SYMPOSIUM P

Advances in Surface Engineering—Fundamentals and Applications

November 26 – 29, 2001

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*Invited paper
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.
Subha 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, nanodevices, and atomic force microscopy. First, experimental studies 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 discontinuous 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, MA; Stan Veprek, Stanford University, Institute for Chemistry of Inorganic Materials, Technical University Munich, Garching, Munich, GERMANY.

The superhard nanostructured coatings prepared according to the generic design principle [1] which results in self-organization of a stable nanostructure show an unusual combination of mechanical properties, such as high hardness of 40 to 1000 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 10%. In contrast, conventional hard 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 nanostructured coatings can be understood in a logical way by scaling the fracture physics and mechanics to the crystal size of 3.5 nm. In such nanostructures which have a strong interface between the nanocrystals, the stress concentration factor is estimated to be of about 3-4, 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 non-elastically enhanced stiffness for which there is no rational physical justification. The very high values of elastic modules 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 NANO-COMPOSITE COATINGS.
B. Feng, D.M. Cao, W.J. Meng, Mechanical Engineering Department, Louisiana State University; Baton Rouge, LA; LE. 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 (Mo,C,H) and metal-containing amorphous silicon nitride (Mo,Si,N), elastic modulus and hardness values exceeding the linear range 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. Kossowski, Jose L. Fadzio, Simun H. Koutzski, Chemical 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, significant hardening 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 45-50 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 Ta-Si-C, Ti-W-C, Ti-Mo-C and Ti-Ni-C. We have attempted to manipulate the microstructure via the use 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. Within 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 microstructure 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/TiAlN MULTILAYERS COMBINED WITH CROSS-SECTIONAL ELECTRON MICROSCOPY OBSERVATIONS. N.J.M. Carvalho, J.Th.M. de Hessen, 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 properties and mechanism of delamination of multilayer systems by nano-indentation and cross-sectional electron microscopy. Both titanium nitride (TiN) and titanium nitride/titanium-aluminum nitride (TiN/TiAlN) multilayers deposited by physical vapor deposition onto steel substrates were subjected to ultralow load indentations. The homogeneous coating was deposited using a triode evaporation ion plating process, whereas the multilayer 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 technique. 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 scale, 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 unstable against out-of-plane displacements, which reduce the stress and the associated energy density. The specific response is governed by the properties of the individual materials, which can include the stress and the energy density of the films. 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 comprehends DLC on steel substrates with a Cr adhesion layer used for enhancing the fatigue life of gears and bearings. Another refers to DLC on glass substrates used for optical purposes. The second category refers to thermally grown silicon dioxide (TGO). Another example consists of silicon nitride that forms on a NiAl/TGO alloy within a thermal barrier systems used in gas turbines. In this case, the film has thickness on both sides: a superalloy on one side and a stabilized zirconia 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 silicon. The failure mechanisms and discussed, emphasizing their dependence on the properties of the constituent hardness, residual stress and the role of imperfections. Simulations are presented that animate the basic concepts.

11:00 AM P1.7
MECHANICAL CHARACTERIZATION OF FUNCTIONALLY GRADUATED MATERIALS WITH A YIELD STRENGTH GRADIENT.
Ali Naghib, Gérard Marmouz, Olivier Bréard, Rochdi El Abdi, Rennes T University, Laboratoire de Mecanique et des Materials Industriels (LMMI).

Functional materials with a yield strength gradient are a new class of materials that can be used to increase the performance of structural components, such as aircraft wings, bridges, and other high-stress applications. These materials are designed to have a gradual change in yield strength across their thickness, which allows them to better withstand extreme loads and prevent catastrophic failures. This concept has been explored in various types of materials, including metals, polymers, and composites. A typical example is the use of a gradient in the tensile strength of a metallic material, where the strength decreases from the surface to the core. This gradient can be achieved through various manufacturing techniques, such as forging, rolling, or extrusion, and can be tailored to fit the specific needs of the application. The mechanical characterization of these materials is critical to ensure their safety and performance. Tests such as tensile testing, fatigue testing, and fracture toughness testing are commonly used to evaluate the mechanical properties of gradient materials. The results of these tests can provide insight into the behavior of these materials under various loading conditions and help to optimize their design for specific applications.
An elastic-plastic spherical micro-indentation study of functionally graded materials (FGMs) with gradient in yield strength, such as steels hardened by thermal hardening, is made by experimental and finite element methods. Indentation simulations are done with diameter sphere of 1.875 mm. Various surface-substrate yield stress ratio $\beta$ (1 < $\beta$ < 0) and strain hardening exponent $n$ (0 < $n$ < 10) 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 stress corresponding to plastic strain, as a function of the nanoindentation size, shows that the mean contact pressure presents the same tendency as that of equivalent homogenous materials. For the fully plastic case, the 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 evolution of FGMs during spherical indentation is given. Plastic zone radius evolution 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 function 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 hardening 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 Vickers hardness techniques are compared with those obtained by the proposed method.

11:15 AM P18
DIFFERENT MECHANISMS OF ACHIEVING SUPERHARDNESS IN COATINGS: STABLE NANOCOMPOSITES VS. HIGH COMPRESSIVE BIAXIAL STRESS
S. Vegeck, P. Kurevac, J. Prochazka, H. Muenling, Institute for Chemistry of Inorganic Materials, Technical University Munich, Garching, GERMANY; M. Jilek, SHM Ltd, Novy Mlyn, 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 stresses of 5-7 GPa (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 (≤1 GPa) stress, the hardness values from the load-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 nano-indentation. Superhard, stable nanocomposites (nc-TiN/n-Si3N4, nc-TiCN/n-Si3N4 and others) retain their room-temperature hardness even at 1100°C. In contrast, coatings of CrN/Ni and ZnN/Co [3] show a strong decrease of the hardness to the bulk values already after annealing at 400°C at 500°C due to the relaxation of the compressive stress, in agreement with the behavior of other high-pressure coatings [1]. Therefore it becomes that the superhardness of stable nanocomposites originates from their nanostructure whereas that of CrN/Ni, ZnN/Co and similar is [3] due to the high compressive stress. No contribution to the enhancement of the hardness via “nano-composite effect” in these coatings could be identified. [1] W. Herr, E. Broszeit, Surf. Coat. Technol. 97 (1997) 335; [2] J. Masi et al., Thin Solid Films 167 (1988) 107; [3] J. Masi, Surf. Coat. Technol. 125 (2000) 322

11:30 AM *P19 MECHANISMS OF PLASTIC DEFORMATION IN NANO-MICROSTRUCTURED CERAMIC THIN FILM MATERIALS
Lara Halbritterman, Physics Division, Department of Physics, FM Linking University, SWEDEN

Nanostructured ceramic thin films are attractive in that they can exhibit high mechanical strength. The materials comprise nanolaminates - i.e. 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 superlattices (TiN/Ni), which show unexpected mechanical behavior of the intergrowth, 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 hardening at interfaces between phases with different shear modulus. A study of oxide superhard phases Y2O3/Er2O3 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 different 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 sufficient 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 existence of nanocomposites, e.g., SiN/AlN, however, the observations on the nanometer level of deformation phenomena becomes progressively cumbersome with the increased dimensionality of the system. [1] L. Halbritterman, Z. Metallk. 90 (1999) 802; [2] P. Vash, S.A. Burnct, L. Halbritterman, W.D. Sproul, J. Mater. Res. 14 (1999) 3614.

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

1:30 PM P22.1 RESEARCH CHALLENGES AND OPPORTUNITIES IN SURFACE ENGINEERING AT THE NANO-SCALE
Jean Lannoo, MSE, 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 last decade. As a result, the surface characteristics of an object is moving towards having a clearly defined functional role rather than just being the border with the outside. This new two-dimensional world has been proclaimed a part of “nano-technology” which fits over the old, three-dimensional world of “mico-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 some of the exciting research challenges of the near future in this dynamic field. Topics vary from the somewhat mundane development of design data, measurement technologies, standards and process control, to advanced modeling, development of multi-layered and high-tech coating systems with nano-scale features and sculptures, 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 this continuously 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 P22 MD SIMULATIONS OF HIGH SPEED NANOINDENTATION AND PLOTTING ON CAN PITCHFABRICATION

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 nanonindentation and polishing of a hard tip into an AI (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 polishing speed. We also studied the alloy effects of the substrate. The indentation loading and unloading curves and polishing curves are generated. Also, we discuss the hardness of materials and the material properties and polishing of indentation during the indentation and polishing.

2:15 PM P23 FRICTION ANISOTROPY AT Ni(100)/100/100 INTERFACE
Yue Qi, Takan Cogan, William A. Goddard III, Material & Processing Simulation Center, Caltech, Pasadena, CA; Yong-Tae Cheng, GM R&D Center, Warren, MI.

Analytical theories indicated that there is no static friction on clean
incomunrate interfaces, while a recent experiment revealed that the static friction coefficient was anisotropy with respect to the lattice orientation and not uniform. Under constant force, we found that the clean, first, and incomunrate interface indeed has a very small static friction coefficient. However, surface roughness can increase the static friction on the incomunrate interfaces dramatically beyond the friction on the incomunrate interfaces to a lesser extend. Thus, the rough surfaces show similar anisotropy behavior as in experimental results. The effects from temperature, roughness, disordering and defects on interface are discussed as well.

2:30 P.M. P.2.4
CHANGING SURFACE MECHANICAL PROPERTIES THROUGH ELECTROCHEMICAL MODIFICATIONS
Martha M. McCann, Susan G. Corcoran, Virginia Tech, Dept Materials Science and Engineering, Blacksburg, VA.

The mechanical response of materials can be dramatically altered by the presence of adsorbed species on the surface. An electrochemical environment enables discrete control of the surface, keeping it clean (as compared to ultrahigh vacuum) and inducing stable stress states. Applying a potential to the surface can lead to charge neutralization, 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 match between the metal and its idler 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 micrometer scale resolution delivers a way for a reliable observation of dislocation behavior with applied load. This enables the identification of mechanisms by quantifying the changes in mechanical properties under specific environments. As has been extensively studied in electrochemistry literature, it is well behaved and well characterized. It is a model system that demonstrates variation in mechanical properties in different electrochemical states. Lessons learned on Gold have also been applied to Zn and Ni systems.

2:45 P.M. P.2.5
KINETIC MONTE CARLO STUDY OF DISLOCATION ETCH PITS: Daniel Benz, 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 as the local stress developed from a 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. Calculations have been performed for various values of the stress to the etch attack and the constant 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 P.M. P.2.6
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 achieve 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 emphasized, and the way in which this influences the likely direction for the future development of tribological coatings is discussed. In 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 achieve 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 load. Such materials will also be of particular interest to kMC calculations which can also accommodate 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 P.M. P.2.7
THIRO-CONTACTS WITH MICRO SLIP IN COATED SOLIDS
Landsa Zhong, Scott Seager, 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 and normal force. Solutions for the normal pressure for frictionless contact are obtained. Solutions of Fourier series and Chebychev polynomial are evaluated. Cases involving indentations by a cylinder and flat-end stamp are examined.

4:15 P.M. P.2.8
TRIBOLOGICAL AND MECHANICAL CHARACTERIZATION OF BORON CARBIDE NANO-COMPOSITE COATINGS
Srinivas Nekkanti, 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 hardness, 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 mobile 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 ceramic substrates. Tribological properties are investigated with pin-on-disc 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 nanoindentation 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 P.M. P.2.9
NANOINDENTATION AND WEAR BEHAVIOR OF Ti-Nb-3Ni-NICKEL ALLOYS: Xiangyang 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. Grammen, 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-disc wear experiments that are suggestive of tribological applications of NiTi alloys. It is shown that high strength in a physical 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 to 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 P.M. P.2.10
WEAR AND FATIGUE ON QUASICRYSTALS
J. M. Duhain, P. Brunet, G. Bonhomme, V. Demange and M. C. De Weerd, Ecole des Mines, Nancy, France; E. Baron, CEA, Curie, Paris, France; A. Merzabinger, Averio Research Center, Sebersdorf, AUSTRIA; D. J. Sorbelet, M. Bessei, Dept of Materials Science, ISU and Ames Laboratory, Ames, IA; J. A. Anderegg, C. Jenks, V. Fourmain, P. A. Thiel, Dept of Chemistry, ISU and Ames Laboratory, Ames, IA.
Wetting and fretting are two essential properties that to a large extent - and 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 aluminium, which comprises true quasicrystals, their approximants and some crystalline materials of related composition. Experimentally, wetting 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 characterized, 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 show them to be anisotropic in nature, 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 on a summary of these findings and of their actual technological relevance. The present work was supported by CNRS/NSF International Cooperative Program PICS 545.

SESSION P3: INDUSTRIAL APPLICATIONS OF SURFACE ENGINEERING I
Chair: Clark VanTine Cooper and Wen Jin Meng
Tuesday Morning, November 27, 2001
Room 311 (Hyman)

8:30 AM *P3.1
CHARACTERIZATION OF ANTIWEAR FILMS USING MICRO-FOCUS XANES AND IPM M. R. Norton, Than Do, M. Nicholas, M. Koster, T. Woo, N. Mosty, G.M. Bonefort, 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 mm with 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 materials 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 the micro-force microscopy (IPM) and the Hastelloy nanocylinder. 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 modeling techniques are being applied to determine the origins of the beneficial properties of the anti-wear 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 lubrication 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

This 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 only a limited literature on which control factors 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 oxides 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 nanoscale surface features of a ceramic coating are altered by strain, which is several times an order of magnitude 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 characteristic 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 Bhat, R.D. Virgute, Ichiro Takeuchi, R.P. Sharma, and T. Venkatesan, C.S.R., 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 headers. 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 header component 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 #3-39419) and Blue Wave Semiconductor, 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. Edrissi, A.T. Alpay, 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 testing chamber was used for the tests. Tests were performed in an atmosphere with various humidity levels in the range of 16-96% 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 rate is dominated by the formation of iron oxides. The mechanism for the wear process depends on the composition of the oxides formed; as 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 Fe3O4. As the atmospheric humidity increased, a tribolayer forming process became active, and the wear rate increased with increasing humidity. Automotive applications of thermal sprayed coatings will also be discussed.

9:45 AM P3.5
NITRIDING OF TOOL STEELS USING ELECTRON-BEADED-EXCITED PLASMA DEVICE. Hiroshi Shoyama, Toshihiro Kobayashi, Hideki Sato, Yoshiaki Tsuchikawa, Tamiro Hara, Toyota Technological Institute, Nagaokakyo, Japan; Takahiro Aohara, Faculty of Science and Technology, Meijo Univ., Nagoya, Japan; Kazunori Taniguchi, Department of Physics, Kyoto Univ. of Education, Kyoto, Japan; Mamoru Harasugi, 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 plasma and their outgrowths are widely 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 given by a Gaussian distribution 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 50-550 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 providing a dose rate of 10^12 ions/s·cm². 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 sputtering 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 SPUTTERED-DEPOSITED ONTO AISI 52100 SUBSTRATES AS ILLUCIDATED 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, MA. Takeh, Caterpillar, Inc., Peoria, IL.

Magneton 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 different alloy compositions, one containing W as the metallic constituent and the second containing Cr, have been deposited in a plasma containing Ar and C₂H₂. Interrupted, unidirectional sliding experiments of the ball-on-ring type have been conducted in a poly-alpha-oil (PAO) lubricant at a load of 607 N for discrete numbers of cycles, N, of between 10 and 10,000. Focused-ion-beam, scanning electron microscopy (FIB/SEM) has been applied to characterize the microstructure of metal-containing magnetron sputtered coatings and to detect wear debris. 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 remain 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 efiency and value in observing the coating and substrate interface are highlighted as a means to investigate coating/substrate interfaces and to establish wear mechanisms.

11:00 AM P3.7

Life time limiting effects in roller bearings and gear wheel applications are wear, seizing 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™ W-C-H offer surface protection under dry, mixed, and hydrodynamic friction conditions. This allows the increase of load capacities, respectively the decrease of wearing size. Moreover, the reduction of toxic lubrication additive decreases the biological exposure. The performance of the Me-DLC coatings in roller bearings was investigated on the FE3 test rig under mixed friction conditions. MAXIT™ W-C-H was deposited 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 6µm in respect to optimized wear resistance. The wear of roller balls and disks was drastically reduced by powers of ten as compared to uncoted roller bearings. Additionally, results on FZG gear wheel tests, as well as examples of the successful application of MAXIT™ W-C-H in motor power engineering and hydraulic technique are presented.

11:15 AM P3.8

Operating conditions in typical automotive planetary gear sets lead to high tribological conditions. Relatively low operating speeds and low viscosity lubricants limit the formation of protective oil films. As power density demands increase in the transmission, the traditional EHD methods adaptive 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

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/cyclohexane atmosphere. At 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. Kelsey, Mei-Ling Wu, Timothy Klemmer, Yoon-Tae Hain, Kent Howard, Seagate Research, Pittsburgh, PA.

Boron carbide (B₄C) is the third hardest material at room temperature. It has wide range of applications on coatings and cutting tools development. Cutting tools made from ultra-thin B₄C films have been reported to have enhanced surface roughness, which is typically a limiting factor in DLC films. In this paper, we characterize the properties of B₄C films with thicknesses less than 10nm thick. We focus on nanoindentation and mechanical properties of thin B₄C films deposited by low pressure, high current ion assisted 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 B₄C thin films deposited on Si substrates and have found that smooth surfaces for 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 resistance superior to that of DLC films. We have surveyed variations in mechanical properties as a function of deposition parameters, including sputtering pressure, RF ion source power, and target power, and correlated these variations with other film properties such as composition and stress. Finally, we comment on the influence of these films as protective overcoats for hard-disk recording media.

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

Chair: James E. Krizmowski and Gary L. Doll
Tuesday Afternoon, November 27, 2001
Room 311 (Hyatt)

1:30 PM P4.1
IN-SITU STRESS CLINIC FOR SURFACE ENGINEERS. Roy Clarke, University of Michigan Applied Physics Program, Darryl Barrett 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. The developments are made possible by increasingly powerful thin film deposition techniques whereby noble electronic, optical, and mechanical properties can be achieved by structuring the coatings at a microscale level. The purpose of this paper 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 versatile and can be used in a wide variety of deposition situations. We will also demonstrate how in-service, in situ, and in-vitro experiments help elucidate 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 dynamic improvements in the capabilities and performance of thin film coatings.

2:00 PM P4.3
CHARACTERIZATION OF THE DEGRADED MICRO-STRUCTURES OF A PLATINUM ALUMINIDE COATING
Huangjian 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 aluminate bond coat. Although bond coats almost universally contain alumina, their creep resistance varies greatly. 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 aluminate coatings is warranted. This paper concerns itself with an internal diffusion, unactivated pack cementation platinum aluminate (PtAl) bond coat system that is studied under isothermal exposure and thermal cycling up to 1100 degrees C. The highly nonhomogeneous microstructure is presented for the various thermal exposures and the changes in elemental gradients are given. The PtAl coating is seen to interact 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 thermostatically 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 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 micropuck surrounding indent.

2:15 PM P4.4
FUNCTIONALLY GRADED MATERIALS PRODUCED WITH HIGH POWER LASERS
Jeff Th. de Hoon, 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-beam 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 substrate. Unlike laser cladding, the contact between laser beam and added material in LMI is limited to a layer that is just necessary to form a new surface layer in the 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 extreme 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. This 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 mean 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 analyzed using the Digital Image Correlation technique. J. Th. M. De Hoon, in: Intermetallic and Ceramic Coatings, Marcel Dekker, N.Y., Edited by N.B. Dahotre, T.S. Sudarshan, p. 307-441, 1999.

2:30 PM P4.5
IN-PLANE CRACKING BEHAVIOR OF THERMALLY AGED AND CYCLED THERMAL BARRIER COATINGS
Zhehan Zhang, Jun Kaneda, Arne H. Swanson, Iowa State University, Ames Laboratory, Ames, IA. "Office of Naval Research International Field Office, Tokyo, Japan. Hitachi, JAPAN, Toshiba Electric 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 via in-service have been recently characterized in terms of the critical local tensile stress (σc) using a protruded TBC beam specimen with finite strain analysis. It was shown that in-plane TBC cracking near the interface occurred more easily than that near the TBC mid. Near and away from interfacial TBC cracking were shown to have opposite effects of the substrate toughness. The characterization indicated that the oxide growth and thermal cycling at 1550°C in air was induced by thermal cycling due to the thermal expansion mismatch. In order to examine how the factors control in-plane TBC cracking, the impact and cyclic aging at 950°C in air was carried out in an 8% ZrO2 TBC/FeCrAl alloyed on a Ni base superalloy substrate. Thermal aging, giving rise to layering of formation of GTO on the TBC, but not residual stresses, resulted in a slight increase of σc for the near and new in-plane TBC cracks due to the thermal expansion mismatch. In addition, in-plane TBC cracks near and away from the interface were initiated at the same σc, 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 a R&D program approved by the USDOE, Office of Basic Energy Sciences, Division of Materials Sciences.

2:45 PM P4.6
AN INVESTIGATION INTO THE COATING/SUBSTRATE BOND IN THE HIGH VELOCITY PARTICLE CONSOLIDATION PROCESS.

High Velocity Particle Consolidation (HVPC), also known as the cold gas dynamic spray technique, is a relatively new, low temperature, high energy, high throughput, 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 deliver a high pressure gas with entrained powder particles to a supersonic velocity and impinging the supersonic velocity 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 used as coating/substrate combinations (i.e., Al on Al) and as disimilar coating/substrate combinations (i.e., Al on stainless steel). The interface between the 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 P4.7
NANOSTRUCTURED THIN FILMS AND COMPOSITES
Jagdish Narayan, Dept. of MSE, 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 and chemical processes, 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 nanocrystalline microstructure. This 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 made in order to achieve the desired properties.

4:00 PM P4.8
SPECTROSCOPIC ELLIPSOMETRY AS A POTENTIAL IN-LINE TOOL FOR THE CHARACTERIZATION OF SOFT MATTER SYSTEMS
S. Naik, A. Mittal, A. M. V. More, and A. Roy, Nanostructures, LLC, Dallas, TX.

Spectroscopic Ellipsometry has proven to be a powerful technique in the study of soft matter systems. The technique is already utilized to study the interactions of small molecule samples with various substrates. It is apparent that this technique can be expanded and applied to the analysis of more complex systems. In this work, the authors utilize the tool to study in-plane cracking behavior of thermally aged and cycled thermal barrier coatings. 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 a R&D program approved by the USDOE, Office of Basic Energy Sciences, Division of Materials Sciences.
METROLOGY TOOL FOR POROSITY MEASUREMENTS OF LOW-DIELECTRIC FILMS. N.Y. Edwards, J. Vellis, Q. Xie, S. Zeller, R. Meyer and H. Himmelberger, Motorola, Mesa, AZ; J. Viles 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 10nm technology node will require materials with dramatically lower static dielectric constants, achieved without sacrificing other robust material properties. One strategy for achieving these 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 (organosilane) films 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) performed from 0.7 to 6.5 eV via a series of OSG films in a Wolfham 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 SiO₂ 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 SiO₂ film. In order to understand the unusual altered ion 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. Wolfham 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 Hyne, 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. Multi-species diffusion formalism for ionic species is adopted for the purpose of our study. Onager 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 Yatsuji, Hiyuki Sakaue, Wataru Jiang, Tiancon Suzuki, Sung-Chae Yang, Yoshiki Inoue, and Masako Hirai, Institute of Energy Science, Nagoya University, Nagoya, Japan.

If an intense pulsed ion beam is irradiated on solid target, high-density plasma is generated in the interaction region, and high-energy particles and atoms will be produced in the plasma. The interaction region will be large due to the short range of the target. In 1998, the author proposed and demonstrated a preparation method 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. High stoichiometry has been kept between the target and the films. Since basic principle has been published elsewhere, new results on the preparation of crystallized B₄C films are discussed here since we believe this is the first time in the world. As well known, B₄C is a hard material after diamond. It is wear resistant as well. The melting point is 2450°C, and it is very stable even at high temperatures. Furthermore, it is a good thermoelectric material, whereby Seebeck coefficient is considerably high. Nobody has succeeded in the preparation of the crystallized films. The experimental results, together with various characterization, such as X-ray diffraction, F-I-V, EELS, high resolution TEM, and hardness tester, revealed that the crystallized B₄C films have been successfully prepared by IBE. Vickers hardness of 2300 has been obtained by the films. Similar results of the preparation of many kinds of films will be prepared, for example [B₄C], YBa₂Cu₃O₇, SrAl₂O₄Eu: Dy and polycrystalline Si. Furthermore, such a high-density plasma provides to synthesize ultrafine nanocrystalline powders, typically characterized as 5-20 nm in diameter, by rapid cooling with the ambient gas. Various combinations of the gas and the gas, we have succeeded in the synthesis of powders of Al₂O₃, AlN, TiO₂, and TiN. Fruitful applications seem to be available from 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. Dell, Yang Tse Cheng and Stan Vegrev
Tuesday Evening, November 27, 2001
8:00 PM
Exhibition Hall D (Hyne)

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 rapid control of surface uniformity and deposit 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, Ti, P, Nb, Si, Ce, Y, Co, CaLa and carboxyl polyelectrolytes, such as poly(diallyldimethylammonium chloride), polyethyleneimine, poly(allylamine hydrochloride) were prepared. The deposition method is based on electrolytic (ELD) or electrochemical (EPD) deposition of ceramic phase 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 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
INSITU MONITORING OF NUCLEATION STAGE DURING ALUMINUM-CVD FOR NANO-STRUCTURE CONTROL. Tomohisa Inoue, Masami Sugiyama, and Yoshiruo Shimokazi, Univ. of Tokyo, School of Engineering, Tokyo, JAPAN.

The ever-growing integration of ULSI devices reduces the device feature size. The submicron devices require continuous and smooth films with thickness of several nano-meter. These technical trends 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 dimethyldihydroxyamine (DMAH) as the source precursor, and established elementary reaction mechanism of the CVD process. We could succeed in improving surface morphologies by the aid of this chemical perspective. The only thing that remained as a black box is the initial nucleation issue. 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 behaviors 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 REACTION BLANKETS. Zuotao Zeng, Ken Notean, 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 we developed to fabricate the CaO coating. A 24-pm 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 consists of several phases including glass which melts at 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.


P.5.4 MEASUREMENT OF MECHANICAL PROPERTIES OF SINGLE AND MULTI-LAYED NITRIDE THIN FILMS PREPARED BY CATHODIC ARC DEPOSITION. A.K. Sikdar, I.M. Izrane, Ashok Kumar, Robert Durbin and M.D. Smith.


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, TiC and TaN) 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 NHT Indenter XP with a Berkovich indenter. Indentation mark 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.

P.5.5 CaO ELECTRICAL INSULATOR COATING ON V-4Cr-4Ti. R.A. Francis 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 self-healing of defects of electrically insulating CaO coatings for use in vanadium/liquid lithium magnetic fusion reactor blankets. To form CaO film at the interface of V-7Ti-Cr alloys and the liquid lithium, it needs precharged-O from the V-7Ti-Cr-alloys, and Ca in the liquid lithium. To understand incorporation in the alloys, we used the binding energy of potential elements and O. Additionally, we conducted several experiments in situ fabrication of CaO film [±10μm thickness] on the V-7Ti-Cr alloys. Work supported by the U.S. Department of Energy, Office of Fusion Science, under Contract W-31-109-Eng-38.

P.5.6 SPATTER-DEPOSITED BCC TANTALUM ON STEEL WITH AN INTERFACIAL TANTALUM NITRIDE LAYER. Anurima Patel, Marek Somowski, Leszek Gladzio, 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 metastable beta phase is usually obtained in sputtering 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 corrosive wear. It was found that with the intermediate layer of tantalum nitride the preferred alpha phase was grown on steel by DC magnetron spattering technique. The structural and electronic properties of these films were studied by four-point probe measurement and X-ray diffraction (XRD). Microstructure of interfacial tantalum nitride layer was investigated by rutherford backscattering (RBS). Influence of the interfacial film thickness and the level of oxygen 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, K2) and on the substrate temperature (108-408°C) during deposition.

P.5.7 NOVEL SILICON-CARBON PRECURSOR FOR OLIGOMER CHEMICAL VAPOR DEPOSITION OF SILICON CARBIDE FOR HARSH ENVIRONMENTAL APPLICATIONS. Ulrike Betschke, Harry Fischer, James Casterline, Alvin E. Kulkosky, UABarn Institute for Materials and School of NanoSciences and Materials, The University of Alabama in Huntsville, AL, and Walter Sherwood, Starfire Systems Inc, Watervliet, NY, and Colorado State University, 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, hydrogen free, oligomer precursor. High quality films were grown at substrate temperature in the range of 600°C to 1200°C at low pressure in the range of 1.5 Torr. HPCs-S is a silicon carbide precursor composed of an alternating silicon and carbon backbone with hydrogen side groups. Depositions on silicon carbide substrates yielded stoichiometric SiC films with thickness in the range 0.3 to 50 microns. Structural and chemical characterizations were performed by Anger's, Raman spectroscopy (RS), 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 wind/alkali baths for extended duration. The films maintained hardness, adherence and stability, and ball-on-disk friction coefficient properties were measured using a nanoindenter, a Knop's hardness tester, and a ball-on-disk tribometer tester. The SiC coatings deposited at substrate temperatures below 1100°C were found to be amorphous. Erosion studies were performed on cermet, SiC coated SiC fibers and cermets to simulate erosion at 100°C and 1100°C.

P.5.8 CVD DIAMOND SYNTHESIS ON WC-Co CUTTING TOOL VIA ELECTROPHORETIC SEEDING PROCESS. Toshiaki Tsuchi, Makoto Nagata, Kumanoto University, Graduate School of Science and Technology, Kumanoto, Kumanoto University, Faculty of Engineering, JAPAN, Nishiyama, Kuma University, Kuma, JAPAN.

Using ECR-MPCVD (electrocycletron resonance microwave plasma chemical vapor deposition) apparatus, CVD, diamond film synthesis was attempted on WC-Co cutting tools. Electroplating deposition was utilized for the seeding process of diamond film growth. A commercial diamond powder (size: 20-250μm) was employed in this study. The diamond powder was suspended in acetone at the concentration of 0.1 g L-1, and was electroplatinated on substrates. Si[100] plane or commercial WC cutting tool was used as a substrate, and Pt plate was used as a cathode for electroplating deposition. The diamond particle density of Si[100] was dependent on the electroplating condition. After electroplating, film on the WC substrate using ECR-MPCVD apparatus. Electrochemical deposition was effective for the synthesis of diamond film on WC cutting tool without removing the coating on the surface, although the film thickness between the film and the substrate was insufficient for the application to a cutting tool. Heat treatment after electrochemical deposition improved the adhesion force of CVD diamond film. The strength of the sample given the electrochemical pretreatment was as good as that for the sample given scratch pretreatment, which is a popular pretreatment.

P.5.9 NEW DEVELOPMENTS IN ELECTRODEPOSITION OF THIN FILMS FOR FUEL CELL APPLICATIONS. Igor Zhitomirsky, A. Petric, McMaster University, Hamilton, Ontario, CANADA.

Two processes were used to prepare ceramic coatings by cathodic electrodeposition: electrochemical deposition (EPD) and electrolyte deposition (ELD). It was demonstrated that the ethyl alcohol-phosphate ester-polyvinyl butyral system is a unique solvent-dielectric system of advanced materials for solid oxide fuel cells, including electrolytes, electrodes and barriers. EPD was used to produce single layers as well as consecutive 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 CHIPPER DIFFUSION BARRIER. Yong-Ming Sun, Ward Englehardt, Tibor Bolom, Junh H. Sim, Cris Cline, John M. White, and John G. Ekerdt, Texas Materials Institute, The University of Texas at Austin, Austin, TX; Steven Smith, Klaus Pfeiffer Sematech International, Austin, TX.

Chemical vapor deposition of tungsten nitride using W(CO)6 and NH3 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 NH3 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 indicate that these nitride films were grown with an amorphous or nano-crystalline structure. This was further proved by cross section transmission electron microscopy. Scanning electron microscopy of these films was taken for copper diffusion resistance. After annealing a Cu/W2N/3SiO2 stack at 360°C for 8 hrs, secondary ion mass spectroscopy (SIMS) depth profile revealed that copper was still intact in the barrier. The film roughness increased at the lower growth temperature range 270°C to 290°C. The increase of roughness was attributed to the fact 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 these two materials is currently under investigation.

P5.11 HYDROGEN FREE, HIGH SP3 CONTENT DLC FILMS PRODUCED BY PULSED LASER ABLATION OF AMORPHOUS GRAPHITE. J. Hawerkamp, R.M. Mayo, Department of Nuclear Engineering, North Carolina State University, Raleigh, NC; J. Narang, T.K. Chait, J. 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 onto the target material on a silicon substrate. Plasma and flow parameters in this plasma 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 peak parameter, and ion density. Collimation of the plume is inferred from plasma parameters. Plasma 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 amount retained within the target and radiation. Film analysis was conducted by electron energy loss spectroscopy (EELS) indicating that DLC films have been successfully deposited with an sp3 concentration as high as 72%.

P5.12 REAL-TIME UV-EXTENDED SPECTROSCOPIC ELLIPSMETRY FOR CHARACTERIZATION OF CUBIC BORON NITRIDE. J.A. Zupan, R.W. Cooney and R. Meszaros, 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 two different needs: the understanding of real-time processes at the surface and the determination of real-time surface properties. These techniques, in particular real-time spectroscopic ellipsometry (RTSE), are well suited for measurement, monitoring, and control of such deposition processes. Recently, we developed a new extended rotating analyzer/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 34.5 ms while maintaining high accuracy, 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 (α-SiOxNy). 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 on 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 reach the film’s surface in a few minutes during the e-beam synthesis of BN films has been documented recently for cBN films grown using magnetron sputtering of BN and B2O3 targets. In this contribution we present new results on the effects of dynamic deposition conditions on the phase evolution of BN films grown by pulsed dc sputtering of a B2O3 target and rf substrate biasing will be presented. In addition, improvements in data acquisition and analysis resulting from the use of a new uv-RTSE design, the rotating compensation 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. Procivencio, S.V. Prasad, Sandin National Laboratories, Albuquerque, NM; J.R. Tregelo, Cutting Edge Products, Poway, CA; M. Kimmura, Kitami Institute of Technology, Dept. of Materials Science, Kitami, JAPAN.

Intense pulsed beams of ions (700 keV, up to 400 A/cm2) 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 wearability of Pd-enriched Ti1−δTi1+δ produced by two different techniques: 1) high-dose ion implantation of Pt into a Ti substrate (70 keV, at 1017 cm−2), and 2) a micron Pt/Ti sputter layered substrate mixed into a Ti substrate by a high-power ion beam. In the case of 1), a metastable Pt/Ti phase was formed in the near-surface region. In both cases, microstructural changes via 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 implant case, 150 microns in the ion beam case. These results suggest that our new experimental techniques may be more generic and can be used to make new materials.

P5.14 LASER WRITING OF NANO-STRUCTURES ON MAGNETIC FILM SURFACES WITH OPTICAL NEAR FIELD EFFECTS. S.-M. Huang, M.-H. Heng, 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 direct writing of nanostructures on magnetic film surfaces with optical near field effects has been investigated. Spherical 0.5 micron sized particles were created on CoFe/CrO2/Cr films. 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 determined and found to be related to 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 materials processing.

P5.15 CHARACTERIZATION OF POLYCRYSTALLINE SILICON THIN FILMS PREPARED BY PULSED ION-BEAM EVAPORATION. Sung-Chae Yang, Ali Fatemi, Hisuaki Shimada, WeiHua Jiang and Kiyoshi Yatsui, Extreme Energy-Density Research Institute, Nagoya University of Technology, Nagoya, Nagoya, 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). The technology is used in a wide variety of applications including flexible displays and microprocessor circuits. Poly-Si films were prepared by a plasma-enhanced chemical vapor deposition (PECVD) method with post annealing (≤810°C) of a silicon film or substrate heated (300-400°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 high throughput of electronic devices, such as...
solvent. 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 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, IEG, ITO, IBI, BN, SiC, TiO₂, ZrO₂, 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 density of the ablation plasma. The crystallinity and the density of poly-Si thin films are increased by (i) film voltage on the substrate. In this presentation, we will report the characteristic 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 Noskov, Larisa Kuznetsova Institute of Solid State and Semiconductor Physics,insk, BELARUS; Patrice Aublanc LMPG ENSPG/CNRS, St Martin d’Heres, FRANCE; Michel Mermoux, LPEMP/LENSEEG/CNRS, St. Martin d’Hères, FRANCE.

Some attempts to synthesize diamond-like carbon coatings on metallic substrates using a new electrochemical technique are presented. The electrolyte was a mixture of potassium hydroxide, sodium formate 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 (maximum amplitude higher than 25V) was applied to the electrolysis cell. The voltage shift was 5 - 10V, the current density was observed to vary from 0.5 to 0.5 A/cm². For each run, the electrolysis duration was about 30 min. Anodic oxidation of carbonaceous 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, grey films were obtained on the substrate surface. Most of 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, 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 TiF₃ THIN FILMS BY PULSED ION BEAM EVAPORATION. H. Suenaga, T. Saito, T. Suzuki, Y. Jiang and K. Yamaoka, National Research Institute, Nippon, JAPAN.

TiF₃ is a hydrogen-storing alloy which can absorb hydrogen atoms as much as 1.8 wt% of the alloy. Due to the high reactivity of Ti with oxygen, this formulation had 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 (~10¹⁸/cm³) is formed. Thus, it was expected that the oxidation of the TiF₃ thin film may be prevented because the number of oxygen atoms in the vacuum chamber (~10¹⁷ particles) is too small to react with all the Ti and F atoms in the high density plasma. In the present work, preparation of TiF₃ thin films by IBE is performed. Thin films of TiF₃ were prepared in a pulsed ion beam generator (ETIG0-1). A pulsed ion beam of proton accelerated at 1 MV (peak) with a repetition rate of 70 kA was focused on a TiF₃ alloy target. The single crystal and SiO₂ 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 SiO₂ glass substrates consist of a TiF₃ phase. Although the films also contain a small amount of TiO₂ as a second phase, there are no TiO₂ or Fe-O phases in the films. Crystallized TiF₃ thin films without oxides were successfully obtained. On the other hand, when the deposited substrate was SiO₂ glass, the single crystal on the SiO₂ glass substrate was consisted of an amorphous TiO₂ 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 SiO₂ glass.


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

P5.19 TIMING EFFECT OF SOLID SOURCE APPLICATIONS ON Si:C:N FILM DEPOSITION. Hsi Lin Chang, Jing Hwa Lin, Cheng Tzu Kuo, Department of MSE, National Chiao Tung University, Hsinchu, TAIWAN.

The Si:C:N films were synthesized on Si substrates by a MPCVD system using a mixture of CH₄ and N₂ as gas sources. The Si columns coated with C 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 source applications plays an important role. The films deposited by condition (1) show crystals with more re-nucleation phenomena, closer to TiSiN₄ crystal structure, less Si content, existence of more nano-hardness and better field emission properties. In contrast, the films of condition (2) reveal the crystals with structure closer to α-Si,N₄ and show an additional amorphous layer under the crystalline layer. The difference in crystal structure and properties between the films deposited by two conditions can be removed by the following facts. The condition (1) is close to the condition of carbon nitride deposition on CoSi substrate, and gives more chance for C atoms to react with N atoms due to less Si content. 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 amorphous layer. The difference in nano-hardness between two conditions may relate to crystal structure. The possible deposition mechanisms will be discussed.

P5.20 DURABLE OPTICAL FILM FORMATION WITH O₂ CLUSTER ION ASSISTED DEPOSITION. Noritsuki Teguda, Shiji Martsu, Laboratory of Advanced Science and Technology for Industry, Hitotsubashi University, Japan.

Formation of high-quality optical film is very important to fulfill the rapid progress of optical components. These films must be durable, dense and very flat. We have developed a new film formation process by cluster ion beam assisted deposition. When cluster ions bombarded a target, the bombarded area experienced high-tempature and high-pressure conditions transiently. It enhances 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 beam have a surface smoothing effect that is important to fabricate a multi-layer structure. In this work, TiO₂/SiO₂ multilayer was fabricated with O₂ cluster ion beam assisted deposition. TiO₂ and SiO₂ were supplied with an electron beam evaporator, and O₂ cluster ion bombardment targets with energy of 3 to 5 eV. The substrate was kept at room temperature. As an average O₂ cluster size was approximately 1000, the kinetic energy of each molecule was less than 10 eV. After an environmental test, the TiO₂/SiO₂ surface without O₂ ion irradiation was scratched, while the irradiated area was completely free from any scratch. Moreover, the XPS analysis of TiO₂/SiO₂ with O₂ 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 O₂ cluster ion beam assisted deposition. Besides durability, characteristic of the optical film was characterized and measured after the film formation process. The optical film was used in semiconductor industry as an anti-reflective layer. #Supported by NEDO.
Science and Technology Development, Chiang Mai University, Chiang Mai, THAILAND; Fast Neutron Research Facility, Physics Dep., Chiang Mai University, Chiang Mai, THAILAND.

Surface properties of carbon ion implanted (at doses ranging from 10²⁰ to 10²⁴ ions/cm² and accelerating voltages from 120 to 141keV) WC/10Co composite (WC grain size ≈ 408 nm) have been studied. Through nanoscience tests, it was found that surface hardness of the implanted (at the dose of 6 × 10²⁴ ions/cm² and accelerating voltage of 120 keV) sample reached a maximum value of ~25 GPa at the depth of ~126 nm into surface, compared to ~18GPa (HK0.6500g) of the virgin material. Auger electron spectroscopy (AES) analysis of the implanted sample indicated that a carbon rich layer (≈ 120 nm thick) was formed in the subsurface. Glancing angle x-ray diffraction (GAXRD) analysis of the subsurface showed there was no evidence of the formation of new compounds and broadening of the peaks which is attributed mainly to the compressive stress (up to ~4 GPa) induced by the implant process and surface roughness. The surface area micros (SAM) of the implanted sample is around 3.5 mm². Effect of implanted ion dose, energy, and species on surface hardness and roughness, friction coefficient, and wear resistance of ultrasonic WC/10Co composite will be presented.

P.5.22
HOMOEPTAXIAL GROWTH ON THE Ge(100) AND THE Si-TERMINATED Ge(100) SURFACE. Ma Li, Eric J. Altman, Yale University Department of Chemical Engineering, New Haven, CT.

The growth of Ge on top of the Ge(100) and the Si-terminated Ge(100) surface was 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, (1 × 130)-oriented islands dominated the surface with very few epitaxial islands oriented across the substrate, but after the deposition of a monolayer of Si, the (1 × 130)-oriented islands disappeared and were replaced by larger Ge epitaxial islands with a structure similar to that of the substrate. The "smooth" Si-terminated surface with 0.1 ML of Si dimer clusters was prepared by washing an Si-covered sample into 8×200 nm. After 0.18 ML Ge deposition at 310 K, epitaxial Ge islands were distributed over the entire substrate. The morphology of the Si(111) was shown to change from a smooth to a rougher surface similar to that of the substrate. The "smooth" Si-terminated surface with 0.1 ML of Si dimer clusters was prepared by washing an Si-covered sample into 8×200 nm. After 0.18 ML Ge deposition at 310 K, epitaxial Ge islands were distributed over the entire substrate. The morphology of the Si(111) was shown to change from a smooth to a rougher surface similar to that of the substrate.

P.5.23
ENGINEERING THE Si(111) 7×7 SURFACE ENERGY USING Ge. J.B. Macun, B. Yang, A. R. Wall, and M. G. Legally, 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 properties has recently been more widely recognized. Modifications in the strain state of a structure can be introduced by the deposition of a heteroepitaxial film even at the monolayer scale. For example, deposition of Ge onto Si(111) can increase the crystallographic defects between the deposited Ge and the Si(111) surface by releasing the strain 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 adsorption at high temperatures. We show that desorption significantly reduces the Ge surface concentration at high temperatures. 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 490°C. Quantitative arguments are presented to show how to stabilize the 7×7 structure by modification of strain and bond energies. The surface energy is reduced by an additional 20 meV per 1×1 unit cell at a coverage of about 8 ML. [1] T. Ichikawa and I. Imai, Surf. Sci. 316, 267 (1994). [2] K. Kojima, T. Takeo, and K. Tsukagoshi, Surf. Sci. 222, 38 (1989). Supported by ONR and NSF.

P.5.24
PRECISE CONTROL OF CVD-ZrO₂ FILM PROPERTIES BASED ON KINETIC INFORMATION. Kiyomoto Takashi and Yukihito Shimogaki, Department 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 insulators to minimize gate leakage current. Various kinds of high-k materials have been studied to replace conventional thermal oxide or gate oxide. Among them, ZrO₂ has attracted a lot of attention recently. We have investigated ZrO₂/CVD reaction system using thermal analysis, x-ray diffraction (XRD) and zirconium tetrabutoxide (ZTB) as a Zr source. We found that ZTB decomposes both in the growing surface and at the gas phase. The gas phase reaction produces intermediate species, which 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 intermediate species). Furthermore, the effect of thermal annealing on deposited ZrO₂ films for the further improvement of film characteristics. We also deposited ZrO₂ films using the other Zr source and compared the film properties.

P.5.25
BICOMPATIBLE THIN FILMS ON RARE EARTH BASED PERMANENT MAGNETS. Benjamin Vasile, University of Bucharest, Romania; Doima Rudnaciu, Lavin Angelescu, Politehnic University of Bucharest, Bucharest, ROMANIA; Constantin Bluc, The Institute of Solid Mechanics, Bucharest, ROMANIA.

The purpose of the paper is focused on the biocompatible coatings for rare earth based permanent magnets which are used as dental materials for prosthesis devices. An important requirement for these alloys belong to Nd-B -Al system with some Dy and Al content. The double layer coatings had different chemical compositions; first layer: 310Ag-70Co, 310Co-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 and the corrosion rates were determined. It resulted that the 30Ni-Dy-B-Al-B alloy with 310Ag-70Co titanium nitride is very stable in artificial saliva. The wear behavior of the coatings in different conditions of contact and loads was tested, also.

P.5.26
SINGLE POLYCRYSTALLINE FERROELECTRIC SBF THIN FILMS OBTAINED FROM SYNTHESIS OPTIMIZATION ON OXIDE PRECURSOR METHOD. Eudes Borges Arajio, Universidade Estadual Paulista, Departamento de Física e Química, Ilha Solteira, SP, BRAZIL; Ricardo Gonçalves Mendes, José Antonio Ferreira, 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 reversed with an external electric field. An important requirement for these materials is flexibility. The development and use of these materials in various applications require a careful understanding of the fundamental properties of these materials. One of the most promising classes of ferroelectric materials is the barium strontium titanate (BST) family. In this work, a single crystal ferroelectric film of Sr0.75Ba0.25Nb2O6 (SBN75) thin films were obtained by the drop-cast technique. The effect of the atmosphere on film crystallization was investigated to remove the undesired Sn0.5Sn0.5O (SNO) phase in SBN films. For this purpose, films were crystallized under air, oxygen and nitrogen atmosphere. Structure and microstructure of the films were characterized 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 single ferroelectric phase. Its 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.

P.5.27
INVESTIGATION OF MAGNETRON SPUTTERING CHARACTERISTICS USING THREE DIMENSIONAL MULTIE CARLO SIMULATION METHOD. Ji-Kwong Shin, Seong-Gu Kim, Young Dong Lee, Jee Joon Oh, Ji Hyun Hur, Won-Tack 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 location of nucleation sites on 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 electron erosion profile. Under conditions where 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.

P5.20
MOTION OF SAPPHIRE SURFACE STEPS. N. Bhushan, C.B. Carter, Dept. of Chem. Eng., 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 determined by the nature of the steps and the behavior of steps and step-kinks, particularly in the presence of impurities. Under conditions where the quality of the surface is 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 sapphire surface steps are considered to be used to prepare the substrate and for subsequent growth. 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 macrosteps will be presented. The lower energy of the macrostep may provide a driving force for the bunching process.

SESSION P6/B10: JOINT SESSION SURFACE ENGINEERING ISSUES IN MEMS

P6/B10.1 SURFACE TREATMENTS FOR MICROSYSTEMS: COATING ISSUES AND TRIBOLOGICAL MEASUREMENT METHODS. M.T. Daguerre 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 self-assembled (LIGA) processing have resulted in complex machines with actuators and countermechanical 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 scale size 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 in space and velocity regimes relevant to system 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 in this context, those tribochemical 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 gaps and selective tungsten to modify the frictional behavior in polymeric siliccon contacts, and a diamondlike nanocomposite coating for LIGA nickel structures.

P6/B10.2 DIAMONDLIKE NANO COMPOSITE (DLC) COATINGS FOR LIGA MEMS: TRIBOLOGICAL BEHAVIOR AND COATINGS METHODOLOGY. Somari Prasad, Todd Christensen, 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 behavior remains somewhat undefined. In a number of microsystems applications such as gear trains, comb drives and transmission linkages, tribological considerations, particularly amongst surfaces, are of paramount importance. The objective of this research is to devise a novel coatings strategy that can be integrated into the mainstream LIGA technology to coat the surfaces of intricate LIGA MEMS elements. As a first step in this direction, we applied a 100 nm thick diamondlike nanocomposite (DLC) 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 by standard LIGA process after backspattering to clear the coating on the wafer surface. Coverage of the DLC coating on the surface was confirmed by XTEM specimens from a DLC coated Ni LIGA gear tooth. Tribological studies were conducted on planar test coupons using a ball-on-disc apparatus in different test environments. As compared with pure electrodeposited Ni, DLC coated Ni showed significant improvements in friction (0.04 versus 0.61-2.1), debris generation and stick-slip behavior.

P6/B10.3 CONFORTAL 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 conformally 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.

P6/B10.4 DEPOSITION OF LOW SURFACE ENERGY, WEAR-RESISTANT FILMS ON MEMS-LIGA DEVICES USING AN ENERGETIC PULSED PLASMA IMMERSION PROCESS. Kamesh Sivalogan, University of Wisconsin, Madison, WI; Alfredo Morton, 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 fluorne, and exhibiting moderately high hardness, have been deposited on geared 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 octane 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-AC04-94AL85000. This work supported by SNL grant No. 16546.

P6/B10.5 STUDIES OF TRIBOLOGICAL PROCESSES ON ULTRA-NANOCRYSTALLINE DIAMOND (UNCD) THIN FILMS FOR MULTIFUNCTIONAL MEMS DEVICES. A.Y. Sumant, O. Audrilli, A.M. Ikuta, D.M. Grun, and J.A. Carlisle, Materials Science Division, Argonne National Laboratory, Argonne, IL; L. Ederer, J. Anderson, and R.A. Erick, Energy Technology Division, Argonne National Laboratory, Argonne, IL; M.N. Gaido, Raytheon Electronic Company, El Segundo, CA
Many MEMS devices involve rolling, sliding, or bending operations that are extremely constrained 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 processes 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 ultraclean monocrystalline diamond (UCD)-based MEMS technology based on a UCD coating technology developed at Argonne National Laboratory. This technology produces phase-pure diamond with extremely smooth surfaces (RMS roughness ~35 nm) and high strength and mechanical properties. This US patent application is currently being processed and is expected to be suitably for MEMS applications. However, before these UCD MEMS components are ready for integration into commercial MEMS devices, it is necessary to determine their functional properties and 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 UCD films in high vacuum and controlled atmosphere (e.g., N₂, O₂, Ar, He, CO₂). We have also studied the role of preparation and handling of the specimen, measurement of small forces, and measurement of strain in the specimen. The author and colleagues at Argonne have developed techniques and procedures for tensile testing of diamond films, polycrystalline diamond, and silicon. This work is being expanded 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 frequencies to determine the modulus of these materials. Their resonances are sharp and well-defined under appropriate conditions and can be measured using resonant frequency to determine the modulus. Measurement of resonances also provides a convenient means for determining the modulus of all these materials, since >10 film materials are nearly hydrophobic as deposited, and they do not develop an oxide. Our preliminary observations were that the modulus of monocrystalline diamond and polycrystalline diamond structures can be released with a simple delamination technique 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 treatment. These measurements are made using an array of single-dipped, 40000-micron brass rinsers electrostatically brought into contact with a ground plane. Two ground plane materials are being tested, both poly-Si and >10. 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 framework, one can extract the energy density 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 cantilever.

**11:15 AM P6.8/B10.8**


Stiction between surfaces of moving thin film structures places a critical limit on the performance and reliability of microelectromechanical devices. Thin film amorphous-Diamond (A-D) structures may be less susceptible to stiction problems than structures built with monocrystalline 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 delamination technique 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 treatment. These measurements are made using an array of single-dipped, 40000-micron brass rinsers 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 framework, one can extract the energy density 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 cantilever.

**11:30 AM P6.9/B10.9**

**SURFACE MECHANICAL PROPERTIES AND TRIBOLOGY: A COMBINED NANOSCALE AND MACROSCALE APPROACH. Kathryn J. Wohl, 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, containing materials, or sliding processes. At all scales, from atomically thin surface films to chunks of wear particles, mechanical, and dynamical properties play an important role in friction and wear. To address these problems, we combine two approaches: 1) in situ macroscale tribological studies allowing visualization and chemistry of the buried interfaces and 2) “hybrid” nanoscale roughness. Combining high spatial resolution and surface sensitive, quantitative mechanical properties measurements of films as thin as a few nanometers. By combining these techniques, the macroscale tribological behavior can be correlated with mechanical properties of the nanoscale films and structures, e.g. the “third body” found in the sliding interface. In this presentation, I address the issues of measuring and interpreting the mechanical response of ultrathin films and nanoroughness. 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 at the stationary contacts, "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 AI INITIATIVE 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. Adair, Arizona State Univ., Chemical and Materials Engineering, Tempe, AZ.

Aluminum alloys hold great promise as substrate 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 laser melting. Alloying agents, such as magnesium and molybdenum, along with sub-surface plastic deformation, have been used in attempts to improve adhesion to these surfaces. For this reason, research on novel tool coating materials has been increased dramatically in 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 adhesive energy and examined the associated electronic structure of supercells with non-stoichiometric flux and tool coating materials (with selected terminations) consisting of Al, O, C, V, N, Ti, Na, and WC. The impact of aluminum alloying agents, sub-surface, and lattice strain (where appropriate) on the work of adhesion were considered in detail along with the nature and extent of adhesive transfer when the slides were separated. Finally, we propose a relationship between the work of adhesion and the surface energies of the interface slides 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. Somananda Basu, Vinod Srin, 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 Si3N4, identified as candidate materials for use at these higher temperatures, are susceptible to hot corrosion and recession. Mullite (3Al2O3·2SiO2) is an excellent candidate material for coating these ceramics for use in high-temperature gas turbine engines. To prevent non-uniform and adherent mullite coatings have been deposited at 950°C by chemical vapor deposition (CVD) on SiC substrates and fibers, using the Al2O3-SiC-CO2-H2 system. Using an extensive thermodynamic database, a guideline for the coating system was optimized, leading to compositionally graded coatings. The high Si content at the interface allowed excellent bonding with the SiC-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 3Al2O3·2SiO2 nanocrystals in a viscous silicate 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 Al2O3/SiO2 ratio, was converted to equixed 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 WITH COMBINED TWO LASER SURFACE PROCESSING. Dimitrios Tristisfylidis, Univ of Manchester Inst of Science and Technology, Dept of Mechanical Engineering, Manchester, UNITED KINGDOM; R. Bernstein, F. Howard Scott, Univ of Manchester Inst of Science and Technology. Corrosion and Protection Centre, Manchester, UNITED KINGDOM; Lim 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 lining 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 erosion-wear damage. Previous research has successfully used short-pulse 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 gradient and cooling rates, with the aim of eliminating crack formation. The surface 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 Inspector, Kennametal Inc., Latrobe, PA.

Strong functional surfaces are 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 well-documented examples of tools, trends in superhard-coated tools and recent developments in nanostructured films.

3:00 PM  P7.5

Carbon-based coatings deliver advantages regarding friction behaviour, dry and lubricated running, abrasive wear resistance, resistance against scoring 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 components is enhanced by increased fuel efficiency, increased technical system performance and lower running cost. The variety of demands of tribological applications requires 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 multipurpose 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-oriented 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, scoring and seizure, increase of lifetime and improvement of sliding behaviour is required. The metal-free c-C:H coatings (DLC) have a higher hardness than Me-C:H-coatings, due to high internal stresses and do not show a microcracked structure, due to the low-diffused structure. 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
THERMAL BEHAVIOR OF CrDLC NANOCOMPOSITE FILMS. Vassilani Singh, Jiehao 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 group elements of 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, and properties of ultrathin films 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 CH₄ 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 varying up to 30 at.%. Mechanical and tribological properties were studied by 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 Hiru, Hajime Sato, Tsuneyuki Shindo, Takeshi Ishida, Keiji Kuriyama, and Kiyoshi Yashima, Extreme Energy-Density Research Institute, Nagasaki University of Technology, Nagasaki, Nagging, 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 (Sₐ = (Sₐ)/ (Sₐ + Sₐ + Sₐ)) under a pressure of 1 × 10⁻⁴ Torr. The composition of the film prepared at the fluence of P = 2.5 J/cm² and Sₐ = 75% was determined to be Cr₄₃Al₅₃N₂₂O₃ by Rutherford backscattering spectroscopy (RBS). This result indicates that the ratio of Cr and Al in the film is one-to-one correspondence. Chromium, aluminum and nitrogen atoms in the film were provided from the target, whereas the oxygen atoms were incorporated from the residual gas in the chamber. The latter may be attributable to the fact that the residual oxygen is chemically absorbed on the film surface during deposition. The hardness of the Cr-Al-N-O film was found to be about 20% higher than the Cr-Al-N target, whereas the absorption of the X-ray diffraction pattern of the Cr-Al-N-O film at 900°C was observed above 900°C. Furthermore, the film was tested at 1000°C consisting mainly of Al₂O₃ structure. From the result of the hardness and X-ray diffraction pattern of the Cr-Al-N-O film, the oxidation resistance of the Cr-Al-N-O film was found to be improved by fact that Cr₂O₃ and Al₂O₃ are formed on the film surface.

SESSION P8: POSTER SESSION
MECHANICAL, TRIBOLOGICAL AND OTHER PROPERTIES
Chairs: Wen Jin Meng, Ashok Kumar, Yi-Wa Ch, Gary D. Doll, Yong, Tseng and Seok Yeo, 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 Echeverria, James Kaczmarek, University of New Hampshire, Dept of Mechanical Engineering, Durham, NH, Jose Nainapamplum, System 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 TiC/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 were used for phase identification. The friction coefficient was obtained in both 50% R. H. Air and in vacuum run for 10,000 cycles in a pin-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 Hensley, 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. Jenny, University of Illinois, Urbana, IL, Jean-Francois Buisson, IRC, Boucherville, CANADA.

Yttria-stabilized zirconia (YSZ) deposits, manufactured by means of atmospheric-pressure magnetron-sputtering onto a steel substrate, were characterized by small-angle scattering of neutrons and X-rays. Depositions such as these are routinely used as thermal barrier coatings. Small angle neutron scattering has proven successful for relatively thin (millimeter) deposits and the scattering from the deposits on substrates cannot be characterized by SAMs without the use of a complex reflection geometry. Amorphous ultra small-angle X-ray scattering (USAXS), using 18 keV X-rays, have made it possible to extract non-invasive 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 YSZ. The high brightness and small beam size make it a third generation technique. We report the results of 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, Tadao Nitta, Hiashi Hagi, Kunisuke Kawashima, Kanagawa University, School of Science, Division of Physics, Sagamihara, 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 relaxation times under applied stress. Then effects of the elastic deformation on the frictional force can be seen more apparent 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 2000 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 friction value is quite different from those previously reported in many other systems such as paper-on-paper system, where the static friction force is constant at a logarithmic law of the duration. From this comparison, the duration dependence of the static friction 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, How Yung, Alex Kvit, Xingzhong Zheng, Carl C. Koch, Jarnyn 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 has been used in grain boundary sliding and grain boundary diffusion related creep phenomena. We have investigated mechanical and electrical properties of TiN as a function of microstructure varying from polycrystalline 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 a micro indentation technique. X-ray diffraction 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. This behavior has been modeled recently involving grain boundary sliding which is particularly relevant in the size of hard coatings such as TiN. The dependence of resistivity of TiN as a function of the deposition temperature is discussed and correlated with hardness results.

PS.5 PHASE ANALYSIS FOR SINGLE CRYSTALLINE SILICON SCHOTTKY BARRIER DEPOSITED BY PHOTOCHEMICAL LAYER COATINGS. Young-Chang Eom, National Institute of Standards and Technology, Gaithersburg, MD.

The photolithography process is a key step in the fabrication of integrated circuits. This study investigated the phase analysis of single crystalline silicon Schottky barriers deposited by photochemical layer coatings. The photocatalytic reaction process was optimized to improve the quality and uniformity of the deposited layers. The results showed that the photocatalytic process effectively reduced the defect density and enhanced the electrical properties of the Schottky barriers.

PS.6 CROSS-SECTIONAL PHASE ANALYSIS FOR SINGLE CRYSTALLINE SILICON SCHOTTKY BARRIER DEPOSITED BY PHOTOCHEMICAL LAYER COATINGS. Young-Chang Eom, National Institute of Standards and Technology, Gaithersburg, MD.

The cross-sectional analysis of single crystalline silicon Schottky barriers deposited by photocatalytic layer coatings was performed to study the interface and bulk properties. The analysis revealed that the photocatalytic coating significantly improved the electrical performance and reduced the defect density at the interface. This finding has important implications for the development of high-performance Schottky barrier devices.

PS.7 INVESTIGATION OF STRUCTURAL AND MECHANICAL PROPERTIES OF LASER-POLISHED CRYSTALLINE HAMmers. Dong-Hyuk Lee, M.S., Department of Materials Science and Engineering, University of South Carolina, Columbia, SC.

The investigation of structural and mechanical properties of laser-polished crystalline hammers was conducted to understand the effects of laser processing on the material properties. The results showed that laser polishing significantly improved the surface roughness and reduced the defect density. This finding has important implications for the development of high-performance hammers for industrial applications.

PS.8 THE EFFECT OF PRE-OXIDATION ON THE OXIDATION BEHAVIOR OF Ti-2Al-2.5Zr ALLOY AT 1050°C IN AN ALKALINE STEAM. Xiao-Qing Liu, J. Xiang, D. Yang, F. Chen, and J. Wang, Department of Materials Science and Engineering, Zhejiang University, Hangzhou, China.

The study investigated the effect of pre-oxidation on the oxidation behavior of Ti-2Al-2.5Zr alloy at 1050°C in an alkaline steam environment. The results showed that pre-oxidation significantly improved the oxidation resistance and reduced the oxidation rate. This finding has important implications for the development of high-temperature alloys for industrial applications.

PS.9 THE MECHANICAL EFFECTS OF CERAMIC THERMAL BARRIER COATINGS ON ENGINE COMPONENTS. Joseph Guida, Manchester University, Manchester, UK.

The study investigated the mechanical effects of ceramic thermal barrier coatings on engine components. The results showed that the thermal barrier coatings significantly improved the thermal efficiency and reduced the thermal stress on the engine components. This finding has important implications for the development of high-temperature gas turbines.

PS.10 INVESTIGATION OF MECHANICAL PROPERTIES OF SINGLE CRYSTALLINE SILICON SCHOTTKY BARRIER DEPOSITED BY PHOTOCHEMICAL LAYER COATINGS. Young-Chang Eom, National Institute of Standards and Technology, Gaithersburg, MD.

The investigation of mechanical properties of single crystalline silicon Schottky barriers deposited by photocatalytic layer coatings was conducted to understand the effects of process parameters on the material properties. The results showed that the photocatalytic coating significantly improved the mechanical properties and reduced the defect density. This finding has important implications for the development of high-performance Schottky barrier devices.
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 metal (steel, aluminum and copper), carbon fiber polymer matrix composite, cement mortar and graphite, due to their relevance to hardening, concrete structures, electronic systems and geothermal projects. Correlation was made between the contact resistivity and the occurrence of elastic/plastic deformation, oxidation, strain hardening, passive layer damage and local fracture. The interface structure was found to depend on the loading history.

**PS.12** MORPHOLOGICAL AND NANO-TRIBOLOGICAL PROPERTIES OF DIAMOND LIKE THIN FILMS ERODED BY A NITROGEN PLASMA. R. Piscioli, 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) on a Si substrates, using substrate self-bias of $-400$ V and a methane precursor flow rate of 5 sccm. After to the high-energy ions were exposed to nitrogen rf plasma with an erosion bias ranging from $-100$ V to $-500$ V, different plasma erosion pressures from $1Pa$ to $10Pa$ at different times of erosion which varied from 5 to 50m$^3$. The films were analyzed in the line of sight with the use of an optical 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$_2^+$ ions plays a role in 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 ion energy is changed from 100eV to 500eV. It is shown that the nitrogen incorporated in 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 the MJHS 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 - 3 mN microscope tip. In our case, it is observed that after 50m$^3$ of erosion the friction coefficient reaches a saturation value of 0.21, which is 20% higher than the fresh $a-C:H$.

**PS.13** DUCTILE MICRO-MACHINING OF SILICON FOR MEMS APPLICATIONS. Yuriy Gogotsi, Tom Juliano, Drexel University, Department of Materials Engineering, Philadelphia, PA; Sabri Ozisikant, Nisar Chopra. University of Illinois at Chicago, Department of Mechanical Engineering, Chicago, IL.

Micro-mechanical micromachining of silicon surfaces has been explored in this work. A single point diamond turning machine (SPDTM) was used to machine the surface of a n-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 piezoelectric actuators and gap sensors working in each axis that push the rotation 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 $\mu m$ 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. Multisegment shapes have been successfully machined with overall dimensions of 10 by 20 $\mu m$. 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 into the cubic silicon crystal structure with mechanical polishing. The ability to control the mechanical properties of the finished silicon can be readily applied to other semiconductors, and can create any material (like silicon) limited only by the resolution of the tool shape itself. Possible applications include creating channels for microfluidic devices, or using the electrical properties of each phase to create electronic devices machined on the surface.

**PS.14** FABRICATION AND MICRO-STRUCTURES 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; K. Liu, Univ. of Technology, 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 strain processing to transform the surface layers of the materials into ultrafine-grained (UFG) structures (both submicrometers 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 (USP). Refined microstructures of three levels of the grain size were present, i.e., microscopic shear bands and elongated subgrains (first level), submicron- (second level), and nano-grained (third level) structures rather than surface 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 misorientation of boundaries was created and then, a more stable, equiaxed, and uniformed UFG structures were formed. The evolution of the surface ultrafine structure and the related mechanism of the formation were both observed using the high-resolution transmission electron microscopy. With the extension of SP time from 5 to 25 min, the depth of the whole deformed layer increased from 26 to 64 $\mu m$ and the final equiaxed nano-crystallized size decreased from 90 to 46 nm.

**PS.15** STRESSES AND MECHANICAL EFFECTS OF OXIDE FILMS ON TUNGSTEN AND MOLYBDENUM SINGLE CRYSTALS. J.E. Talia, Dept. of Mechanical Engineering, Virginia State University, VA; R. Gibala, Dept. of Materials Science and 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 77K to 500K 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 ambient melting temperature, the coated-machined surfaces are strained 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 a micron and etching diffusion.

**PS.16** Nanostructured ultrathin films of Silicate Clay and Polyenelectrolytes: Deposition Parameters and Mechanical Properties by Nanoindentation. Hidlerdsen Advincula, Xianwu Fan, Department of Chemistry, University of Alabama in Birmingham, Birmingham, AL.

Recently, we have investigated the layer-by-layer (LbL) deposition of polyelectrolyte and clay platelet ultrathin films. We have investigated the properties of these films using techniques including 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 indenter penetration depth and load. The ultrathin films have remarkable mechanical properties very different from polyelectrolyte ultrathin films. Practical applications of these films are important for the preparation of thin film electro-optical and membrane devices using the (LbL) technique.
Since anisotropic stainless steels provide a high corrosion resistance combined with a high mechanical strength and a good formability, they are in common use for orthopedic (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 addition, a fungal-like corrosion in the anisotropic magnetic structure occurs. The use of stainless steels needs to be highly corrosion-resistant and thus, the amount of nickel must be added in fairly high contents. The interstitial solution of nickel enhances the tensile strength, ductility [1] and pitting resistance [2] when compared to nickel-free stainless steels. Together with a high working hardening capacity, these properties predict excellent wear characteristics in corrosive environments. Metallic implants, which are chemically and electrically not isolated, are typically electrically connected to the implantation site. The aim of this paper is to investigate the influence of a novel surface topology on the tribological behavior of high nitrogen steels. Therefore, an anisotropic nickel-free stainless steel with the trade name P2300 (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 (\(R_s = 0.02 \mu m\)) and a microscopically rough surface with features in the micrometer. The wear-corrosion behavior of mechanically polished (\(R_s = 0.02 \mu m\)), electropolished (\(R_s = 0.1 \mu m\)) and wet-chemically modified samples was studied on a pin-on-disc apparatus in distilled water at 300°C. A normal force of 5 N (helium 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 mass loss after the experiment. The samples were imaged using a SEM and the loss, respectively. In all experiments, a region with a constant wear rate \(W = 1.2 \times 10^{-7} \mu m^3/m^S\), was observed, which starts after approximately 500 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 (< 500 m), the sample surface is more influenced. P2300 samples, which were wet-chemically polished were much smoother in high acid water already after 25 m, whereas 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 scars were observed in regular intervals using FE-SEM. Secondary electron images show the local formation of wear particles 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. Repaired 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 thus, adhesion becomes improbable. As a result, wear rates as low as \(2.8 \times 10^{-12} \mu m^3/m^S\) (280 m) are measured in distilled water before repaired loading initiates segmentation and loss of the protective hydrogen. The experiments show that a novel surface topography process leads to an improved sliding wear behavior of anisotropic 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]. Thomas, I., Wear-corrosion behavior of biocompatible stainless steels. Wear 239 (2000) 48-58 [2] Olejford, I., The Influence of nitrogen on the passivation of stainless steels, Corrosion Science 38:7 [1996] 1293-1320 [3] Jennisen, H.P., Zumbach, T., Chumakhoziou, M. and Steppehn, T. (1999) J. Materwiss. Werkstofftech. 30, 838-845

**PS.18 PROPERTIES OF CVD-GROWN TiSiN MATERIAL FOR COPPER DIFFUSION BARRIER APPLICATIONS**

Dahane Anjun, Katharine Dovidenko, Sergei Oktubyan, Eric Eisenmann, Alisa E. Kaloyeros, Univ of Albany, Institute for Materials at Albany, SUNY, Albany, NY, USA

TiSiN film is thermally grown at low substrate temperature (370°C) using TiCl_4 and SiCl_4 as Ti and Si precursors, respectively. The mixture of NH_3 and H_2 was utilized as a reducing gas. The stoichiometry of the deposited TiSiN film is determined by X-ray Photoelectron Spectroscopy (XPS) and is given by Ti_xSi_{1-x}N_{y}Si_{2+y}. Using the binding energy peak shift technique in XPS analysis, it is determined that deposited film have Ti and Si 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 resulting Ti/Si ratio is around 0.5 and the thickness of 40 nm. The deposited film exhibits low surface roughness (~1 nm) as determined by Atomic Force Microscopy (AFM). Both XPS and Rutherford Backscattering Spectroscopy (RBS) showed Cu diffusion upon one hour annealing of Cu/TiSiN/Si at 950°C. The Cu diffusion of Cu in TiSiN film is obtained by measuring the amount of diffused Cu through the TiSiN film and the obtained Arhenius relation is given by \(D_{Cu} \sim 10^{-6} \exp \left[2.1 \pm 0.48 \text{ eV/RT} \right] \text{cm}^2/\text{sec}\). The obtained results showed that Cu diffusion barrier is employed in Cu diffusion barrier for sub-100 nm device generations.

**PS.19 INTERFACIAL FORCE MICROSCOPY AND ITS APPLICATION IN METAL MATRIX COMPOSITES**

Rob M. Winter, Jan A. Puzynska, South Dakota School of Mines and Technology, Dept of Chemistry and Chemical Engineering, Rapid City, SD, USA and 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–Al203, SiC–Al, Al–Al203, Al–B/C-Ni–N4. Mechanical or thermal properties such as strain-impact behavior or thermal conductivity 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 mesoscopic 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 mechanical properties of metal matrix composites on nanoscale 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 modulus and individual phase Young's moduli 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–Al203, SiC–Al, Al–Al203 composites will be discussed in detail. Furthermore, a comparison of experimental data with mechanical properties calculated from first principles will be discussed.

**PS 24 NOVEL NANOSTRUCTURED AMORPHOUS DIAMOND-TN AND TiC COMPOSITES FOR BIOMEDICAL APPLICATIONS**

R. A. Parish, B. J. Keaveny, and J. C. Paton, Naval Research Laboratory, Washington, DC.

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 the carbon target was excited by a laser 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 a 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 nanocomposites for biomedical applications.

**PS 25 DISSOLUTION PROPERTIES OF NITROGEN-DOPED DIAMOND-LIKE CARBON FILMS DEPOSITED BY A MAGNETRON SPATTER TYPE POSITIVE ION SOURCE**

K. W. Moon, D. M. Yoon, and S. H. Oh, Department of Mechanical Engineering, University of New Hampshire, Durham, NH.

It has been proposed that metal carbide-metal nanocrystalline structures have improved mechanical properties over solid metal carbide films for use as hard coatings. The improved wear resistance of nanocrystalline structures has been attributed to several sources, among them crack blunting, the presence of slip planes at the carbide/metal interface 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 nanocrystalline structures have improved wear resistance compared to 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 nanodentor under a reciprocating load. It was found that TiC-metal nanocrystalline 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.

**PS 26 ELECTRODE PROPERTIES OF B234-C34 Thin Films Prepared by Pulsed Ion-Beam Evaporation**


Boron carbide (B234-C34) is known as an excellent thermoelectric material particularly at high temperatures. Seebeck coefficient of B234-C34 is as high as 300 μV/K. Electrical and thermoelectric properties of B234-C34 vary with carbon content in the B234-C34 phase. Although crystallized B234-C34 thin films were successfully deposited on Si single crystal substrates at room temperature by a pulsed ion-beam evaporation (IBE) method, preparation of B234-C34 thin films with various carbon contents have not been attempted. Furthermore, measurements of electrical properties of B234-C34 thin films deposited on glass substrates were conducted. In the present study, preparation of B234-C34 thin films on the glass substrates is carried out and the thermoelectric properties of the B234-C34 thin films were measured. B234-C34 films were grown on Si substrates using 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 the B234-C34 targets. Pyrex and quartz glass substrates were placed 840 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 the thin films were found to consist of a B234-C34 phase and lattice parameters of the phase were estimated. The B234-C34 thin films with various carbon contents have been successfully prepared by the IBE method on glass substrates without substrate heating or single annealing. Thermoelectric properties of the thin films were measured with a 0.6 mm thick film exhibits the highest power factor at room temperature among B234-C34 samples.
reported.


PS.27
EFFECT OF Co SEED LAYERS ON THE MAGNETIC ANISOTROPY OF Au/Co METALLIC MULTILAYERS. M. Kuroko, H. Kuga, T. Shiraishi, H. Yamauchi Institute of Engineering, University of Tokyo, Meguro-ku, Tokyo, JAPAN.

Au/Co(111) multilayers and Au buffer layer were grown by MBE on Al2O3 (0001) substrates using a thin Co seed layer. The influence of the Co layer on the structure of the Au/Co multilayer 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 Al2O3 (0001) substrates display a large fraction of (111) twins, giving rise to a lack of interface continuity in the film. The initial deposition of a few Å of Co onto Al2O3(0001) substrates prior to deposition of the Au buffer layer yielded (111) epitaxial films with no twins. The use of 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 clearly shows that the use of Co seed layer improved the periodicity of Au/Co multilayers.

PS.28
MICROTTEXTURE OF COPPER-LOADED CARBON AEROGELS PREPARED BY AN ION EXCHANGE METHOD. Noriko Yoshizumi, Masayoshi Hisamatsu, Massachusetts Institute of Technology, Dept of Physics, Cambridge, MA; Joe Stadler, Ted Baumann, Lawrence Livermore National Laboratory, Livermore, CA; Kasumi Kaneko, Chiba Univ, Dept of Chemistry, Chiba, JAPAN; Morishoto Endo, Univ, Dept of Electrical & Electronic Engineering, Nagano, JAPAN.

Copper-loaded organic aerogels were prepared by an ion exchange method of gels polymerized with a 2,4-dihydroxybenzilic acid and formaldehyde. This sample was heat-treated at 1320°C in a nitrogen flow to obtain the carbon aerogel. After heat-treatment, the density of the sample was increased from 204 to 250 g/cm³ to 350 g/cm³. According to TEM observations, the sample before heat-treatment had a densely packed 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. Copper-related copper(II) oxide 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 denser than that of the non-carbonized sample, but the network of carbon particles seems more collapsed after carbonization. The carbon aerogel particles are 1.6-1.9 μm in diameter and keep their round shapes. Mesopores about 15-20 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 size range of 0.1 to 1 μm. The determination of the crystallographic 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
Chair: Ashok Kumar and Stan Veprek
Thursday Morning, November 29, 2001
Room 311 (Hynes)

8:30 AM #P9.1
SUPERFLUIDITY AND WEARLESS SLIDING IN DIAMOND-
LIKE CARBON FILMS. Ali Erederem, Argonne National Laboratory, Energy Technology Division, Argonne, IL.

Diamond-like 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. Systems studies on carbon-based materials in our laboratory have resulted in the development of a new class of amorphous diamond-like carbon films providing extremely low friction and wear coefficients of 0.001 to 0.01, 0.01 to 0.1, and 0.1 to 1.0, 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 surface) plays a very important role in the superfluidity and wearless sliding behavior of these films. Based on these studies, a mechanical model is proposed to explain the superlow friction and wear properties of the new DLC films.

9:00 AM P9.2
PLASMA DEPOSITION OF A MÖRFH Pornhub CARBON FILMS FROM CH4 AT HIGHLY DILUTED IN Ar. Luiz Gustavo Jocobsen, Fernando Lázaro Freire Jr., Departamento de Física, Pontificia Universidad Católica do Rio de Janeiro, Rio de Janeiro, BRAZIL.

Recently, strong indications pointed that C2 species, instead of CH2 radicals, are the building blocks of n-C6H films when CH4 is highly diluted in argon. In this work, we systematically study the deposition of n-C6H films in these conditions and correlate them with the film properties. The films were deposited by plasma decomposition of CH4:Ar mixtures with a total pressure of 13 Pa, total inlet gas flow of 50 sccm and a fixed self-bias voltage of 350 V. The CH2 partial pressure ranged from 1 to 100%. The effect of the residence time of the plasma species was investigated by varying the inlet CH4 partial pressure from 5 to 50 sccm and the total pressure for a fixed CH4 partial pressure of 5%. The deposition rate decreased by a factor of ~1.8 as the CH2 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 CH2 partial pressure increases, the fraction of hydrogen bonded to carbon increases, while the total hydrogen content remains constant. The calculated external 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. Bini, M. Fantoni and P. Toai, Chem. Phys. Lett., 328, 60 (2000).

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

Continuous miniaturization of the device dimensions and the reduced 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 (< 5 μm) have to be removed very precisely while maintaining the precise contour of the remaining structures. Because CMP correlates at the slurry/wafer interface, slurry pads and film surface play an important role in the successful implementation of this process. Surface roughness, elastic and viscous properties, thickness and pore sizes of the film 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 oxide 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 Preston's equation was also verified.

9:30 AM P9.4
MOLECULAR DYNAMICS SIMULATIONS OF CMP OF A-SiOx. Eugene Chiangrov 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 n-SiOx. Specifically, the simulations involve n-SiOx slurries interacting with various SiO2 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 changing conditions affect these processes. Visualization of the results allows an easy interpretation of how temperature and local stress change when slurry particles abrade the surface, and reveals new metal removal. A wide variety of parameters are investigated, including degree of hydrolysis, surface roughness, contact speed, load, and temperature.
09:45 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 Kurihara, Hua Zhao, Seichi Takami, Momoyo Kako, Akira Mijamoto, Tokyo 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

The application of hard and lubricious coating materials to components subject to rolling and sliding contact is currently an 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 of superstoichiometric TiC 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. 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: pure Ti target, a Ti-12% Si target, and a Ti-25% Si target. 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 0.19 to 0.47 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 superstoichiometric levels of carbon were found to have either a nano-crystalline or amorphous structure. 1. Voievodin et al., J. Appl. Phys., 82 (2), 855 (1997) 2. Joseph R. Nainprampli et al., JVSTA 17 (3), 809 (1999).

10:15 AM P9.7
IONIZING RADIATION EFFECTS ON INTERFACES IN CARBON NANOTUBE-POLYMER COMPOSITES. Julie P. Farmer, Patricia Anne O. Quinter, Lori Adorno, LuNea Clayton, John D’Angelo, Department of Chemistry, University of South Florida, Tampa, FL; Arun K. Siker, Ashok Kumar, Center for Microelectronics Research, University of South Florida, Tampa, FL; Alan M. Cassell, Elercor Corporation, NASA Ames Research Center, Moffett Field, CA.

The purpose of this research was to probe polymer nanotube composites for evidence of radiation induced chemistry at the interface of the host polymer and the nanotube structure. Single wall carbon nanotube (SWNT) / poly (methyl methacrylate) (PMMA) composites were fabricated and exposed to ionizing radiation with a Co60 source. Next nanotube paper and pure PMMA were also exposed. The dose was 5.9 Mrads at a dose rate of 1.08 X 106 rad/hour in an air environment. Both irradiated and non-irradiated samples were compared. Glass transition temperature 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-indentation 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.

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