsequent growth will be discussed. The influence of impurities on the surface and their role on the step motion is investigated. Illustrations of extensive step bunching which results in the formation of macrofacets will be presented. The lower energy of the macrofacet may provide a driving force for the bunching process.

SESSION P6/B10: JOINT SESSION SURFACE ENGINEERING ISSUES IN MEMS STRUCTURES AND DEVICES

Chairs: Kathyrn J. Wahl and S. Mark Spearing
Wednesday Morning, November 28, 2001
Room 311 (Hynes)

8:30 AM *P6.1/B10.1
SURFACE TREATMENTS FOR MICROSYSTEMS: COATING ISSUES AND TRIBOLOGICAL MEASUREMENT METHODS. M.T. Dugger and S.V. Prasad, Sandia National Laboratories, Albuquerque, NM.

Several fabrication routes are available to realize mechanical devices with structural elements that are microns to tens of microns in size. In particular, recent developments in surface micromachining (SMM) and patterned electrodeposition (LIGA) have resulted in complex machines with actuators and countermeshing gears. Such machines include impacting and sliding surfaces in which friction and wear will determine the machine's performance and reliability. The materials in contact are usually determined by processing constraints or material properties such as strength, density or magnetic behavior, rather than friction and wear performance. Efficient operation of these devices will require an engineered surface that is tailored to meet friction and wear requirements. Application of surface treatments to three-dimensional shapes at this size scale presents significant challenges, including modification of hidden surfaces, control of treatment thickness relative to gap dimensions, and the generation and trapping of third bodies. Further, understanding the behavior of surface treatments at pressure and velocity regimes relevant to microsystem operation requires the development of new tools for quantifying interface performance. A focus of our research is the development of special SMM and LIGA structures that contain isolated tribological contacts from which the friction forces may be extracted. Methods of quantifying static and dynamic friction in surface micromachined contacts will be shown, including measurements where the interface is parallel to the wafer surface (planar) and where the interface is perpendicular to the wafer surface (sidewall). Newly developed techniques for quantifying dynamic friction in LIGA contacts will be presented. Use of these approaches will be illustrated with several examples, including coupling agents and selective tungsten to modify the frictional behavior in polycrystalline silicon contacts, and a diamondlike nanocomposite coating for LIGA nickel structures.

9:00 AM P6.2/B10.2
DIAMOND LIKE NANOCOMPOSITE (DLN) COATINGS FOR LIGA MEMS: TRIBOLOGICAL BEHAVIOR AND COATINGS METHODOLOGY. Somuri Prasad, Todd Christenson, Sandia National Laboratories, Albuquerque, NM.

Many microelectromechanical systems (MEMS) fabricated by LIGA utilize electrodeposited metals such as nickel and Ni alloys. While Ni alloys may meet the structural requirements for MEMS, their tribological (friction and wear) behavior remains somewhat undefined. In a number of Microsystems applications such as gear trains, comb drives and transmission linkages, tribological considerations, particularly amongst sidewalls, are of paramount importance. The objective of this research is to device a novel coatings strategy that can be integrated into the mainstream LIGA technology to coat the sidewalls of intricate LIGA MEMS elements. As a first step in this direction, we applied a 100 nm thick diamond like nanocomposite (DLN) coating on a wafer containing LIGA MEMS elements by commercial plasma enhanced chemical vapor deposition (PECVD) technique. The MEMS elements were subsequently released from the wafer per standard LIGA process after backsputtering to clear the coating on the planar surface. Coverage of the DLN coating on the sidewalls was confirmed by cross sectional TEM analysis. Focused ion beam technique was used to prepare XTEM specimens from a DLN coated LIGA gear tooth. Tribological studies were conducted on planar test coupons using a ball-on-disk apparatus in different test environments. As compared with pure electrodeposited Ni, DLN coated Ni showed significant improvements in friction (0.04 versus 0.6-1.2), debris generation and stick-slip behavior.
*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.

9:15 AM P6.3/B10.3
CONFORMAL DEPOSITION OF AMORPHOUS HYDROCARBON BASED COATINGS ON METALLIC HIGH-ASPECT-RATION MICRO-SCALE STRUCTURES (HARMs) BY LIGA MICRO-FABRICATION. D.M. Cao, T. Wang, W.J. Meng, K.W. Kelly, Mechanical Engineering Department, Louisiana State University, Baton Rouge, LA.

A high-density plasma assisted hybrid CVD/PVD tool was used to deposit Ti-containing amorphous hydrocarbon (Ti-C:H) coatings comformally over electrodeposited Ni high-aspect-ratio micro-scale structures (HARMs) fabricated by the deep X-ray lithography based microfabrication technique LIGA. Mechanical properties and tribological characteristics of Ti-C:H coatings are reviewed. Ti-C:H deposition over Ni HARMs substrates was studied as a function of the HARMs dimension and aspect ratio. Potential applications of surface engineered metallic HARMs will be discussed.

9:30 AM P6.4/B10.4
DEPOSITION OF LOW SURFACE ENERGY, WEAR-RESISTANT FILMS ON MEMS-LIGA DEVICES USING AN ENERGETIC PULSED PLASMA IMMERSION PROCESS. Kumar Sridharan, University of Wisconsin, Madison, WI; Alfredo Morales, Sandia National Laboratory, Livermore, CA; Erik Wilson, University of Wisconsin, Madison, WI; and Joseph Woodworth, Sandia National Laboratory, Albuquerque, NM.

Low surface energy diamond-like carbon films modified with fluorine, and exhibiting moderately high hardness, have been deposited on gear-shaped MEMs-LIGA parts. Film deposition was performed with the non-line-of-sight plasma immersion ion implantation and film deposition process operated in the low energy regime, using a mixture of acetylene and a fluorinated precursor gas. The film-substrate interface region was compositionally-graded by adjustments in energy and deposition precursor content. Conformality to the device features was observed, and improvements in conformality of the film to the contours of the devices were achieved by adjusting the plasma process parameters. Conformality studies are being supported by modeling of plasma-target interactions during pulse-biasing of the MEMs-LIGA devices in the plasma, with the goal of optimizing process parameters. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94-AL8500. This work supported by SNL grant No. 16546.

9:45 AM P6.5/B10.5
STUDIES OF TRIBOLOGICAL PROCESSES ON ULTRA-NANOCRYSTALLINE DIAMOND (UNCD) THIN FILMS FOR MULTIFUNCTIONAL MEMS DEVICES. A.V. Sumant, O. Auciello, A.M. Dhote, D.M. Gruen, and J.A. Carlisle, Materials Science Division, Argonne National Laboratory, Argonne, IL; A. Erdemir, J. Andersson, and R.A. Erck, Energy Technology Division, Argonne National Laboratory, Argonne, IL; M.N. Gardos, Raytheon Electronic Company, El Segundo, CA.

Many MEMS devices involve rolling, sliding, rotating or bending operations that impose severe constrains on their performance and durability imposed by the tribological and mechanical properties of the base materials. In terms of mechanical and tribological properties, diamond clearly outperforms almost all materials. Additionally, diamond has other outstanding properties such as chemical inertness, very high thermal conductivity, high flexural strength and negligible stiction. All these properties make diamond an outstanding candidate material for fabrication of MEMS devices. Conventional CVD thin film deposition methods can be used to fabricate diamond MEMS structures. However, these films have large grain size, high internal stress, poor intergranular adhesion, and very rough surfaces, and are consequently ill-suited for MEMS applications. We have recently demonstrated a novel ultrananocrystalline diamond (UNCD)-based MEMS technology based on a UNCD coating technology developed at Argonne National Laboratory. This technology produces phase-pure diamond with extremely smooth surfaces (RMS roughness ~30-40 nm) with morphological and mechanical properties that are ideally suited for MEMS applications. However, before these UNCD-MEMS components are ready for integration into commercial MEMS devices, it is necessary to perform extensive research on their mechanical and tribological properties in various gas environments and under a wide range of test conditions. We have performed comprehensive friction and wear studies on UNCD films in high vacuum and controlled atmospheres (e.g., N_2, O_2, H_2, OH_2, inert gases) at room temperature to explore the specific roles of surface adsorbates in frictional properties. We will discuss results from tribological tests in correlation with studies of the effect of surface adsorbates on the UNCD friction coefficient, using integrated time of flight mass spectroscopy of recoiled ions (MSRI) and X-ray photoelectron spectroscopy techniques to determine the nature of the adsorbates and their chemical state on the UNCD surface.
Work supported by the U.S. Department of Energy, BES-Materials Sciences and Office of Transportation Technology, under Contract N0. W-31-109-ENG-38.

10:30 AM *P6.6/B10.6
MECHANICAL TESTING OF FREE-STANDING THIN FILMS.
W.N. Sharpe, Jr., Johns Hopkins University, Department of Mechanical Engineering, Baltimore, MD.

Microelectromechanical systems (MEMS) are usually planar microdevices with the mechanical or structural part consisting of freestanding thin-film material. Young's modulus and Poisson's ratio are needed for elastic response, and the strength of the material is needed to determine the allowable forces and displacements. Tensile testing is the preferred approach for structural materials because its uniform stress and strain fields enable direct determination of mechanical properties according to their definitions. Tensile testing of small thin-film specimens presents three challenges - preparation and handling of the specimen, measurement of small forces, and measurement of strain in the specimen. The author and colleagues at Hopkins have developed techniques and procedures for tensile testing of polysilicon, silicon nitride, and silicon carbide thin films. It is easier to measure mechanical properties of MEMS materials indirectly by modeling microdevices and extracting properties. One can fabricate a comb-driven resonant structure and use the measured resonant frequency to determine the modulus. Thin membranes of different shapes can be pressurized, and the measured displacements used to determine both Young's modulus and Poisson's ratio. Cantilever or fixed-end beams can be deflected electrostatically to measure modulus. However, none of these indirect approaches permit simultaneous measurement of all three properties (modulus, ratio, strength) as does the tension test. This presentation summarizes the current state-of-the-art in terms of the test methods and the values of the properties of polysilicon and other materials used in MEMS. Similar techniques have been used to conduct tensile tests of the bond-coat layer in thermal barrier coatings and those will be discussed. This research was conducted under the sponsorship of DARPA F30602-99-2-0553.

11:00 AM P6.7/B10.7
ROLE OF MICROSTRUCTURE IN FRACTURE AND FATIGUE PROCESSES IN MICRON-SCALE SILICON STRUCTURAL FILMS.
Christopher L. Muhlstein, University of California, Dept of Materials Science and Engineering, Berkeley, CA; Eric A. Stach, National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, CA; William G. Stratton, University of Minnesota, Dept of Materials Science and Engineering, Minneapolis, MN; Stuart B. Brown, Exponent Inc., Natick, MA; Robert O. Ritchie, University of California, Dept of Materials Science and Engineering, Berkeley, CA.

Fracture and fatigue resistance are important properties for the design and long-term durability of micromechanical structures. A thorough understanding of these phenomena is particularly important to avoiding failure of brittle, silicon-based, structural films in the high-performance and safety critical applications commonly found in computing, biological, and aerospace components. Recent work by some of the authors (CLM,EAS,SBB,ROR) have established that such thin, micron-scale, films of single- and polycrystalline silicon are susceptible to premature failure under cyclic loading conditions, with studies focused on characterizing the fatigue life behavior and mechanisms of fatigue crack initiation and growth. These investigations emphasized the importance of the surface chemistry and environment in the fatigue process; in addition, the underlying microstructure was found to play an important role in the failure of the material. The current work is centered on examining the general features of the polycrystalline silicon thin film microstructure that are relevant to the fracture and fatigue processes. Results are based on fifty stress-life fatigue tests that have been conducted on surface micromachined polysilicon films using Exponent fatigue test structures with a variety of surface and environmental conditions. High voltage transmission electron microscopy was used to observe the crack path, surface morphology, and underlying microstructure of polycrystalline silicon. In addition, cross-sections of the patterned films were thinned and evaluated using conventional transmission electron microscopy. Particular attention is given to the importance of grain boundary structure, oxide precipitates, and grain morphology in fracture and fatigue of polysilicon structural films.

11:15 AM P6.8/B10.8
STICTION IN AMORPHOUS-DIAMOND (A-D) THIN FILM STRUCTURES.
R.V. Ellis, T.A. Friedmann, J.P. Sullivan, M.P. de Boer, J.A. Knapp, W.K. Schubert, M. Mitchell, Sandia National Labs, Albuquerque, NM.

Stiction between surfaces of moving thin film structures places a critical limit on the performance and reliability of micromechanical devices. Thin film amorphous-Diamond (a-D) structures may be less susceptible to stiction problems than structures built with other materials, since a-D film surfaces are nearly hydrophobic as deposited, and they do not develop an oxide. Our preliminary observations were that surface micromachined a-D structures can be released with a simple dehydration bake at 200 - 400°C under inert atmosphere, and that these structures do not re-adhere over time. To better quantify these observations, we are measuring adhesion and surface wetting as a function of surface termination. These measurements are made using an array of singly-clamped a-D cantilever beams that are electrostatically brought into contact with a ground plane. Two ground plane materials are being tested, both poly-Si and a-D. An interferometric microscope is used to measure the length of the beam that is adhered to the ground plane. Using this measurement and simple beam mechanics within a Griffith crack formalism, one can extract the adhesion energy per unit area. We will discuss the effects of various surface treatments and humidity on the adhesion in these systems and compare the results to those obtained from poly-Si based devices. We are also investigating the number of contacts to failure and the effects of electrical current across the contact.
*This work was supported by the U.S. DOE under contract DE-AC04-94AL85000 through the Laboratory Directed Research and Development Program, Sandia National Laboratories.

11:30 AM *P6.9/B10.9
SURFACE MECHANICAL PROPERTIES AND TRIBOLOGY: A COMBINED NANOSCALE AND MACROSCALE APPROACH.
Kathryn J. Wahl, U.S. Naval Research Laboratory, Washington, DC.

Mechanical properties of surfaces and interfaces are important for understanding the behavior of tribological contacts, where changes in interfacial properties can result from surface treatments, contaminant films, or sliding processes. At all scales - from atomically thin surface films to chunks of wear particles - interfacial mechanics and dynamics play an important role in friction and wear. To address these problems, we are combining two approaches: 1) *in situ* macroscopic tribological studies allowing visualization and chemistry of the buried interface and 2) "hybrid" nanoindentation, coupling high spatial resolution and surface sensitive, quantitative mechanical properties measurements of films as thin as a few nanometers. By combining these techniques, the macroscopic tribological behavior can be correlated with mechanical properties of the nanoscale films and structures, e.g. the "third bodies" found in the sliding interface. In this presentation, I address the issues of measuring and interpreting the mechanical response of ultrathin films and nanostructures. Combining these nanomechanical techniques with the *in situ* tribological studies yields a powerful approach to examine worn surfaces and interpret tribological response. For example, one can learn "how" third body films form on the stationary counterface, "what" are their composition and mechanical properties, and "why" they provide low friction and prevent wear. Such studies can provide a better understanding of the transformation and behavior of tribological interfaces, which is a key need for devices and applications at all scales.

SESSION P7: INDUSTRIAL APPLICATIONS OF SURFACE ENGINEERING II
Chairs: Gary L. Doll and Yip-Wah Chung
Wednesday Afternoon, November 28, 2001
Room 311 (Hynes)

1:30 PM *P7.1
INTRINSIC ADHESION AT ALUMINUM/CERAMIC INTERFACES: AN AB INITIO APPROACH TO SURFACE ENGINEERING. Louis G. Hector, Jr., Thomas A. Perry, General Motors R&D Center, Tribology and Surface Eng. Dept., Warren, MI; Donald J. Siegel, Univ. of Illinois, Dept. of Physics, Urbana, IL; James B. Adams, Arizona State Univ., Chemical and Materials Engineering, Tempe, AZ.

Aluminum alloys hold great promise as substitute materials for automotive components traditionally manufactured from steel. However, aluminum adhesion to forming tool surfaces is notoriously difficult to control due to the chemical reactivity of nascent aluminum liberated during plastic formation. Alloying agents, such as magnesium and manganese, along with sub-surface plastic deformation also enhance aluminum adhesion through mechanisms that are not fully understood at the present time. The challenge therefore remains to minimize aluminum adhesion by controlling the chemical and physical properties of the tool surface. For this reason, research on novel tool coating materials has increased rather dramatically over the past decade. Unfortunately, tool coating selection is based less upon the intrinsic or chemical component of adhesion, and more upon empiricism. To gain a more quantitative understanding of adhesion, we conducted a study of different material interfaces, in which one of the materials was aluminum, using a first principles methodology based upon density functional theory. We calculated the work of adhesion and examined the associated electronic structure of supercells with atomistically flat aluminum and tool coating materials (with selected terminations) consisting of Al_2O_3, CrC, CrN, TiC, TiN, VC, VN, TiB_2, and WC. The impact of aluminum alloying agents, slab stoichiometry, and magnetism (where appropriate) on the work of adhesion were considered in detail along with the nature and extent of adhesive transfer when the slabs were separated. Finally, we propose a relationship between the work of adhesion and the surface energies of the interface slabs that can be used to provide insight into the selection of coating materials that reduce aluminum adhesion.

2:00 PM P7.2
FUNCTIONALLY GRADED CVD MULLITE COATINGS. Soumendra Basu, Vinod Sarin, Boston University, Dept of Manufacturing Engineering, Boston, MA.

In order to improve fuel efficiency and reduce emissions, the future generation of gas turbines and internal combustion engines will rely on higher operating temperatures. Silicon-based ceramics such as SiC and Si_3N_4, identified as candidate materials for use at these higher temperatures, are susceptible to hot corrosion and recession. Mullite ($3Al_2O_3 \bullet 2SiO_2$) is an excellent candidate material for coating these ceramics for use in high temperature corrosive atmospheres. Dense, uniform and adherent mullite coatings have been deposited at 950°C by chemical vapor deposition (CVD) on SiC substrates and fibers, using the $AlCl_3$-$SiCl_4$-CO_2-H_2 system. Using an extensive thermodynamic analysis as a guideline, the coating system was optimized, leading to compositionally graded coatings. The high Si content at the interface allowed excellent bonding with the Si based substrate, while the higher Al content of the outer coating surface in contact with the corrosive atmospheres accounted for the superior hot-corrosion resistance of the coatings. The typical coating microstructure consists of a thin layer of γ-Al_2O_3 nanocrystallites in a vitreous silica-rich phase at the coating-substrate interface. Above this layer, crystalline mullite grains formed with a columnar morphology. The nano-crystalline layer, whose thickness was controlled by adjusting the input $AlCl_3/SiCl_4$ ratio, was converted to equiaxed mullite grains after annealing at 1250°C without any loss of coating adherence. These mullite coatings exhibited excellent high temperature oxidation and hot corrosion resistance and were very effective in protecting the SiC substrates from corrosive atmospheres. The coatings also exhibited excellent adhesion during cyclic oxidation tests. The microstructural features of the mullite coatings, some of which are unique to the CVD deposition process, will be presented and their role in providing the excellent oxidation and hot corrosion resistance will be discussed.

2:15 PM P7.3
CHARACTERIZATION OF HIGH ALUMINA REFRACTORY CERAMICS TREATED WITH COMBINED TWO LASER SURFACE PROCESSING. Dimitrios Triantafyllidis, Univ of Manchester Inst of Science and Technology, Dept of Mechanical Engineering, Manchester, UNITED KINGDOM; Johanna R. Bernstein, F. Howard Stott, Univ of Manchester Inst of Science and Technology, Corrosion and Protection Centre, Manchester, UNITED KINGDOM; Lin Li, Univ of Manchester Inst of Science and Technology, Dept of Mechanical Engineering, Manchester, UNITED KINGDOM.

Alumina-based refractory materials are extensively used in high-temperature industrial applications, such as for linings in waste and other incinerators. The existence of porosity and material inhomogeneities can promote chemical degradation due to molten slag penetration, while impacting solid or liquid feedstock can cause erosive-wear damage. Previous research has successfully used single laser energy sources to alter the surface properties of similar ceramics, with emphasis on sealing porosity and enhancing degradation resistance. However, this process has resulted in some solidification cracking at the surface due to large temperature gradients developed during processing. In the present, ongoing work, the surface of the refractory ceramic is modified by combining two laser energy sources to control the thermal gradients and cooling rates, with the objective of eliminating crack formation. The surface morphologies and microstructures of the laser-treated areas are analyzed and the wear properties determined. This paper presents some initial results from the programme.

2:30 PM *P7.4
COATINGS AND SURFACE ENGINEERING FOR METAL CUTTING APPLICATIONS. Aharon Inspektor, Kennametal Inc., Latrobe, PA.

Strong functional surface is the first line of defense of the cutting tool and thus, is vital to the performance and to the reliability of the tool. This paper will present and critically discuss principles of surface engineering for metal cutting applications. An emphasis will be on the design and preparation of the cutting edge as a complete system consisting of substrate and coating designed to work together. This concept will be illustrated by case studies in modern cutting tools, trends in superhard-coated tools and recent developments in nano-structured films.

3:30 PM *P7.5
INDUSTRIAL PRACTICE OF CARBON-BASED COATINGS. O. Massler, R. Herb, J. Karner, M. Grischke, Balzers Limited, Balzers, LIECHTENSTEIN.

Carbon-based coatings deliver advantages regarding friction behaviour, dry and lubricated running, abrasive wear resistance, resistance against scuffing and seizure, and even corrosion. Carbon coatings can decrease cost of running, design and maintenance, increase lifetime, improve service behaviour and enable higher performance of tribological systems. Carbon-based coatings can provide the automotive and other industries with improved performance on precision components in tribological applications. This broad range of properties improve the surface characteristics of selected functional surfaces and parts. Additionally, the performance of systems is enhanced by increased fuel efficiency, increased technical system performance and lower running cost. The variety of demands of tribological applications require a high flexibility of the properties of the coatings. The bonding structure of the coatings is of major importance for the coating behaviour. But also the designs of the multilayer coating does significantly influence the behaviour of the coating in the system. Test results and practical applications show the range of possibilities of a system-orientated coating design. Carbon-Coatings on the basis of Me-C:H have superior frictional properties. The low friction coefficient causes a much improved frictional behaviour compared to the uncoated tribological system. This type of coating is becoming widely distributed in industrial applications, where protection against adhesive wear, scuffing and seizure, increase of lifetime and improvement of sliding behaviour is required. The metal-free a-C:H coatings (DLC) have a higher hardness than Me-C:H-coatings, due to high internal stresses and do not show a nanolayered structure, due to the different growth mechanism of the material. The high hardness gives the base for a much higher abrasion resistance in tribosystems with highly abrasive tribocomponents. Thus the friction coefficient can be similar to Me-C:H systems, depending on the partners in the tribosystem.

4:00 PM P7.6
TRIBOLOGICAL BEHAVIOR OF Cr-DLC NANOCOMPOSITE FILMS. Varshni Singh, Jiechao Jiang, E.I. Meletis, Louisiana State University, Materials Science and Engineering Program of Mechanical Engineering, Baton Rouge, LA.

Extensive studies have been conducted in the past on Diamondlike Carbon (DLC) films, known for exhibiting attractive combination of properties. A significant drawback with these films is their low thermal stability above 400°C and low fracture toughness. Our recent studies showed that incorporation of carbide formers such as Cr into the DLC structure produces a nanocomposite (with 2-5 nm diameter nanoparticles) offering the possibility to stabilize the film structure and enhance DLC properties. The present work focuses on the synthesis, characterization of structure and properties with emphasis on tribological behavior, of Cr-containing nanocomposite DLC films. Cr-containing DLC films were deposited on Si substrates in an intensified plasma environment using magnetron sputtering of a Cr target with a CH_4 and Ar gas mixture. The film morphology and composition were characterized by SEM-WDS. The role of Cr in the DLC structure was analyzed by high resolution X-TEM. The effect of Cr content on the mechanical and tribological behavior of DLC films was studied with the percentage of Cr content varying up to 30 at.%. Mechanical and tribological properties were studied by nano-indentation and pin-on-disc experiments, respectively. Thermal annealing experiments were conducted to study Cr-DLC stability.

4:15 PM P7.7
CHARACTERISTICS OF Cr-Al-N-O THIN FILMS PREPARED BY PULSED LASER DEPOSITION. Makoto Hirai, Hajime Saito, Tsuneo Suzuki, Hisayuki Suematsu, Weihua Jiang and Kiyoshi Yatsui, Extreme Energy-Density Research Institute, Nagaoka University of Technology, Nagaoka, Niigata, JAPAN.

Chromium aluminum oxynitride (Cr-Al-N-O) films have been successfully prepared by pulsed laser deposition (PLD). The Cr-Al-N-O film, which is expected to exhibit high hardness and oxidation resistance, is promising as the coating material for high-speed cutting tools. Experiments were carried out by changing the surface area ratio of the target ($S_R = (S_{AlN} / (S_{Cr_2N} + S_{AlN}))$ under a pressure of 1×10^{-5} Torr. The composition of the film prepared at the fluence of $F = 5$ J/cm^2 and $S_R = 75$ % was determined to be $Cr_{0.11}Al_{0.39}N_{0.25}O_{0.25}$ by Rutherford backscattering spectroscopy (RBS). This result indicates that the ratio of cation and anion in the film is one-to-one correspondence. Chromium, aluminum and nitrogen atoms in the film were provided from Cr_2N and AlN targets, whereas oxygen atoms were incorporated from the residual gas in the chamber. The latter may be attributed by that the residual oxygen is chemically adsorbed on the film surface during deposition. The hardness of the Cr-Al-N-O film was found to be above HV 4000 when the aluminum content in cations was 25 at. %. In addition, it is higher than that of α-SiC bulk measured under the same condition. One of the reasons to explain the high hardness is the pinning of dislocations by distortion associated with the dissolved aluminum atoms in the lattice. The oxidation of the Cr-Al-N-O film was observed above 900°C. Furthermore, the film heat-treated at 1100°C consisted mainly of B1 (NaCl) structure. From the result of grazing angle X-ray diffractometry (GXRD), the oxidation resistance of the Cr-Al-N-O film was found to be improved by fact that Cr_2O_3 and α-Al_2O_3 are formed on the film surface.

SESSION P8: POSTER SESSION MECHANICAL, TRIBOLOGICAL, AND OTHER PROPERTIES

Chairs: Wen Jin Meng, Ashok Kumar, Yip-Wah Chung, Gary L. Doll, Yang Tse Cheng and Stan Veprek
Wednesday Evening, November 28, 2001
8:00 PM
Exhibition Hall D (Hynes)

P8.1
MICROSTRUCTURE AND TRIBOLOGICAL PROPERTIES OF DLC/TiC/Ag COMPOSITE COATINGS IN VACUUM AND AIR ENVIRONMENTS. Jose Endrino, James Krzanowski, University of New Hampshire, Dept of Mechanical Engineering, Durham, NH; Jose Nainaparampil, Systran Inc, Dayton, OH.

The development of composite coatings that can provide low friction in both air and vacuum has become important to meet the demand for lubricant mechanisms capable of operating in both ambient and space. In a previous study, TiC/Ag coatings were successfully deposited using the hybrid technique of MS-PLD (magnetron-sputtering pulsed laser deposition). The deposited coatings were proven to be extremely effective to reduce both friction and wear in high vacuum but failed in ambient. In this study, MS-PLD DLC/TiC/Ag coatings were obtained by co-deposition of carbon by ablation and Ti/Ag (60:40) by DC sputtering. The power on the sputtering gun was varied to obtain films with different DLC to TiC/Ag ratio. XRD analysis and TEM of the deposited films was used for phase identification. The friction coefficient was obtained in both 50% R. H. Air and in high vacuum run for 10,000 cycles using the ball-on-disc friction test. SEM images, EDX mapping and electron diffraction of the wear track were used to further analyze the lubrication mechanism.

P8.2
STUDIES OF ANISOTROPIC VOIDS MICROSTRUCTURE OF YSZ DEPOSITS BY SMALL-ANGLE X-RAY SCATTERING. Jan Ilavsky, University of Maryland, College Park, MD and National Institute of Standards and Technology, Gaithersburg, MD; Andrew J. Allen and Gabrielle G. Long, National Institute of Standards and Technology, Gaithersburg, MD; Pete R. Jemian, University of Illinois, Urbana, IL; Jean-Francois Bisson, NRC, Boucherville, CANADA.

Yttria-stabilized zirconia (YSZ) deposits, manufactured by means of atmospheric-plasma-spraying onto a steel substrate, were characterized by small-angle scattering of neutrons and X-rays. Deposits such as these are routinely used as thermal barrier coatings. Small angle neutron scattering has proven successful for relatively thick (millimeter) deposits. Industrially more applicable thin deposits on substrates cannot be characterized by SANS without the use of a complex reflection geometry. Anisotropic ultra small-angle X-ray scattering (USAXS), using 10 keV X-rays have made it possible to extract anisotropic void information on deposits of lower-density materials such as calcium disilicate. Extension of the USAXS method to higher energies (17 keV) now allows studies of even relatively dense materials, such as is YSZ. The high brightness and small beam size available at a third generation X-ray synchrotron source permit the study of deposits less than 500 μm thick in a plane perpendicular to the substrate. Our results demonstrate that we can obtain the complete anisotropic surface area distribution from the Porod scattering. Furthermore, the anisotropy in the microstructure can be studied as a function of scale.

P8.3
DURATION DEPENDENT STATIC FRICTION FORCE OF POLYMER GEL-ON-GLASS SYSTEM. Takahiro Nitta, Hisashi Haga, Kazushige Kawabata, Hokkaido University, Graduate School of Science, Division of Physics, Sapporo, JAPAN.

We have a study on the static friction when polymer gel slides on glass plate in water. Polymer gel is easily deformable with long retardation times under applied stress. Then effects of the elastic deformation on the static friction can be seen more apparently in this system than in metal-on-metal systems. We measured the static friction force varying the duration of stationary contact from 10 up to 7200 sec. We found that the static friction force increased as a power of the duration. The value of the exponent was about 0.7. This duration dependence is quite different from those previously reported in many other systems such as paper-on-paper system, where the static friction force increases as a logarithmic law of the duration. From this comparison, the duration dependence of the static friction force is the characteristic of the polymer gel-on-glass system. The relation between this characteristic and the polymer gel structure will be discussed.

P8.4
MECHANICAL AND ELECTRICAL PROPERTIES OF NANOCRYSTALLINE AND EPITAXIAL TiN FILMS. Haiyan Wang, Alex Kvit, Xinghang Zhang, Carl C. Koch, Jarayan Narayan, Department of MS&E, North Carolina State University, Raleigh, NC.

High-temperature materials such as TiN have been successfully applied as wear corrosion protection, decorative coatings, electrical contacts and diffusion barriers in electronic devices. However the poor toughness and ductility have limited some of these applications. To alleviate some of these problems, reduction of grain size can enhance grain boundary sliding and grain boundary diffusion related creep phenomena.[1] We have investigated mechanical and electrical properties of TiN as a function of microstructure varying from nanocrystalline to single crystal TiN films deposited on (100) silicon substrates. By varying the substrate temperature from 25°C to 700°C during pulsed laser deposition, the microstructure of TiN films changed from nanocrystalline (having uniform grain size of 8 nm) to a single crystal epitaxial film on the silicon (100) substrate. The microstructure and epitaxial nature of these films were investigated using X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM). Hardness measurements were made using nanoindentation techniques. Resistivity measurements were performed by van der Pauw method. The nanocrystalline TiN contained numerous triple junctions without any presence of amorphous regions. The width of the grain boundary remained constant 1 nm as a function of boundary angle. Similarly the grain boundary structure did not change with grain size. The hardness of TiN films decreased with decreasing grain size in nanoscale.[2] This behavior has been modeled recently involving grain boundary sliding which is particularly relevant in the case of hard materials such as TiN.[3] The dependence of resistivity of TiN as a function of the deposition temperature is discussed and correlated with hardness results.
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[2]H. Wang, A. Sharma, A. Kvit, Q. Wei, X. Zhang, C.C. Koch and J. Narayan, J. Mater. Res. (in press)
[3]J. Narayan, J. Nanoparticle Res. 2, 91 (2000); Scripta Mater. 42, 1025 (2000).

P8.5
PHASE ANALYSIS FOR SINGLE CRYSTALLINE SILICON SCRATCHED BY SPHERICAL DIAMOND TIP. Seong-Min Jeong, Han-Seog Oh, Sung-Eun Park, Hyun-Ho Kim, Hong-Lim Lee, Department of Ceramic Engineering, Yonsei University, Seoul, KOREA.

The production of optical quality surfaces on semiconductor silicon wafer is an emerging technology, so called ductile regime machining. Machining processes must be more precisely controlled in large diameter silicon semiconductor industry by the shrinkage of design rule. Turning technique is used to control the machining parameters of ductile regime. But in ductile regime machining, the response of material is also meaningful. Silicon is a brittle material and undergoes a series of phase transformations when subjected to high pressures, using conventional high pressure devices, such as diamond anvils or hydrostatic pressure cells, or under indentation. In this study, diamond scratching test was performed to study the machining parameters and the response of material during machining. Scratching on a silicon surface in the various conditions introduces various kinds of mechanical damage and stressed states. Micro-Raman spectroscopy was used to observe the phase transition of single crystal silicon. As a result, some different phases were observed as functions of scratching speed and scratched locations.

P8.6
CROSS-SECTIONAL PHASE ANALYSIS OF SINGLE CRYSTALLINE SILICON INDENTED BY ROCKWELL INDENTOR. Sung-Soon Kim, Han-Seog Oh, Seong-Min Jeong, Hong-Lim Lee, Yonsei Univ, Seoul, KOREA.

The response of crystalline silicon to indentation has been a topic of interest for many years, and it is now well established that this material undergoes a series of high-pressure phase changes when subjected to high pressures. But most results of investigation used to directly confirm the phase transformation by indentation are plane view. The information from plane view observation is limited on studying the actual affected region of indentation on the material from surface to inside. In order to get a better understanding of the phenomenon occurring during indentation, the cross-sectional study is required. Lack of this kind of information is mainly because of the difficulty in preparing a suitable cross-section sample for observing by TEM or other instruments. In this work, the stress field induced by indentation was simulated to predict phase transformation region. The simulation results was compared with experimentally observed region. Micro-Raman spectroscopy was used to observe the phase transition of the single crystalline silicon.

P8.7
INVESTIGATION OF STRUCTURAL AND MECHANICAL PROPERTIES OF LASER DEPOSITED MICROLAMINATE HARD COATINGS. Manoj Radder and Ashok Kumar, Department of Electrical Engineering, University of South Alabama, Mobile, AL.

Microlaminate coatings produced by physical vapor deposition (PVD) are increasingly applied to mechanical components such as metal cutting tools, forming tools and machine elements. Nitride and carbide coatings, such as TiN, TiC and SiC, TiC, B4C prepared by physical vapor deposition (PVD) can considerably increase the tool lifetime. It was observed that thin film with multilayer structure have better quality crystallinity and hence carry better hardness and modulus values as compared to the single layer coating of the respective materials. PVD hard material coatings on Si (100) were deposited by laser ablation method and were characterized by standard analytical techniques. Nanoindentation method was used to evaluate the mechanical properties. Tribometer was used to measure the tribological properties. Cross-sectional TEM method was used to investigate the interfacial properties of layered coatings. This paper discusses detailed investigation of structural, mechanical and tribological properties of single and multilayer coatings of nitrides (TiN/TaN, TaN/TiN, TiN/TaN/TiN, TiN/TaN/TiN) and Carbide (SiC/TiC, TiC/B4C, B4C/SiC).
Now at the University of South Florida, Department of Mechanical Engineering, and Center for Microelectronics Research. This research was supported by Alabama NASA EPSCoR Program.

P8.8
ASSESSMENT OF MICROSCALE TEST METHODS OF PEELING AND SPLITTING ALONG SURFACE OF THIN FILM/ SUBSTRATES. Yueguang Wei, LNM, Institute of Mechanics, Chinese Academy of Sciences, Beijing, CHINA.

Peeling and splitting tests at micro-scale are important and effective experimental methods, and have been used extensively to estimate the interfacial fracture toughness or adhesive behavior of thin film/substrate system or surface coating. In the present research, two kinds of test methods will be assessed and studied based on the viewpoint of the elastic-plastic fracture mechanics and comparison for several experimental results of metal thin film/ceramic substrates. For the peel test method, the thin film is subjected to the peeling force at the terminal of delaminated part along some direction and is delaminated from interfacial surface. During peeling, the thin film undergoes a very complicated deformation process from elastic, elastic-plastic, unloading, reversed plastically yielding (or bending), finally to unloading. Applied energy will be dissipated in each deformation steps. Due to the reversed plastically bending behavior in the peel test, theoretical and experimental researches for the material interfacial and adhesive properties using peel test method have become difficult, and limited considerably. For the split test method, the split arm does not undergo the reversed plastic yielding and the split arm residual curvature becomes a measurable parameter. Comparing with the conventional peel test method, the split test has remarkable advantages in measuring the interfacial fracture properties or interfacial adhesive strength of thin film/substrate. Moreover, comparing with the peeling force, the split force also has the connection with the total energy rate, further is related with the crack tip separation energy (or material fracture toughness) and separation strength, as well as plastic dissipation work. Through measuring the driving force and the residual curvature, the fracture toughness and separation strength are obtained.

P8.9
THE EFFECT OF PRE-OXIDATION ON THE OXIDATION BEHAVIOUR OF Ti-2Al-2.5Zr ALLOY AT 300°C IN AN ALKALINE STEAM. Xiaotao Zu[a,b], Xiangdong Feng[a], Zhiguo Wang[a], Guangting Zeng[a], and Libin Lin[a], [a]Key Laboratory for Radiation Physics and Technology of Ministry of Education, Department of Physics, Sichuan University, Chengdu, PR CHINA; [b]Department of Nuclear Engineering and Radiological Sciences, University of Michigan, Ann Arbor, MI.

The oxide scales on a Ti-2Al-2.5Zr alloy with and without pre-oxidation oxidized at 300°C in an alkaline steam for about 130000h were studied by SEM, XRD, XPS and in-situ AES techniques. Some of the samples were subjected to 400°C deionized water steam at a pressure of 10Mpa for 72 hours for pre-oxidation. The results showed that the oxide scales on the Ti-2Al-2.5Zr alloy were composed of $Al_2TiO_5(TiO_2{\cdot}Al_2O_3)$, TiO_2, Ti_3O_5, Ti_2O_3, Al_2O_3 and TiO. A comparison study has been carried out between the pre-oxidized and without pre-oxidized Ti-2Al-2.5Zr to determine the influence of pre-oxidation upon the properties of oxidation resistance. The oxidation kinetics showed that the weight gains of the pre-oxidized samples were much less than that of the controlled samples, which was consistent with the results by in-situ AES analysis. The AES results showed that the whole thickness of the pre-oxidized sample (about 33000Å) was thinner than that of the controlled one (about 40000Å), in contrast the pattern for the stable oxide scale was reversed, i.e. the pre-oxidized sample was much thicker. Thus pre-oxidation is an effective method to improve the oxidation resistance of Ti-2Al-2.5Zr.

P8.10
THERMO-MECHANICAL EFFECTS OF CERAMIC THERMAL BARRIER COATINGS ON DIESEL ENGINE PISTON. Jesse Muchai, David E. Klett, Ajit D. Kelkar and Jag Sankar, NSF Center for Advanced Materials and Smart Structures, North Carolina A&T State University, Greensboro, NC.

Coating the piston crown with ceramic thermal barrier coatings (surface engineering) can improve the thermal efficiency and reduce the NO_X, CO and hydrocarbons emissions in direct injection diesel engines. Effect of Yttria Stabilized Zirconia (YSZ) thermal barrier coating (TBC) thickness on the piston surface was studied for Ricardo single cylinder diesel engine. The piston thermal boundary conditions were obtained from 1-D engine thermodynamic cycle analysis. A 2-D Finite Element Analysis using ANSYS was performed to evaluate the temperature distribution and heat transfer on the piston as a function of coating thickness. The paper will present the results of five different YSZ-TBC ranging from 0.5 to 2.0 mm. The transient thermal analysis was carried out followed by a steady state temperature analysis. Simulation was performed at steady state during combustion, the most severe case. Analysis included piston stresses due to thermal and pressure loads, piston/coating interfacial properties, engine performance and emissions It was shown that coating thickness decreases heat transfer by 8-20% for 0.5-2 mm coat and coating thickness increases surface temperature by 21-53%. The paper will also discuss the use of this analytical route in understanding the surface engineered piston.

P8.11
TRIBOLOGY OF MATERIAL CONTACTS UNDER DYNAMIC LOADING, STUDIED BY ELECTRICAL RESISTANCE MEASUREMENT. Xiangcheng Luo, D.D.L. Chung, Composite Materials Research Laboratory, University at Buffalo, The State

University of New York at Buffalo, Buffalo, NY.

The tribology of material contacts under cyclic compression in the direction perpendicular to the plane of the contact was studied by measurement of the contact electrical resistivity of the contact in real time during the dynamic loading. The real-time monitoring allowed observation of both reversible and irreversible effects. The material contacts studied were those involving metals (steel, aluminum and copper), carbon fiber polymer-matrix composite, cement mortar and graphite, due to their relevance to fastening, concrete structures, electric brushes and electrical pressure contacts. Correlation was made between the contact resistivity and the occurrence of elastic/plastic deformation, oxidation, strain hardening, passive layer damage and local fracture. The interfacial structure was found to depend on the loading history.

P8.12

MORPHOLOGICAL AND NANOTRIBOLOGICAL PROPERIES OF DIAMOND LIKE THIN FILMS ERODED BY A NITROGEN PLASMA. R. Prioli, S. Castaneda, F.L. Freire Jr., Dept of Physics, Pontificia Universidade Catolica do Rio de Janeiro, Rio de Janeiro, BRAZIL; W.H. Schulte, Dept of Physics and Astrophysics, Rutgers Univ, NJ.

In this work we present a study of the morphological structure and nanotribological properties of hydrogenated amorphous carbon thin films ($a-C:H$) eroded by nitrogen plasma. The carbon films were deposited by rf plasma enhanced chemical vapor deposition (PECVD) onto a Si substrates, using substrate self-bias of $-400V$ and a methane pressure of $3Pa$. After to the films deposition, they were exposed to nitrogen rf plasmas with an erosion bias ranging from $-100V$ to $-500V$, different plasma erosion pressures from $1Pa$ to $10Pa$ at different times of erosion which varied from 5 to $50min$. The films morphological structure were measured with the use of a force microscope, operated in tapping mode. Its nanotribological properties were analyzed using the force microscope operated in the lateral force mode. The growth and erosion of the $a-C:H$ films were modeled with the use of scaling laws. It is shown that the energy of the impinging $N-2^+$ ion plays a role on the final state of the films surface. As the energy of the impinging ions is increased the correlation length increases leading to changes in the films surface final state, from columnar to very smooth surfaces when the ions energy is changed from $100eV$ to $500eV$. It is shown that the nitrogen incorporated on the films, during the erosion process, is located in the top layers of the film, i.e., first 20 Angstroms, and its amount is almost independent on the ion energy as revealed by MEIS experiments. The incorporation of nitrogen, by the erosion process, causes an increase in the friction coefficient of the films measured with the use of a $Si-3N^4$ microscope tip. In our case, it is observed that after $5min$ of erosion the friction coefficient reaches a saturation value of $0,21$, which is 20% higher than the fresh $a-C:H$.

P8.13

DUCTILE MICROMACHINING OF SILICON FOR MEMS APPLICATIONS. Yury Gogotsi, Tom Juliano, Drexel University, Department of Materials Engineering, Philadelphia, PA. Sabri Cetinkunt, Nishan Bopearatchy, University of Illinois at Chicago, Department of Mechanical Engineering, Chicago, IL.

Mechanical micromachingin of silicon surfaces has been explored in this work. A single point diamond turning machine (SPDTM) was used to machine the surface of a (111) p-type single-crystal silicon wafer at room temperature. The SPDTM machine consists primarily of an X-Y stage (100 nm resolution) controlled by servomotors and a Z-axis linear motor (100 nm resolution). Attached to these components, there are piezo-actuators and gap sensors working in each axis that push the resolution of the machine to about 2.5 nm. During machining, the pressure-induced metallization of silicon yields a ductile regime of mechanical micromachining on the wafer surface. Scratch tests in this ductile regime with three degrees-of-freedom have been performed at depths from a few nanometers up to about 3 μm with both sharp and spherical diamond tools. Greater depths will start to yield brittle fracture, and we have illustrated that the tool shape determines the precise value of the critical depth of cut. Multi-segment shapes have been successfully machined with overall dimensions of 10 by 20 μm. Depending on the cutting tool and depth of cut, material removal mechanisms were different and the amounts of ductile chips present were shown to change. It was found that a mixture of metastable silicon polymorphs and amorphous silicon covered the surface of the grooves after machining. These phases can, in turn, be transformed to cubic silicon by annealing. The developed technique can be readily applied to other semiconductors, and can create any machined shape (unlike etching) limited only by the realization of the tool shape itself. Possible applications include creating channels for micro-fluidic devices, or using the electrical properties of each phase to create electronic devices machined on the surface.

P8.14

FABRICATION AND MICROSTRUCTURES OF MECHANICALLY INDUCED SURFACE NANOCRYSTALLIZATION IN AN ALUMINUM ALLOY. Y. Hong, X. Wu, State Key Lab of Nonlinear Mechanics, Institute of Mechanics, Chinese Academy of Sciences, Beijing, PR CHINA; J. Lu, LASMIS, Univ of Technology of Troyes, Troyes, FRANCE; K. Lu, State Key Lab for RSA, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, PR CHINA.

Significant interest exists in the materials science community in creating nanocrystalline microstructures on the surface layer of the metallic materials in an effort to obtain improved properties. We have recently proposed the concept of mechanically induced surface nanocrystallization and developed a novel intense straining process to transform the surface layers of the materials into ultrafine-grained (UFG) structures (both submicrometer- and nano-grained structures) without changing the overall composition and/or phases. Experiments were conducted to investigate the development of UFG structures in the surface layer of an aluminum alloy by using an ultrasonic shot peening (SP). Refined microstructures of three levels of the grain size were present, i.e., microscopic shear bands and elongated subgrains (first level), submicro- (second level), and nano-grained (third level) structures respectively, within the deformed layer. The microstructural evolution consisted of two stages. First, the high density of dislocations resulted in the subdivision of the initial grains and the formation of subgrains. Second, the high misoreintation of boundaries was created and then, a more stable, equiaxed, and uniformed UFG structures were formed. The evolution of the sub-boundary of dislocation walls into the high-angle boundary was visible with an increase in plastic straining. Formed structures were highly non-equilibrium. A mechanical subgrain rotation model was suggested in which mechanically-driven subgrain rotations assist the formation and evolution of UFG structures during repetitive dynamic plastic straining. With the extension of SP time from 5 to 25 min, the depth of the whole deformed layer increased from 26 to 64 μm and the final equiaxed nano-crystallized size decreased from 90 to 46 nm.

P8.15

STRESSES AND MECHANICAL EFFECTS OF OXIDE FILMS ON TUNGSTEN AND MOLYBDENUM SINGLE CRYSTALS. J.E. Talia, Dept of Mechanical Engineering, Wichita State Univ, Wichita, KS; R. Gibala, Dept of Materials Science & Engineering, Univ of Michigan, Ann Arbor, MI.

Experimental results are reported on the effects of thin oxide films on the mechanical properties of tungsten and molybdenum single crystals oriented for single slip. Film thicknesses were in the range 40-400 nm and were deposited on 2-3 mm diameter crystals. The materials were deformed in tension and compression at temperatures from 77 K to 500 K at strain rates of 10^{-3} to 10^{-4} s^{-1}. In both tension and compression, these metal oxide systems exhibited surface film softening, i.e., at temperatures below approximately 0.15 of the absolute melting temperature, the oxide-coated materials deformed at lower stresses and exhibited larger plasticities than their uncoated counterparts. However, the effects are larger in tension for tungsten and larger in compression for molybdenum. These results are shown to be expected for oxides formed by anion and cation diffusion, respectively.

P8.16

NANOSTRUCTURED ULTRATHIN FILMS OF SILICATE CLAY AND POLYELECTROLYTES: DEPOSITION PARAMETERS AND MECHANICAL PROPERTIES BY NANOINDENTATION. Rigoberto Advincula, Xiaowu Fan, Department of Chemistry, University of Alabama at Birmingham, Birmingham, AL.

Recently, we have investigated the layer-by-layer (LbL) deposition of polycation and clay platelet ultrathin films. We have investigated the properties of these films using techniques such as ellipsometry, X-ray diffraction, surface plasmon spectroscopy (SPS), and atomic force microscopy (AFM), and quartz crystal microbalance, and X-ray Photoelectron Spectroscopy (XPS). In this talk, we would like to report our results regarding the formation of this type of hybrid ultrathin films focusing on their mechanical properties as probed by nanoindentation experiments. Structural information such as film thickness, platelet coverage, surface morphology, roughness, etc., are important parameters for their potential use as coatings. We have investigated the relationship of several of these parameters with their mechanical hardness and modulus properties as a function of indentor probe depth in nanoindentation experiments. The ultrathin films have remarkable mechanical properties very different from polymer ultrathin films. Practical applications of these films are important for the preparation of thin film electro-optical and membrane devices using the (LbL) technique.

P8.17
SLIDING WEAR BEHAVIOR OF NANOSTRUCTURED AUSTENITIC HIGH-NITROGEN STEELS. Robin Buescher, Andreas Krause, Alfons Fischer, University of Essen, GERMANY.

Since austenitic stainless steels provide a high corrosion resistance combined with a high mechanical strength and a good formability, they are in common use for orthopaedic (bone plates) and cardiovascular (stents) implant devices. Allergic reactions from nickel as an alloying element lead to the development of nickel-free stainless steels. In order to preserve the austenitic nonmagnetic phase without the use of nickel, nitrogen must be added in fairly high contents. The interstitial solution of nitrogen enhances the tensile strength, ductility [1] and pitting corrosion resistance [2], when compared to nitrogen-free stainless steels. Together with a high work hardening capacity, these properties predict excellent wear characteristics in corrosive environments. Metallic implants, which are exposed to wear and corrosion in contact with human tissue are usually electro- or mechanically polished prior to implantation. The aim of this paper is to investigate the influence of a novel surface topography on the tribological behavior of high nitrogen steels. Therefore, an austenitic nickel-free stainless steel with the trade name P2000 (VSG Energie- und Schmiedetechnik GmbH, Essen, Germany) was wet-chemically modified using chromosulfuric acid ($H_2SO_4 + CrO_3$) at 190 - 240°C for 30 - 90 min [3]. This treatment creates a macroscopically smooth (R_a = 0,8 μm) and a microscopically rough surface with features in the nm-range. The wear-corrosion behavior of mechanically polished (R_a = 0,02 μm), electropolished (R_a = 0,1 μm) and wet-chemically modified samples was studied on a pin-on-disc apparatus in distilled water and Ringer's solution. A normal force of 5 N (hertzian pressure of 370 MPa) was applied at a sliding speed of 0,1 m/s (sliding distance: 10 km). All experiments were carried out at RT. The resulting wear rate W was determined from the materials density, system parameters (sliding distance, wear scar area) and the mass loss, respectively. In all experiments, a region with a constant wear rate (Wc = 1.2×10^{-10}) can be observed, which starts after approximately 560 m of sliding distance. Although the wear rate does not change significantly up to 10 km, the polished samples constantly loose 1.4 to 2 times more material, when compared to the modified ones. During the running-in period (< 560 m), the surface topography seems to be even more influential: P2000 samples, which were wet-chemically modified, reach Wc in distilled water already after 25 m, whereas it takes the polished samples roughly 500 m of sliding distance. Although a slightly higher wear arises, the same tendencies can be observed in Ringer's solution. In order to analyse the acting wear mechanisms and to explain the lower wear on the rougher surfaces, respectively, the wear scar was observed in regular intervals using FE-SEM. Secondary electron images show the local formation of wear protective layers merely on the wet-chemically modified stainless steels in both media. They originate from wear debris particles, which are trapped in the structural cavities of the surface. Repeated loading leads to a compacted agglomerate of oxide debris and generates a smooth surface. An enhanced oxide content in the surface may reduce the friction coefficient and adhesion becomes less probable. As a result, wear rates as low as 2.8×10^{-11} (280 m) are measured in distilled water before repeated loading initiates segmentation and loss of the protective layer. One may conclude from these results that the novel surface modification process leads to an improved sliding wear behavior of austenitic high nitrogen steels. The benefit that less debris leaves the tribological system might be favourable for implant devices, which are exposed to wear in corrosive environments. [1] Thomann, I., Wear-corrosion behavior of biocompatible austenitic stainless steels. Wear 239 (2000) 48-58 [2] Olefjord, I., The influence of nitrogen on the passivation of stainless steels, Corrosion Science 38-7 (1996) 1203-1220 [3] Jennissen, H.P., Zumbrink, T., Chatzinikolaidou, M. and Steppuhn, T. (1999) J. Materialwiss. Werkstofftech. 30, 838-845

P8.18
PROPERTIES OF CVD-GROWN TiSiN MATERIAL FOR COPPER DIFFUSION BARRIER APPLICATIONS. Dalaver Anjum, Katharine Dovidenko, Serge Oktyabrsky, Eric Eisenbraun, Alain E. Kaloyeros, Univ of Albany, Institute for Materials at University at Albany-SUNY, Albany, NY.

TiSiN film is thermally grown at low substrate temperature (370°C) using TiI_4 and SiI_4 as Ti and Si precursors, respectively. Whereas the mixture of NH_3 and H_2 was utilized as a reacting gas. The stoichiometry of the deposited TiSiN film is determined by X-ray Photoelectron Spectroscopy (XPS) and is given by $Ti_{28\pm2}$ $Si_{21\pm1.5}$ $N_{39\pm3}$. Using the binding energy peak shift technique in XPS analysis, it is determined that deposited film have TiN and SiN_x phases present in the bulk. Furthermore, the presence of TiN phase in the TiSiN film is confirmed by using Transmission Electron Microscopy (TEM) analysis which is separated by amorphous SiN_x phase. The resistivity of the deposited film is 2000 $\mu\Omega$-cm at a thickness of 40 nm. The deposited film exhibits low surface roughness (~1 nm)as determined by Atomic Force Microscopy (AFM). Both XPS abd Rutherford Backscattering Spectroscopy (RBS) showed Cu diffusion upon one hour annealing of Cu/TiSiN/Si stacks at 500°C. The diffusivity of Cu in TiSiN film is obtained by estimating the amount of diffused Cu through the TiSiN film and the obtained Arrhenius relation is given by $D_{gb} \sim 10^3$ Exp [2.1 ± 0.48 eV /kT] cm^2/sec. The obtained results showed that CVD-grom TiSiN material is a promising candidate that may be employed as a Cu diffusion barrier for sub-100 nm device generations.

P8.19
DIAMOND COATED WC TOOLS FOR MACHINING WOOD AND PARTICLE BOARD. M.S. Raghuveer, S.N. Yoganand, K. Jagannadham, North Carolina State University, Department of Materials Science and Engineering, Raleigh, NC; R.L. Lemaster, North Carolina State University, Department of Wood and Paper Science, Raleigh, NC; J.A. Bailey, North Carolina State University, Department of Mechanical Engineering, Raleigh, NC.

Diamond coating was provided to improve the performance of WC-Co tools used in wood machining. Microwave plasma chemical vapor deposition was used to deposit diamond using a gas mixture with CH_4:H_2 in the ratio 0.5:100 at a temperature of 900°C. The microwave energy was set at 900W and a pressure of 35Torr was maintained in the chamber. An essential factor that determines the life of polycrystalline diamond coated tools is poor film adhesion. To counter this problem, we have developed a process that includes etching away cobalt from surface regions, treatment with H_2 plasma and use of TiC/TiN intermediate layers. The TiC/TiN layers were deposited by reactive magnetron sputtering. These layers embed diamond crystallites and improve adhesion, and in addition act as good diffusion barriers for Co. The diamond coated and uncoated tools have been characterized in the as deposited conditions and after prescribed wear by machining wood stock using SEM and X-ray mapping. It was also found that the limited contact area with diamond on the cutting edge effects the adhesion of the coating. Improvement in contact area by providing a larger radius to the cutting edge is discussed.

P8.20
CORROSION RESISTANCE AND STABILITY OF SELF ASSEMBLED SILANE MONO- AND MULTI-LAYERS ON ALUMINIUM AND ALUMINIUM ALLOY SURFACES. A.P.G. Robinson, Q. Guo, Nanoscale Physics Research Laboratory, School of Physics and Astronomy, The University of Birmingham, UNITED KINGDOM; J.A. Preece, School of Chemistry, The University of Birmingham, UNITED KINGDOM; M. Hebbron, S. Harris, G.A. Johnson, Sowerby Research Centre, BAe Systems, Filton, Bristol, UNITED KINGDOM.

Silanes have been widely investigated in the aerospace industry as adhesion promoters between metals and surface coatings. Here, the properties of the silanes themselves as functional surface coatings have been examined. Self assembled monolayers (SAMs) of five different short chain silanes have been prepared on the oxide surface of aluminium silicon copper oxide (AlSiCuO) film deposited on silicon wafers, and on plates of bare and aluminium oxide clad 2024 aluminium. SAMs were prepared using both the simple dipping technique, and via vapour deposition at standard temperature and pressure. The formation of monolayers has been probed using contact angle microscopy, to observe changes in the surface wetting properties of the samples. Atomic force microscopy has been extensively used to characterise the topology of the surface and thus distinguish between monolayers and physisorbed multilayers. The long term stability of the samples has been observed using contact angle microscopy and x-ray photoelectron spectroscopy when stored in an ambient environment. The corrosion resistance of the SAMs was evaluated using electron impedance spectroscopy, with a 3.5% sodium chloride solution. It was seen that a single monolayer of silane could provide at least 13 hours of corrosion resistance before the initial pitting event on 2024 aluminium plate. In order to improve the corrosion resistance self assembled multilayers, in which several layers of silane molecules are bonded head to tail, have been investigated. Several chemical processes have been utilised to convert the SAM functional group to an alcohol, whereupon further silane SAMs have been deposited. In this way it has been possible to build up homo- and hetero-geneous multilayers of silanes.

P8.21
INTERFACIAL FORCE MICROSCOPY AND ITS APPLICATION IN METAL MATRIX COMPOSITES. Robb M. Winter, Jan A. Puszynski, South Dakota School of Mines and Technology, Dept of Chemistry and Chemical Engineering, Rapid City, SD; Anthanasios N. Chantis, Berthold E. Liebig, South Dakota School of Mines and Technology, Materials Science Ph.D. Program, Rapid City, SD.

Metal matrix composites (MMCs) combine the properties of metal and ceramic or intermetallic materials. Common examples of metal matrix composites are Cu-Al2O3, SiCw-Al, Al-Al2O3, Al-B4C,Ni-NiAl3. Mechanical or thermal properties, such as strain-stress behavior, or thermal expansion coefficient can be tailored by changing the content of the reinforcing phase. The most common techniques of measuring mechanical properties of composite materials rely on macroscopic approach. During the past fifteen years, a significant effort has been made to develop various techniques of measuring mechanical properties on a microscopic level. These techniques include atomic force microscope (AFM) and indentation techniques, based on Hertzian mechanics. However, up to now, there is no reliable quantitative method of measuring Young's modulus and Poisson's ratio of individual phases as well as properties at the interfaces. This presentation will focus on fundamental aspects of measuring of mechanical properties of metal matrix composites at nano-scale using Interfacial Force Microscopy (IFM). The IFM is a scanning probe microscope which utilizes a unique self-balancing capacitance force sensor. Force-displacement curves obtained with the IFM are analyzed using Hertzian contact mechanics to extract the Young's moduli of the individual phases and interface region with nanometer spatial resolution. Special attention is paid to properties at interfaces between the metal matrix and the reinforcing ceramic materials. The properties of Cu-Al2O3, SiCw-Al, Al-Al2O3 composites will be discussed in detail. Furthermore, a comparison of experimental data with mechanical properties calculated from first principles will be discussed.

P8.22
ASSESSING TRIBOLOGICAL PROPERTIES OF METAL CARBIDE-METAL NACREOUS NANOSTRUCTURES USING NANOSCRATCH METHODS. Rachel W. Obbard, Todd S. Gross, Department of Mechanical Engineering, University of New Hampshire, Durham, NH.

It has been proposed that metal carbide-metal nacreous structures have improved mechanical properties over solid metal carbide films for use as hard coatings. The improved wear resistance of nacreous structures has been attributed to several sources, among them crack blunting, the presence of slip planes at the carbide-metal interface or within the ductile layers, and the effect of periodic interruptions on the metal carbide grain structure. We have used a nanoscratch technique to show that TiC-metal nacreous structures can have improved wear resistance over comparable solid TiC films. TiC-metal multilayer hard coatings have been deposited on Si and steel substrates using RF magnetron sputtering and pulsed laser deposition. Variables studied include TiC layer thickness, metal type, and thickness of metal interlayers. To assess the wear resistance of these films, we used the two-dimensional scratch capability of a commercially available nanoindentor under a reciprocal load. It was found that TiC-metal nacreous structures produced lower wear rates than solid TiC coatings for certain load ranges. The wear rate as a function of normal force was compared for various films to determine the mechanism producing improved wear resistance.

P8.23
PREPARATION AND CHARACTERISATION OF SELF ASSEMBLED MONOLAYERS FOR THE REDUCTION OF ICE ADHESION ON OXIDE SURFACES. A.P.G. Robinson, Q. Guo, Nanoscale Physics Research Laboratory, School of Physics and Astronomy, The University of Birmingham, UNITED KINGDOM; J.A. Preece, School of Chemistry, The University of Birmingham, UNITED KINGDOM; D. Hammond, S. Harris, G.A. Johnson, Sowerby Research Centre, BAe Systems, Filton, Bristol, UNITED KINGDOM.

Prevention of the accretion of ice on surfaces is of great importance in several fields where structures are exposed to low temperatures. In particular icing of aircraft can dramatically affect flight characteristics and safety, whilst ice accretion on transmission line insulators can lead to arcing and pylon collapse. This study has examined the effects of highly hydrophobic self assembled monolayers (SAMs) on the adhesion of ice to oxide surfaces. Films of trichloro(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silane were prepared using a simple dipping technique and by vapour deposition at standard temperature and pressure. The monolayers have been produced on the oxide surface of aluminium silicon copper oxide (AlSiCuO) films deposited on silicon wafers, on glass substrates, and on 2024 aluminium plates. Samples prepared under a variety of conditions have been characterised using contact angle microscopy, and atomic force microscopy. The SAMs are seen to substantially increase the contact angle on AlSiCuO, glass samples and 2024 aluminium plate. Films stored in ambient conditions have been examined using x-ray photoelectron spectroscopy and shown to be stable with time. The effect of the SAMs on the adhesion of ice to the surfaces has been investigated using plane-strain fracture-energy testing at -5°C. At this temperature ice on the anodised aluminium control samples was removed by a mainly cohesive process (failure within the ice) or a mixed mode (cohesive and adhesive) process. The fracture mode of ice on the SAM treated samples was completely adhesive (failure at the ice/sample interface) and the pressure of nitrogen required to remove the ice was reduced by 50% which implies a reduction of the work of adhesion of a factor of 4. It was observed that this reduction was repeatable, suggesting the SAM films are not significantly damaged by the removal of the ice.

P8.24
NOVEL NANOSTRUCTURED AMORPHOUS DIAMOND-TiN AND TiC COMPOSITES FOR BIOMEDICAL APPLICATIONS.
Roger J. Narayan, Jerome J. Cuomo, Gary Poeling and Jagdish Narayan, Dept of Materials Science and Engineering, NCSU, Raleigh, NC, and Wake Forest University, School of Medicine, Medical Center Blvd, Winsten-Salem, NC.

We have investigated novel nanocrystalline amorphous diamond composites where TiN and TiC nanocrystallites are embedded into amorphous diamond films. These films were synthesized by ablating amorphous carbon-TiN and amorphous carbon-TiC targets where carbon rotating targets are covered partially by TiN and TiC, respectively. Some of these films were also deposited by sequentially depositing amorphous diamond and TiN or TiC. The fraction of TiN and TiC nanocrystallites was controlled as function of distance from the original interface to create functionally gradient materials. Functionally gradient concept is used to control internal stresses and adhesion of thin films, and thereby improve wear of the novel amorphous diamond nanostructured composites for biomedical applications.

P8.25
FIELD EMISSION PROPERTIES OF NITROGEN-DOPED DIAMOND-LIKE CARBON FILMS DEPOSITED BY A MAGNETRON SPUTTER TYPE NEGATIVE ION SOURCE.
Kie Moon Song, Department of Applied Physics, Konkuk University, KOREA; Namwoong Paik, Steven Kim, Daeil Kim, and Sungjin Kim, SKION Corporation, Hoboken, NJ.

Nitrogen-doped diamond-like carbon (DLC) films were deposited on a silicon substrate using a magnetron sputter type negative ion source. Partial pressures of nitrogen gas and applied bias voltages were parameters of film deposition. The structural property and surface morphology of the films were examined using Raman spectroscopy, atomic force microscope, and scanning electron microscopy. Effect of deposition parameters on field emission property was studied. This measurement was carried out DLC or nitrogen-doped DLC films as the cathode and ITO-coated glass as the anode. The field emission data indicated that the nitrogen doping could lower the turn-on field and increase the current density. It was believed that doping of nitrogen into the DLC film plays an important role in enhancement of the field emission. This enhancement of field emission could be explained by the improvement of electron transport through nitrogen-dope DLC layer.

P8.26
THERMOELECTRIC PROPERTIES OF $B_{12+x}C_{3-x}$ THIN FILMS PREPARED BY PULSED ION-BEAM EVAPORATION.
H. Suematsu, K. Kitajima, I. Ruiz, T. Suzuki, W. Jiang and K. Yatsui Extreme Energy-Density Research Institute, Nagaoka University of Technology, Niigata, JAPAN; K. Kobayashi, D. Shimbo, Nob. Harada, M. Takeda Faculty of Engineering, Nagaoka University of Technology, Niigata, JAPAN.

Boron carbide ($B_{12+x}C_{3-x}$) is known as an excellent thermoelectric material particularly at high temperatures. Seebeck coefficient of $B_{12+x}C_{3-x}$ is as high as 300 μV/K. Electrical and thermoelectric properties of $B_{12+x}C_{3-x}$ vary with carbon content in the $B_{12+x}C_{3-x}$ phase. Although crystallized $B_{12}C_4$ thin films were successfully deposited on Si single crystal substrates at room temperature by a pulsed ion-beam evaporation (IBE) method[1], preparation of $B_{12+x}C_{3-x}$ thin films with various carbon contents have not been attempted. Furthermore, measurements of electrical properties requires thin films deposited on glass substrates. In the present study, preparation of $B_{12+x}C_{3-x}$ thin films on the glass substrates are carried out and the thermoelectric properties of the $B_{12+x}C_{3-x}$ thin films are measured. $B_{12+x}C_{3-x}$ bulks with nominal carbon contents of 3-x = 2.0 to 3.0 were synthesized by a spark plasma sintering. A pulsed ion beam of proton accelerated at 1 MV (peak) with a pulse width of 50 ns and a current of 70 kA bombarded on the $B_{12+x}C_{3-x}$ targets. Pyrex and quartz glass substrates were placed 80-100 mm apart from the target. After 10 shots, thin films with a thickness of 1.0 to 4.0 μm were obtained. X-ray diffraction results indicated that thin films were found to consist of a $B_{12+x}C_{3-x}$ phase and lattice parameters of the phase were comparable to that of the target. $B_{12+x}C_{3-x}$ thin films with various carbon contents have been successfully prepared by IBE method on glass substrates without substrate heating or sample annealing. Thermoelectric properties of the thin films were measured and the $B_{13.0}C_{2.0}$ thin film exhibits the highest power factor at room temperature among $B_{12+x}C_{3-x}$ samples

reported.
1) K. Kitajima et al., Jpn. J. Appl. Phys., 40 (2001) 1030

P8.27
EFFECT OF Co SEED LAYERS ON THE MAGNETIC ANISOTROPY OF Au/Co METALLIC MULTILAYERS. M. Kamiko, H. Mizuno, J. Xu and R. Yamamoto, Institute of Industrial Science, University of Tokyo, Meguro-ku, Tokyo, JAPAN.

Au/Co(111) multilayers and a Au buffer layer were grown by MBE on $Al_2O_3(0001)$ substrates using a thin Co seed layer. The influence of the Co layer on the structure of the Au/Co multilayers was studied by X-ray diffraction and reflection high-energy electron diffraction (RHEED), and compared to its effect on the magnetic anisotropy. The Au buffer layer grown on $Al_2O_3(0001)$ substrates display a large fraction of (111) twins, giving rise to a lack of lateral continuity in the film. The initial deposition of a few Å of Co onto $Al_2O_3(0001)$ substrates prior to deposition of the Au buffer layer yielded (111) epitaxial films with no twins. The use of the Co seed layer results in a highly improved structural quality of Au/Co(111) multilayers. From the results of Low-angle X-ray diffraction and RHEED observations, we confirmed that the interfaces of Au/Co multilayers with Co seed layer are sharper than those without Co seed layer. It cleary shows that the use of Co seed layer improved the periodicity of Au/Co multilayers.

P8.28
MICROTEXTURE OF COPPER-LOADED CARBON AEROGELS PREPARED BY AN ION EXCHANGE METHOD. Noriko Yoshizawa, Mildred S. Dresselhaus, Massachusetts Institute of Technology, Dept of Physics, Cambridge, MA; Joe Satcher, Ted Baumann, Lawrence Livermore National Laboratory, Livermore, CA; Katsumi Kaneko, Chiba Univ, Dept of Chemistry, Chiba, JAPAN; Morinobu Endo, Shinshu Univ, Dept of Electrical & Electronic Engineering, Nagano, JAPAN.

Copper-loaded organic aerogels were prepared by an ion exchange method of gels polymerized with a K-salt of 2,4-dihydroxybenzoic acid and formaldehyde. This sample was heat-treated at 1323K in a nitrogen flow to obtain the carbon aerogel. After heat-treatment, the density of the sample was increased from 200-250 g/cm^3 to 350-400 g/cm^3. According to TEM observations, the sample before heat-treatment had a highly dense packing texture with a network of carbonaceous particles, 15-20 nm in diameter. Mesopores with almost the same, or often larger, size relative to these particles were found among the particles. There were not any Cu or related compound particles large enough to be seen by TEM. The carbonized sample also has a dense packing texture. Its particulate structure shows less crystallinity and is much clearer than that of for the non-carbonized sample, but the network of carbon particles seems more collapsed after carbonization. The carbon aerogel particles are 10-15 nm in diameter and keep their round shapes. Mesopores about 10-20 nm in size are still present among these carbonized particles. We also found a lot of round Cu metal particles dispersed almost uniformly in the carbon aerogel texture. These Cu particles have a cubic lattice, according to their electron diffraction patterns, and their sizes are distributed in the 10-30 nm range. The dispersion and chemical conditions of the Cu species, as well as their effect upon the carbon aerogel texture, will be discussed in terms of their characterization using EELS, XRD, and molecular adsorption methods.

SESSION P9: MACRO-, MICRO-, AND NANO-TRIBOLOGY II
Chairs: Ashok Kumar and Stan Veprek
Thursday Morning, November 29, 2001
Room 311 (Hynes)

8:30 AM *P9.1
SUPERLUBRICITY AND WEARLESS SLIDING IN DIAMOND-LIKE CARBON FILMS. Ali Erdemir, Argonne National Laboratory, Energy Technoloy Division, Argonne, IL.

Diamondlike carbon (DLC) films have attracted great interest in recent years mainly because of their unusual optical, electrical, mechanical, and tribological properties. Such properties are currently being exploited for a wide range of engineering applications. Systematic studies on carbon-based materials in our laboratory have resulted in the development of a new class of amorphous diamondlike carbon films providing extremely low friction and wear coefficients of 0.001 to 0.005 and 10 -11 to 10-10 mm3/N.m, respectively when tested in inert-gas environments. These films were produced in a highly hydrogenated gas discharge plasma of a plasma enhanced chemical vapor deposition (PECVD) system at room temperature. Tribological studies established a very close correlation between the composition of the gas discharge plasma and the friction and wear coefficients of the DLC films. Specifically, DLC films grown in source gases with higher hydrogen-to-carbon ratios had much lower friction and wear coefficients than did films derived from source gases with lower hydrogen-to-carbon ratios. Fundamental and surface analytical studies have led us to conclude that hydrogen (within the film, as well as on the sliding surfaces) is extremely important for the superlubricity and wearless sliding behavior of these films. Based on these studies, a mechanistic model is proposed to explain the superlow friction and wear properties of the new DLC films.

9:00 AM P9.2
PLASMA DEPOSITION OF AMORPHOUS CARBON FILMS FROM CH_4 ATMOSPHERES HIGHLY DILUTED IN Ar. Luiz Gustavo Jacobsohn, Fernando Lázaro Freire Jr., Departamento de Física, Pontifícia Universidade Católica do Rio de Janeiro, Rio de Janeiro, BRAZIL.

Recently, strong indications pointed that C_2 species, instead of CH_3 radicals, are the building blocks of a-C:H films when CH_4 is highly diluted in argon[1]. In this work, we systematically study the deposition of a-C:H films in these conditions and correlate them with the film properties. The films were deposited by plasma decomposition of CH_4-Ar mixtures with a total pressure of 13 Pa, total inlet gas flux of 50 sccm and a fixed self-bias voltage of -350 V. The CH_4 partial pressure ranged from 1 to 100%. The effect of the residence time of the plasma species was investigated by varying the total inlet gas flux from 5 to 50 sccm and the total pressure for a fixed CH_4 partial pressure of 5%. The deposition rate decreased by a factor of ~10 as the CH_4 partial pressure decreased from 100 to 1%. The atomic arrangement was investigated by Raman spectroscopy and x-ray diffraction, while chemical bonding was revealed by infrared spectroscopy. As the CH_4 partial pressure increases, the fraction of hydrogen bonded to carbon increases, while the total hydrogen content remains constant. The internal stress was determined by measuring the substrate curvature. The behavior of the composition, density and stress are correlated and were explained by means of the ion bombardment during film growth. [1]C. Riccardi, R. Barni, M. Fontanesi and P. Tosi, Chem. Phys. Lett., 329, 66 (2000).

9:15 AM P9.3
TRIBOLOGICAL PROPERTIES OF FILMS AND POLYURETHANE PADS IN CHEMICAL MECHANICAL PLANARIZATION PROCESS. A.K. Sikder, Frank Giglio, John Wood, Ashok Kumar and Mark Anthony, Center for Microelectronics Research, College of Engineering, University of South Florida, Tampa, FL.

Continued miniaturization of the device dimensions and the related need to interconnect an increasing number of devices on a chip have led to building multilevel interconnection on planarized levels. In chemical mechanical planarization (CMP) very thin materials ($\leq$ 5 μm) have to be removed very precisely while maintaining the precise control on the remaining thickness. Because CMP occurs at an atomic level at the slurry/wafer interface, slurries, pads and film surface play a critical role in the successful implementation of this process. Surface roughness, elastic and viscoelastic properties, thickness and pore sizes of pad play an important role in this process. The films surface properties along with the mechanical properties also affect the within–wafer–nonuniformity, removal rate and roughness. We have studied the CMP process of oxide on different polyurethane pads with colloidal silica slurry at different conditions. The friction coefficient and acoustic emission signal was monitored during process. Surfaces of the pads were investigated before and after polishing using scanning electron microscopy (SEM). The oxide film surfaces were characterized using both SEM and atomic force microscopy. The removal rate was calculated by the initial and final thicknesses of the oxide film, measured by Ellipsometer. The validity of Prestons equation was also verified.

9:30 AM P9.4
MOLECULAR DYNAMICS SIMULATIONS OF CMP OF A-SiO_2. Evgueni Chagarov and James B. Adams, Arizona State University, Dept of Chemical and Materials Engineering, Tempe, AZ.

Molecular dynamics simulations have been carried out to investigate CMP of a-SiO_2. Specifically, the simulations involve a-SiO_2 slurry particles abrading various a-SiO_2 surfaces, for a variety of conditions. The composition of the surface is varied to mimic the effect of varying degrees of hydrolysis reactions at the surface. These simulations provide a detailed microscopic insight into the physical processes that occur during CMP, and how chemical reactions can affect those processes. Visualization of the results allows an easy interpretation of how temperature and local stress change when slurry particles abrade the surface, and reveal how material is removed. A wide variety of parameters are investigated, including degree of hydrolysis, surface roughness, contact speed, load, and temperature.

9:45 AM P9.5
DEVELOPMENT AND APPLICATION OF NEW ACCELERATED QUANTUM CHEMICAL MOLECULAR DYNAMICS PROGRAM TO SIMULATE CHEMICAL-MECHANICAL POLISHING PROCESS. Toshiyuki Yokosuka, Daisuke Kamei, Hitoshi Kurokawa, Hui Zhou, Seiichi Takami, Momoji Kubo, Akira Miyamoto, Tohoku Univ., Dept. of Materials Chemistry, Sendai, JAPAN; Akira Imamura, Hiroshima Kokusai Gakuin Univ., Dept. of Mathematics, Hiroshima, JAPAN.

Recent advancement of the silicon technology requests the ultimate integration technique for the development of new devices. Especially, the global planarization technique of the silicon wafer is strongly demanded for new device development. Recently, the chemical-mechanical polishing (CMP) process has gained much attention as a key technology to realize the planarization of the silicon wafer. The CMP is expected to solve all problems related to the roughness of the silicon surface such as the aspect ratio, focus depth, and so on. Although a lot of experimental results related to the CMP processes have been accumulated, the detailed chemical and mechanical mechanism of the CMP process has not been clarified on atomic and electronic level. Recently, computational chemistry has been applied to a lot of silicon technology, however no simulation study on the CMP processes has been performed, to the best of our knowledge, because of the lack of the software which can simulate the CMP processes. First-principles molecular dynamics method cannot simulate the CMP processes since it requests huge calculation time. Hence, in order to solve the above problem, we developed a new accelerated quantum chemical molecular dynamics program, based on our tight-binding theory. It is more than 5000 times faster than the first-principles molecular dynamics program. In this program, the shear process on the silicon wafer can be simulated by sliding the polishing particles, considering the electron transfer and chemical reactions. We successfully applied our accelerated quantum chemical molecular dynamics program to various CMP processes as well as the electronic and atomistic dynamics of the CMP processes were well elucidated.

10:00 AM P9.6
STOICHIOMETRIC Ti-C AND Ti-Si-C FILMS DEPOSITED BY MAGNETRON SPUTTER/ PULSED LASER DEPOSITION. Jose J. Nainaparampil, Systan Federal Inc., Dayton, OH; James E. Krzanowski and A.R. Phani, University of New Hampshire, Durham, NH.

The application of hard and lubricous coating materials to components subject to rolling and sliding contact is currently area of considerable research and development efforts. It is well known that carbide-based films containing excess carbon can exhibit excellent friction and wear properties in air environments. In the present study we have examined the friction and wear behavior super-stoichiometric Ti-C and Ti-Si-C films. The films were deposited by a hybrid magnetron sputtering/pulsed laser deposition process (independent source process) which was effectively used for the deposition of crystalline TiC, SiC and WC [1,2]. In this method carbon is ablated by PLD, while the Ti and Si are simultaneously sputter deposited, allowing independent control over the carbon stoichiometry. Films for this study were made using three types of sputtering targets: a pure Ti target, a Ti-12% Si target, and a Ti-25% Si targets. The hardness of the deposited films ranged from 10 to 28 GPa. The friction and wear properties were evaluated using a ball-on-disk method in an atmosphere of ambient air containing 50% r/h. Friction values in the range of 0.1-0.3 were obtained, and the films exhibited a very long wear life. X-ray diffraction and transmission electron microscopy were used to evaluate film structure. In most cases, the films with super-stoichiometric levels of carbon were found to have either a nano-crystalline or amorphous structure. 1. Voevodin et al., J. Appl. Phys, 82 (2), 855 (1997) 2. Josekutty J. Nainaparampil et al., JVST A 17 (3), 909 (1999).

10:15 AM P9.7
IONIZING RADIATION EFFECTS ON INTERFACES IN CARBON NANOTUBE-POLYMER COMPOSITES. Julie P. Harmon, Patricia Anne O. Muisener, Lori Adornato, LaNetra Clayton, John D'Angelo, Department of Chemistry, University of South Florida, Tampa, FL; Arun K. Sikder, Ashok Kumar, Center for Microelectronics Research, University of South Florida, Tampa, FL; Alan M. Cassell, Eloret Corporation, NASA Ames Research Center, Moffett Field, CA.

The purpose of this research was to probe polymer nanotube composites for evidences of radiation induced chemistry at the interface of the host polymer and the nanotube structures. Single wall carbon nanotube (SWNT) / poly (methyl methacrylate) (PMMA) composites were fabricated and exposed to ionizing radiation with a Co60 source. Neat nanotube paper and pure PMMA were also exposed. The dose was 5.9 Mrads at a dose rate of 1.28 X 106 rad/hour in an air environment. Both irradiated and non-irradiated samples were compared. Glass transition temperatures were characterized by differential scanning calorimetry. Dynamic mechanical analysis and dielectric analysis evidenced changes in relaxations induced by irradiation. Irradiated composites exhibited radiation induced chemistry distinct from degradation effects noted in the pure polymer. Nano-identation experiments were performed on the composites and pure PMMA to determine their respective hardness and modulus characteristics. Scanning electron microscopy and atomic force microscopy provided images of the nanotube and PMMA interface before and after irradiation. This investigation imparts insight into the nature of chemical reactions in these materials initiated by ionizing radiation.