SYMPOSIUM P

Advances in Surface Engineering—Fundamentals and Applications

November 26 – 29, 2001

Chairs

Wen Jin Meng
Mechanical Engineering Dept
Louisiana State Univ
2508 CEBA Bldg
Baton Rouge, LA 70803
225-578-5832

Ashok Kumar
Ctr for Microelectronics Research
Univ of South Florida
ENB 118
Tampa, FL 33620
813-974-3942

Yip-Wah Chung
Dept of M$&$E
Northwestern Univ
Evanston, IL 60208-3108
847-491-3112

Gary L. Doll
Timken Company
MC RES-04 PO Box 6930
Canton, OH 44706-0930
330-471-3522

Yang Tse Cheng
Maths and Processes Lab
General Motors R&D Ctr
MS 480-106-224
Warren, MI 48090
810-986-0939

Stan Veprek
Inst for Chemistry of Inorganic Mats
Technical Univ of Munich
Garching Bavaria, D-85747 GERMANY
49-89-28913625

Symposium Support
Balzers Limited
General Motors Corporation
Hauzer Techno Coating USA
†Hysitron, Inc.
‡k-Space Associates, Inc.
†2001 Fall Exhibitor

Proceedings to be published in both book form and online
(see ONLINE PUBLICATIONS at www.mrs.org)
as Volume 697
of the Materials Research Society
Symposium Proceedings Series

*Invited paper
SESSION P1: MECHANICAL AND TRIBOLOGICAL PROPERTIES OF NANO- AND MICRO-SCALE CONTACT AT SURFACES. EXPERIMENT, SIMULATION AND APPLICATIONS
Suhana 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 quantum inelasticity and molecular dynamics computations, will be delivered 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 macroscopic 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 discrete changes 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, Institute for Chemistry of Inorganic Materials, Technical University Munich, Garching, Munich, GERMANY.

The superhard nano composite coatings prepared according to the generic design principle [1] which results in selforganization of a stable nanostructure show an unusual combination of mechanical properties, such as high hardness up to 40 to 100 GPa, high elastic modulus measured by the load-depth sensing indentation technique, high elastic recovery up to 95% 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 nanocomposites can be understood in a logical way by scaling the fracture physics and mechanics to the nanocrystallite size of 3-5 nm. In such nanocomposites which have a strong interface between the nanocrystals, the stress concentration factor is estimated to be of about 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 invoke other mechanisms for which there is no rational physical justification. The very high values of elastic modulus are probably due to a high pressure under the indent. [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, L.E. Rehn, P.M. Baldo, Materials Science Division, Argonne National Laboratory, Argonne, IL.

Ceramic nanocomposite coatings have been intensely researched in recent years. In selected coating systems, such as metal-containing amorphous hydrocarbon (Me-C-H) and metal-containing amorphous silicon nitride (Me-SiN), 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. Konstantatos, Jose L. Estroino, Simha H. Kovatski, General 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 advances in hardness levels, even exceeding that of diamond, have been reported in microstructurally modified nitride thin films. However, others report maximum hardness levels only in the range of 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 TiC-SiC, TiC-WC, TiC-Mo-C and Ti-HfC. We have attempted to manipulate the microstructure via the use of alloying, as well as by controlling deposition parameters such as substrate 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 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. We find that substrate bias levels at which the hardness maximum was achieved depended on alloy content, the material 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 Hoon, Department of Applied Physics, MRS Science Center and Netherlands Institute of Metals Research, University of Groningen, Groningen, THE NETHERLANDS.

This investigation is aimed at examining the mechanical performance and mechanism of delamination of 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 utilizing a reactive hybrid deposition process consisting of a combination of electron beam evaporation of Ti and dc magnetron sputtering of Ti-Al alloy. The mechanical properties, i.e., hardness and effective Young's modulus - were measured by nano-indentation tests using the continuous stiffness techniques. The information from load-displacement curves were critically analyzed and the cracking mechanisms were characterized using a new technique for cross-sectional electron microscopy of the nano-indentations. The information retrieved with this technique eliminates problems inherent in assessing, at this small contact scales, whether delamination of the coating occurs along the substrate or by interfacial failure inside the multilayer.

10:00 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, the magnitude of the stress and the characteristics of the thin film thickness. The presence of imperfections and their morphology are also crucial. Two categories of response are presented. The first consists of diamond-like carbon (DLC) films on a range of different substrates, which fail by buckle delamination. One example in this category comprises DLC on steel 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 relates to highly grown silicon carbide TGOs. In this latter example, the TGO attaches to a silicon carbide TGO that forms on a NiAl alloy within a thermal barrier systems used in gas turbines. In this case, the film on both sides is a superalloy on one side and a stabilized zirconia thermal barrier on the other. Failure occurs through a displacement instability vectors into the alloy, as the system thermally cycles, resulting in delamination of the zirconia. These phenomena and discussed, emphasizing their dependence on the properties of the constituent materials, and their role in the failure of the thin film.
An elastic-plastic spherical micro-indentation study of functionally graded materials (FGMs) with gradient in yield strength, such as steels having a thermal hardening gradient, is made by experimental and finite element methods. Indentation simulations are done with diameter sphere of 1.8675 mm. Various surface-substrate yield stress ratio \( \beta = (1 < \beta < 6) \) and strain hardening exponent \( n = 0.5 < n < 1 \) 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 force stress corresponding to the plastic strain, as a function of depth, of indentation of FGMs, shows that the mean contact pressure presents the same tendency as in 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 of equivalent homogenous materials are very similar, which confirms the definition of equivalent yield stress for FGMs. Based on finite element results, a functional equation is developed to predict the hardness variation as a function of indentation depth, which depends on mechanical and geometrical properties of studied materials. Lastly, a theory based on effective hardness evolution is proposed to determine the yield stress evolution and hardness profile for materials with a decreasing yield stress with depth.

Results for carbo-nitriding steels obtained by the standard Vickers micro hardness techniques are compared with those obtained by the proposed method.

**SESSION P2**: MACRO-, MICRO-, AND NANO-TRIBOLOGY I

Chairs: Yang-Tse Cheng and James B. Adams

Monday Afternoon, November 26, 2001
Room 311 (Hyne)

1:30 PM P2.1

**RESEARCH CHALLENGES AND OPPORTUNITIES IN SURFACE ENGINEERING AT THE NANO-SCALE.**

Jorn Larsen-Jensen, National Science Foundation, National Engineering and Materials Design Program, Arlington, VA.

Developments in the many different aspects of surface engineering have been very rapid during the past decade. As a result, the surface properties 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 "paleo-technology", becoming its skin. Much research is in progress in this area but much more is needed to take advantage of its promises. In this brief overview I present a personal view of some of the current research, opportunities and needs and I try to extrapolate to some of the exciting research challenges of the near future in this dynamic field. Topics vary from the somewhat mundane design of new materials and micro-structure, metrology and testing standards, processes and control, to advanced modeling, development of multi-layered and nano-composite coating systems with nano-scale features and sculpting, low-friction MEMS surfaces, and superhard coatings, and even further on to smart or intelligent surfaces, self-healing coatings, etc. Further into the future we may see even more exciting developments if, as expected, there will be a scramble for wholesale new ways of dealing with and manipulating information as well as to incorporate nano-structures into surface layers and MEMS and micro-technological devices into coating finishes. In conclusion, in order for society to consistently evolving nano-technology to become reality there will need to be many advances made in materials and surface engineering and some of these are outlined as well.

2:00 PM P2.2

**MO S I M U L A T I O N S O F HIGH SPEED NANOINDENTATION AND PLOTTING ON Si SURFACE.**

Takanori Yo, Arizona State University, Science and Engineering of Materials Program, Tempe, AZ.

James Adams, Arizona State University, Dept of Material and Materials Engineering, Tempe, AZ, Ying-Tse Cheng, Louis Hector Jr. General Motors R&D Center, Warren, MI.

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

2:15 PM P2.3

**FRIC T I O N A N I S T R O P Y AT N(100)/(110) INTERFACE.**

Yue Qi, Takamori Ogi, William A. Goddard III, Material & Processing Simulation Center, Caltech, Pasadena, CA, Ying-Tse Cheng, GM R&D Center, Warren, MI.

Analytic theories indicated that there is no static friction on clean
incommensurate interfaces, while a recent experiment revealed that the static friction coefficient was anisotropic with respect to the lattice orientation but not vanishing on two Ni(110)-misoriented surfaces. To understand this friction anisotropy and the difference between theory and experiment, we carried out a series of Non Equilibrium Molecular Dynamics (NEMD) simulations for sliding of Ni(110)/Ni(100) interfaces under a constant force. We found that the clean, flat, and incommensurate interface indeed has a very small static friction coefficient. However, surface roughness can increase the static friction on the incommensurate interfaces dramatically, while the friction on the commensurate interfaces to a lesser extent. Thus, the rough surfaces show similar anisotropy behavior as experimental results. The effects from temperature, roughness, disordering and defects on interface are discussed as well.

2:30 PM P2.4
CHANGE IN SURFACE MECHANICAL PROPERTIES THROUGH ELECTROLUMINESCENT 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 absorbed 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), discrete monolayers of metal can be added to a surface. The degree of batter, that is, the difference between the metal and its upd layer will also control the degree of surface stress. The changes in the mechanical properties of these highly controlled surfaces are measured in situ nanoindentation at various potentials. Nanoindentation of single crystals with this method and location defines for the first time observation of dislocation behavior with applied load. This enables the identification of mechanisms by quantifying the changes in mechanical properties under specific environments. Au has been extensively studied in electrochemistry literature; it is well behaved and well characterized. It is a model system that has demonstrated variation in mechanical properties in different electrochemical states. Lessons learned on Gold have also been applied to Zn and Ni systems.

2:45 PM P2.5
KINETIC MONTE CARLO STUDY OF DISLOCATION ETCH PITS
Daniele Ratti, 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 due to 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. Simulation results have been performed for various values of the strength of the etch attack and the constraint of the stress generated by the dislocation. By using kMC in conjunction with molecular dynamics and quantum calculations we are able to increase the length and time scales of both these methods to make direct comparisons to experimentally observed phenomena.

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

With the availability of advanced (mostly plasma-based) coating and treatment methods, coating process developers can now 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 emphasised, and the way in which this influences the likely direction for the future development of tribological coatings is discussed. 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 be used in the development of low coefficient of friction 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 loads. These developments will be illustrated using the microlayer etching process, 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 PM P2.7
TRIBO-CONTACTS WITH MICRO SLIP IN COATED SOLIDS
Luisa Zheng, Seagate, Minneapolis, MN, and S. Ramalingam, University of Minnesota, Minneapolis, MN.

In a frictional contact, both stick and slip zones exist between two contacting bodies. It leads to changes in frictional stresses at the contact interface. A theoretical solution for the frictional contact on a layered solid involving stick-slip zones is obtained using Chebyshev 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 the replacement method. Solutions are obtained for the normal pressure for frictionless contact are first obtained. Solutions of Fourier series and Chebyshev polynomial are evaluated. Cases involving indentations by a cylinder and flat-end stamped are examined.

4:15 PM P2.8
TRIBOLOGICAL AND MECHANICAL CHARACTERIZATION OF BORON CARBIDE N/COMPOSITE COATINGS
Srikanta Nedkoti, Mark Walker, 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 hydrogencontaining gases has been used to produce novel nano-composite boron carbide thin films comprised of BC nano-crystals embedded in a matrix of hydrogenated amorphous carbon (DLC). The microstructure of these thin films is similar to that of other metal carbide/DLC nano-composite films. This paper presents results of the characterization of the mechanical and tribological properties of boron carbide nano-composite thin films that have been sputter deposited onto both silicon and titanium steel disks. 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, the nano-indentation experiments, information regarding cohesive and interfacial strengths is inferred. Ultimately, the results of the characterization will lead to microstructural models that advance the scientific understanding of boron carbide nano-composite coatings.

4:30 PM P2.9
NANOINDENTATION AND WEAR BEHAVIOR OF THE M-NiAl ALLOYS
Xiaoliang 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. Grammon, 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 load tests of spring-back reversibility together with high hardness, as measured by nanoindentation experiments, correlate with improved wear resistance in both bulk nitinol and NiTi thin films. Amorphous thin films of equiatomic NiTi are readily produced by physical vapor deposition and are found to be especially hard and wear resistant. Finally, stress induced B2→B19 transformation is shown to occur during wear-loading of martensitic NiTi, indicating that wear processes are capable of inducing superelastic effects in B2 NiTi alloys.

4:45 PM P2.10
WEUTING AND FRETTING ON QUASICRYSTALS
Wetting and fretting are two essential properties of materials that have a large extent and yet for quasicrystals - embody their technological potential when employed in the form of coatings. Quasicrystals, one considers here the whole family of complex intermetallics based on aluminum, which comprises true quasicrystals, their approximants and some crystalline materials of related composition. Experimentally, wetting these surfaces by water is largely reduced in comparison to conventional metal surfaces. A clear correlation is observed between the irreversible adhesion energy of water on the one hand and the density of states at the Fermi energy on the other. Such surfaces are necessarily octahedral on average 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 ridges are reduced in an ambient atmosphere; thus indicating that the oxide layer is involved to some extent in determining the tribological mechanisms. Nevertheless, reduction of friction is far more important on the true quasicrystal than on its neighboring crystals. Our data show that the specific crystallographic structure of quasicrystals is responsible for this effect. Hence, the paper will focus on a summary of these findings and on 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 (Hynes)

8:30 AM *P3.1
CHARACTERIZATION OF ANTIWEAR FILMS USING MICRO-FOCUS XANES AND IFM. P.R. Norton, Than Do, M. Nicholls, M. Kouri, T. Woo, N. Mosey, G.M. Bondolfi, 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 micrometers. An understanding of wear films requires the use of modern surface techniques and modeling, 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 instrumental force microscopy (IFM) and the Hysitron nanoindentor. 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 antiwear films. Materials include cast iron, thermal spray and high silicon aluminum alloys. This presentation will illustrate how the structure of antiwear films, formed under lubricated conditions influence the friction properties based on both mechanical and chemical studies. These data provide new fundamental insights into the mechanics of the lubricated wear, which can be used to design better engineered surfaces for automotive applications.

9:00 AM P3.2
CHEMICAL-AND MECHANICAL POLISHING BETWEEN STEEL AND CARBON-CONTAINING CERAMIC COATINGS. Stephen J. Herring, 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 counterpart, reducing stresses from asperities. Thus, a coating's ability to polish or abrade without damaging the counterpart may determine its usefulness. Yet there has been little work examining how these factors influence polishing by such coatings. We have analyzed the abrasiveness of diamondlike carbon and boron carbide coatings for this study. We find an extremely steep dependence of abrasiveness on hardness. We show that nanometer-scale features on the coating surface are strongly correlated with abrasiveness, while micron-scale features are not. The nano-scale but not the microscale-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 steel, which is several times softer than the coating. We derive quantitative scaling relationships that show how the time dependence of the abrasion rate varies with important parameters of sliding wear, and use these relationships to predict abrasion kinetics for new experiments. Damped contact mechanisms 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 Bathe, R.D. Vignate, Ichiro Takeda, R.P. Sharma, and T. Venkatesan, CSR, Dept. of Physics, Univ of Maryland, College Park, MD.

Protective coatings of ceramic materials are of great interest for high temperature applications. Boron nitride is an ideal candidate for protective coating applications for high temperature elements and components due to its structural and chemical stability at very high temperatures (>2000°C), high thermal conductivity, and high chemical inertness to corrosive gases and oxidizing atmospheres. In this paper, we report on fabrication, characterization, and processing of boron nitride films on metallic components of high temperature wafer heaters. The hexagonal BN films have been fabricated by pulsed laser deposition and spray techniques. The deposited films were characterized by x-ray diffraction, FTIR, Rutherford backscattering spectrometry, scanning electron microscopy, atomic force microscopy, and electrical resistivity. The deposited BN films have been found to be poorly crystalline, however, the films annealed at 900°C have been found to be polycrystalline. The deposited films were annealed at various temperatures ranging from 500°C to 1200°C in order to densify the films. Adhesion of the films with the heater components was also greatly improved for the high temperature annealed samples due to 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 #3-29319) and Blue Wave Semiconductors, Inc. is acknowledged.

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

Low carbon steel coatings were applied on 319 Al alloy substrates using a plasma transfer wire arc (PTWA) type thermal spraying process. A pin on disc type wear tester placed in an environmental test chamber was used for the wear tests. Tests were performed in an atmosphere with various humidity levels in the range of 10-90% RH. It was shown that the wear rates of the coatings were a strong function of the testing environment in addition to the applied load and test speed. The wear is dominated by the formation of iron oxides. The mechanism for the wear process depends on the composition of the oxides formed; at low sliding velocity the oxides degrade and dominate the material removal from the surface. At high velocity more oxides are formed that coat the surface and act as a tribo-lubricant that reduces the wear rate. The addition of moisture to the test atmosphere alters the ratio of the various iron oxides formed, strongly favoring FeOx. As the atmospheric humidity increased, a tribo-lubricating 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-Beam EXCITED PLASMA DEVICE. Hiroshi Shoyama, Toshihiro Kobayashi, Hideo Sato, Yoshiki Tasekimura, Tatsuo Hara, Toyota Technological Institute, Nagoya, JAPAN; Takanori Arahata, Faculty of Science and Technology, Meijo Univ., Nagoya, JAPAN; Kazunori Taniguchi, Department of Physics, Kyoto Univ. of Education, Kyoto, JAPAN; Mambu Hanyukaga, 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 concentrically a highly reactive species, primarily atomic nitrogen, which is generated Uniform etal. surface nitriding of structural materials. However, in the conventional
plasma sources, there are only few electrons with energy enough to break the molecular bond, because the electron energy distribution is generally confined to a region where the electron temperature is of 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 500 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 substrate current of 6 l/s. 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. Furthermore, 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 nitride the disks, it was found that the modified region extended to 5 mm in the radial direction from the edge where 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 SP EUTTERED DEPOSITED ONTO AISI 52100 SUBSTRATES AS ILLUCIDATED USING F OCUSED-ION-BEAM SEM. C.V. Cooper, United Technologies Research Center, East Hartford, CT; R. Wang, A.G. Evans, Princeton University, Princeton, NJ; H.K. Yoon, M.A. Taker, Caterpillar, Inc., Peoria, IL.

Magneton sputtering has been used to deposit metal-containing, diamond-like carbon (Mo-DLC) coatings onto substrates composed of AISI 52100 steel in quenched-and-tempered condition. Coatings of two different forms, one containing W as the metallic constituent and the second containing Cr, have been deposited in a plasma containing Ar and H2. Oriented, unidirectional sliding experiments of the block-on-ring type have been conducted in a poly-alpha-olefin (PAO) lubricant at a load of 0.67 N for discrete numbers of cycles, N, of between 10 and 1000. Focused-ion-beam, scanning electron microscopy (FIB/SEM) has been applied to characterize the microstructure of metal-containing magnetron sputtered coatings. This technique has resulted in the determination that the Cr-DLC coating, deposited using the investigated processing parameters, fractures in a brittle manner through the formation and propagation of “channel cracks,” which unpin 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 coatings has produced a coating that wears by gradual recession, consistent with polishing wear. Distinctive characteristics of the FIB/SEM technique and its efficacy and value in observing the coating and substrate subsurface will be highlighted as a means to investigate coating/substrate interfaces and to establish wear mechanisms.

11:00 AM P3.7

LOW FRICTION W-C-H COATINGS FOR WEAR RESISTANCE IN ROLLER BEARINGS AND GEAR WHEELS. Thorsten Kiesick, Metallurgische Louis GmbH. Bergisch Gladbach, GERMANY; Peter Werner Gold, Jörg Loos, Institute for Machine Elements and Machine Design, RWTH Aachen, GERMANY.

Life time limiting effects in roller bearings and gear wheel applications are wear, sizing and fatigue damages like micro pitting. These mechanisms are related to a number of parameters: lubrication conditions, surface roughness, and the hardness of the bulk material, for example. Nowadays, Mo-DLC coatings like MAXITM W-C-H offer surface protection under dry, mixed, and hydrodynamic friction conditions. This allows the increase of load capacities, respectively the decrease of gearing size. Moreover, the reduction of toxic lubrication additives is of increasing interest. The performance of the Mo-DLC coatings in roller bearings was investigated on the FEStest rig under mixed friction conditions. MAXITM W-C-H was deposited via the PVD technique of magnetron sputtering onto case hardened steel bulk material. The deposition temperature was 100°C. The coating thickness was varied from 1.5 to 6 μm with respect to optimized wear resistance. The wear of ball bodies and disks was drastically reduced by powers of ten as compared to uncoated roller bearings. Additionally, results on P2G gear wheel tests, as well as examples of the successful application of MAXITM 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 grow and heat generation is several °C, 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 nitride the disks, it was found that the modified region extended to 5 mm in the radial direction from the edge where 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.
focus on optical reflective methods which are very versatile and can be used in a wide variety of deposition situations. We will also demonstrate how these materials, known as in-plane TBCs, led to a better understanding of the mechanisms of TBC failure and to the design of the TGO layer. 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 composition can vary greatly, and the mechanisms of TBC failure indicate that bond coat properties have a determinant effect on the ultimate TBC performance. The study of the deformation of the alumina coatings is warranted. This paper focuses on the effect of thermal aging and cycling on the TGO layer, and it is particularly focused on the in-plane TBC cracking behavior. This study was carried out as part of the Office of Basic Energy Sciences, Division of Materials Science.

2:45 PM P4.5

High Velocity Particle Consolidation (HPC) is known for the cold spray technology. Cold spray is a relatively new, low temperature, low pressure, and high velocity spray process that can be used to coat substrates. This process involves the use of a converging-diverging nozzle to accelerate a high pressure gas with entrained powder particles to supersonic velocity and impinging the supersonic powder particles onto a substrate. The mechanism by which the powder particles initially impact 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 the cold welding processes. The bond between coating and substrate materials has been investigated for three different metallic materials: Al, Cu, and Ti6Al4V. In this work we explore the effect of the cold spray process on the mechanical and/or chemical nature of the bond between the coating and the substrate.

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

We review our research on the formation and properties of 'artificial-free' nanocrystalline metallic and ceramic films and composites using controllable plasma deposition processes. The source materials include, for example, W and Ta in Cu and Zn, and NaAl in WC, which can be used to produce multilayer structures for various applications such as tungsten carbide deposition of polycrystalline Wolfram and tantalum intermetallic compound films. In this work we investigate the formation of a new, nanostructured material system, NaAl in WC, which can be used to produce multilayer structures for various applications such as tungsten carbide deposition of polycrystalline Wolfram and tantalum intermetallic compound films.
METROLOGY TOOL FOR POROSITY MEASUREMENTS OF LOW-K DIELECTRIC FILMS. N.V. Edwards, J. Vella, Q. Xie, S. Zheludev, N. Allred, Motorola Microelectronics, Mesa, AZ; J. Vires and K.H. Junker, Motorola Materials and Structures Laboratories, Austin, TX.

The International Technology Roadmap for Semiconductors predicts that the progressive downward scaling of device dimensions required for the 10nm technology node will require materials with dramatically lower static dielectric constants, achieved without sacrificing robust mechanical properties. One strategy for achieving these ultra-low-k materials is to incorporate porosity into otherwise dense dielectrics, yet there is no definitive in-line metrology solution that yields porosity and mechanical property information. Our results obtained on OSZ (organosiloxane) 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 0.5 eV on a series of OSZ films with Wolfram 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 bonded methyl groups in the OSZ 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 absorption behavior of the films and its connection to film mechanical properties, the ellipsometry measurements were extended into the Vacuum Ultraviolet (to 8.7 eV) with a J.A. Wolfram 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. Ramnathan Krishnamurthy, Brian W. Sheldon, Division of Engineering and Computer Science, Pennsylvania State University, PA; John Allen, Haynes, Oak Ridge National Laboratory, 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 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 O₂. SiO₂ mulls with different Si/Al compositions were deposited on SiC. The coating thickness was varied so as to allow for the study of diffusion for mullite specimens with different compositions for the appropriate surface layer thickness. This model calculation was compared to 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. Toshihiko Isshiki, Tetsuya Yamanaka, and Takeshi Kato, Department of Physics, Nagoya University, Nagoya, Japan.

If an intense pulsed ion beam is irradiated on solid target, high-density plasma is produced because the energy density will be high due to short range in the target. In 1998, the author proposed and demonstrated quick preparation of thin films of ZnS by the ion beam plasma, aimed 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 B₂C₃ films are discussed here since we believe this is the first time in the world. As well known, B₂C₃ is a hard material after diamond. It is wear resistant as well. The melting point is 2,450°C, and it is very stable even at high temperatures. Furthermore, it is a good thermoelectromotive material, where Seebeck coefficient is considerably high. Nobody has succeeded in the preparation of the crystallized films. The experimental results, together with various characterization, are presented by SEM, EELS, high resolution TEM, and hardness tester, revealed that the crystallized B₂C₃ films have been successfully prepared by IBE. Vickers hardness of 2,300 has been obtained by the films. Similar results of the preparation of many kinds of films will be presented, for example, [Ba,Sr, Y]Ba₂Ca₃O₇-δ, SrAl₂O₄:Eu,Dy and polycrystalline Si. Furthermore, such a high-density plasma provides to synthesize ultrafine nanosize powders, typically characterized as 5 - 20 nm in diameter, by rapid cooling with the ambient gas. 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
Chair: Wen Jin Meng, Ashok Kumar, Yip-Wah Chung, Gary L. Dell, Yang Tse Cheng and Stan Vregek
Tuesday Evening, November 27, 2001
8:00 PM
Exhibition Hall D (Hynes)

P5.1 ADVANCES IN CATHODIC ELECTRODEPOSITION OF ORGANOCERAMIC FILMS. Igor Zhitomirsky, A. Petric, Dep't. 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 high control of surface uniformity and deposition rate as well as the possibility of formation of multilayer deposits of controlled thickness on substrates of complex shape and on selected areas of the substrates. Organoceramic films based on oxides or hydroxides of Zr, Ti, Ge, Sn, Si, Ce, Y, Co, Cu, La and carboxylic polyelectrolytes, such as poly(diallyltrimethanimmonium chloride), polyethyleneimine, poly(allylamine hydrochloride) were prepared. The deposition method is based on electrolytic (ELD) or electrophoretic (EPD) deposition of inorganic phases and EPD of polymers. Cathodic electrodeposition of polyvinyl alcohol (PVA) involves a pH increase and electrochemical crosslinking of PVA molecules near the cathode surface. EPD and ELD were used for intercalation of ceramic particles into growing polymer films. By varying the current density and concentration of polymer, ceramic, electrolyte, the amount of the deposited material and its composition could be controlled. Deposition rate was evaluated at different experimental conditions. Films in the range of thickness up to 10 microns were prepared as monolayers or laminates of different materials. Possible applications of the prepared materials are discussed.

P5.2 IN-SITU MONITORING OF NUCLEATION STAGE DURING ALUMINUM-CVD FOR NANO-STRUCTURE CONTROL. Tomohiko Inoue, Masakazu Sugiyama, and Yoshiohiro Shimogaki, 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 trend arouse the interest and importance of initial nucleation during film growth by chemical vapor deposition (CVD). We have examined the kinetic of aluminum CVD using dimethylaluminumhydride (DMAlH) as the source precursor, and established elementary reaction mechanism of this CVD process. We could succeed in improving surface morphologies by the aid of this chemical perspectives. The only thing that remains 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 DMAlH concentration and the substrate temperature. The higher concentration of DMAlH provides shorter incubation time and higher reflectivity reflection. These nucleation behavior of Al-CVD will be discussed in conjunction with the elementary surface reaction mechanism.

P5.3 FABRICATION OF CaO INSULATOR COATINGS BY MOCVD FOR APPLICATION IN FUSION REACTOR BLANKETS. Zuotao Zeng, Ken Nisemara, 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 metallicorganic chemical-vapor deposition method used to fabricate the CaO coating. A 24 μm thick CaO coating was successfully obtained by this method. Composition and phase analyses of the coating were performed by energy dispersive X-ray analysis and X-ray diffraction. Scanning electron microscopy images show that the coating consists of four different phases. The resistance of the coating is high enough for an insulating coating on the liquid lithium blanket of fusion reactors.


Mechanical properties of these films differ significantly from those of similar materials. In this study we will present the results of nanoindentation tests to evaluate mechanical properties of nitride (TiN, TiC, TiCN and TiAIN) single and multi-layered nitride thin films. Films were coated on steel substrates using cathodic arc deposition technique. We have extended the measurement to the multiply coating with indentor displacements increasing to different layer thicknesses. Nanoindentation was performed by MTNL's Nanoindentor XP with a Berkovich indenter. Indentation marks and deformation 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 elastoplastic deformation, cracking, phase transformation etc.

P.5.5 CaO ELECTRICAL INSULATOR COATING ON V-4Cr-4Ti-3Al. FUNDAMENTALS AND APPLICATIONS. J. H. Park, K. Nataev 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 forming CaO and/or the self-healing of defects of electrically insulating CaO coatings for use in vacuum/filament/magnetic fusion reactor blankets. To form CaO film at the interface of V-5%Cr-alloys and the liquid lithium, it needs preheating of O from the V-5%Cr-alloys, and Ca in the liquid lithium. To understand the mechanism in the alloys, we used the binding and/or formation energies between the metal elements and O. Additionally, we conducted several experiments on in-situ fabrication of CaO film on Thickness V-5%Cr-alloys by electron beam evaporation. 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. A. A. I. Arminus Patel, Marek Sanowski, Leszek Gladczuk, New Jersey Institute of Technology, Dept. of Electrical Engineering, Newark, N.J.

Tantalum has mainly two phases: alpha phase (bct structure) and beta phase (tetragonal structure). The metastable beta phase is usually obtained in spatter films. Alpha phase is preferred over the beta for some applications as beta phase is very brittle. One of such applications 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 microstructural properties of these coatings were studied by four-point probe measurement and x-ray diffraction (XRD). Stocometry of interfacial tantalum nitride layer was investigated by rutherford backscattering (RBS). Influence of the interfacial film thickness and the ratio of oxygen to 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 spattering gas (Ar, Kr) and on the substrate temperature (1000-1100°C) during deposition.

P.5.7 STABLE SILICON-CARBON PRECURSOR FOR OLIGOMER CHEMICAL VAPOR DEPOSITION OF SILICON CARBIDE FOR HARSH ENVIRONMENTAL APPLICATIONS. Ulrike Patschek, Harry Efthimiadis, James Cattermole, Ahim E. Kudzero, UABz pH Material Institute for Matl. and School of Nanosciences and Materials, The University of Alabama in Huntsville, AL. Mark MacDonald, Susan Hayes, and Walter Sherwood, Starfire Systems Inc, Watervliet, NY.

Silicon carbide (SiC) films have been successfully deposited on various substrates by low pressure oxygen chemical vapor deposition (CVD) from a novel, hydrogen free, oligomer precursor gas. The high quality films were grown at substrate temperature in the range of 600°C to 1200°C at a rate of pressure in the range of 1.5 Torr. HPCs is a silicon carbide precursor gas 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 Auger electron spectroscopy (AES), x-ray diffraction (XRD), electron microprobe, Fourier transform infrared spectroscopy (FTIR), and optical and scanning electron microscopy (SEM). Environmental studies were carried out by exposing the films to oxidizing flame jets and to wind/alcohol baths for extended duration. The film morphologies, hardness, microstructure and secondary ions yield were affected by the environment. The electrical properties were measured using a nanosensor, a Knops hardness tester, and a ball-on-disc tribometer tester. The SiC coatings deposited at substrate temperatures below 1100°C were found to be amorphous. Erosion post deposition etching in inert gas above 1100°C converted the SiC films to a polycrystalline phase. The CVD SiC coatings are being examined for applications such as rocket nozzle, furnace hardware and other high temperature and corrosive systems. The films are also being investigated for use in Nano/Thermal fluidic structures for custom designed components such as valves, pumps and channels in corrosive or high temperature environments.

P.5.8 CVD DIAMOND SYNTHESIS ON WC-Co CUTTING TOOL VIA ELECTROPHORETIC SEEDING PROCESS. Toshiaki Tatsuhito, Minoru Nagata, Kumanoto Industrial Research Institute, Material Development Dept., JAPAN; Naoki Okada, Shintaro Ida, Yasunori Masumoto, Kumanoto University, Faculty of Engineering, JAPAN, Nobutomi Yu-Yoshino, Kumaizuck Metal, Kumanoto, JAPAN.

Using ECR-MPCVD (electrochemical resonance microwave plasma chemical vapor deposition) apparatus, CVD, diamond film synthesis was attempted on WC-Co cutting tools. Electrohydrodynamic deposition was utilized as a seeding process in the synthesis of CVD diamond films. A commercial diamond powder (grain size: 250 nm) was employed in this study. The diamond powder was suspended in acetone at the concentration of 0.1 g/L, and it was electrochemically deposited on substrates. Si(100) plane or commercial WC cutting tool was used as a substrate, and Pt plate was used as a cathode for electrochemical deposition. The diamond particle density of Si(100) substrate depended on the electrochemical condition. After electrochemical pretreatment, CVD diamond was deposited on the WC substrate using ECR-MPCVD apparatus. Electrohydrodynamic deposition was effective for the synthesis of diamond film on WC cutting tool without removing the coatings on the surface, although the deposition force between the CVD diamond and the sample was not sufficient for the application to a cutting tool. Heat treatment after electrochemical deposition improved the adhesion force of CVD diamond films. The strength of the sample given the electrochemical pretreatment was as same as that of 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 Zhidomirsky, A. P. Petrie, McMaster Univ., Hamilton, Ontario, CANADA.

Two processes were used to prepare ceramic coatings by cathodic electrodeposition: electrochemical deposition (EPD) and electrolytic deposition (ELD). It was demonstrated that the ethyl alcohol-phosphate ester-polyvinyl butyral system is an effective solvent-dissolution system of the advanced ceramics. EPD of these ceramics was studied by four-point probe measurement and x-ray diffraction (XRD). EPD was used to produce single layers as well as composite layers of different materials. EPD has been utilized for deposition of thin electrolyte layers or intermediate layers preventing electrode/electrolyte degradation and production 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 technique used for deposition of polymers and organoceramic materials include EPD, ELD and electrochemical ablation. In the case of organoceramic deposits, a two-fold beneficial effect was expected: the possibility of deposition of dense electrolyte layers on porous electrodes and formation of barrier ceramic layers in the solid products. Application of electrodeposition in various fuel cell technology configurations is discussed.
P.5.10 CHEMICAL VAPOR DEPOSITION OF TUNGSTEN NITRIDE AS CHIPPER DIFFUSION BARRIER. Young-Min Sim, Wei Lin, Englebrecht, Tiber Bolom, Jung H. Sim, cris Chin, John M. White, and John G. Ekerdt, Texas Materials Institute, The University of Texas at Austin, Austin, TX, Steven Smith, Klaas Pfeffer 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) analysis revealed that at the temperatures ranging 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 indicated that nitride films were grown with an amorphous or nano-crystalline structure. This was further proved by cross section transmission electron microscopy. Using a combination of these techniques, it was shown that the films consist of copper diffusion resistance. After annealing a Cu/W2N/SiO2 stack at 360°C for 8 hrs, secondary ion mass spectroscopy (SIMS) depth profile revealed that copper was still 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 increase of surface reaction 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 Cu and W2N will reduce lown temperature low dielectric materials was also investigated by in-situ XPS study.

P.5.11 HYDROGEN FREE, HIGH SP³ CONTENT DLC FILMS PRODUCED BY PULSED LASER ABLATION OF AMORPHOUS GRAPHITE. J. Haverkamp, R.M. Mayo, Department of Nuclear Engineering, North Carolina State University, Raleigh, NC, J. Narayan, T.K. Zhang, Jin, Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC.

Pulsed laser ablation is a unique technique for the deposition of a wide variety of thin films. These films include magnetic and optical films, novel semiconductors, high temperature superconductors, and diamond-like carbon films. Amorphous Carbon material is evaporated from a solid target and ionized by a high-energy KrF laser and ejected as a plasma plume. The plume expands outwards and deposits the target material on a silicon substrate. Plasma and flow parameters in this plume determine the quality of the thin film deposited on the substrate. In these experiments, a triple Langmuir probe is used to determine various plasma properties in the plume as a function of laser energy density on target, laser spot size on the target and probe position on target. These properties include electron temperature, ion flow speed, ion kinetic energy, plasma 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 small fraction 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%.


The demand for real-time characterization techniques in thin film science and technology is motivated by the need for complex graded deposition sequences that yield improved film characteristics. Optical characterization techniques, in particular real-time spectroscopic ellipsometry (RSTE), are well suited for measurement, monitoring, and control of such deposition sequences. Recently, we developed an extended rotating polarizer multichannel ellipsometer with spectral capabilities covering the photon energy range from 1.5 to 6.5 eV (uv-RSE). Given its minimum acquisition time of 34 ms while maintaining 4 nm sensitivity, the uv-RSE is ideal for studying wide band gap thin film deposition in real time, including cubic, cubic boron nitride (cBN), and silicon oxynitrides (sSiONₓ), among many other materials. cBN is a promising material for a number of applications ranging from hard protective coatings for cutting tools and optical elements to high temperature and high power electronic devices. To date, most of the research in cBN focuses in the study and control of c-BN 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-RSE to reach the phase evolution of BN films has been documented recently for cBN films grown using magnetron sputtering of BN and B₄C targets. In this contribution, we present the effects of dynamic deposition conditions on the phase evolution of BN films grown using pulsed dc sputtering of a B₄C target and rf substrate biasing will be presented. In addition, improvements in data measurement and analysis resulting from the use of a new uv-RSE design, the rotating configuration, will be presented.

P.5.13 COMPARISON OF MICROSTRUCTURES PRODUCED BY HIGH-KINETIC ENERGY PULSED INTENSE ION BEAMS WITH THOSE FROM MORE CONVENTIONAL TECHNIQUES. T.J. Renk, P.P. Provencio, S.V. Prasad, Sandia National Laboratories, Albuquerque, NM; J.R. Tregilgo, Cutting Edge Products, Paway, CA; M. Kammura, Kitami Institute of Technology, Dept. of Material Science, Kitami, JAPAN.

Intense pulsed beams of ions [700 keV, up to 400 A/cm², 150 ms 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 Ti produced by pulsed 15 keV (1 s) beams. In these experiments, the following techniques were used: high-dose ion implantation of Pt into a Ti substrate (70 keV, at 10¹⁷ cm⁻²), and 1) a micron Pt/Ti sputtered layer 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, x-ray diffraction and transmission electron microscopy (XTEM) shows that microstructural changes are observed that extend well beyond the ion range and heat-affected zone. 1 micron thick deposited case, 150 microns thick in the implant beam case. These structural changes are likely to be due to the beam interaction both with the substrate and the film. XTEM observations show that 1) produces a polycrystalline micron-scale Pt layer, in contrast to the sub-micro grain size produced by 2b). Layers were deposited both at room temperature, and at 350°C. More XTEM is planned, and latest results will be presented.

P.5.14 LASER WRITING OF NANOSTRUCTURES ON MAGNETIC FILMS 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 directly writing of nanostructures on magnetic film surfaces with optical near field effects has been investigated. Spherical 0.5 micron sized particles were written on Co30/Cr70 thin film. After laser illumination with a pulsed Ti:Sapphire laser, hole with size of about 350 nm were observed at the original position of the particles. The mechanism of the formation of nanostructure pattern with optical near field effect has been suggested. The observation of nanostructure effect induced by particles on the surface. A comparison with relative theoretical calculations of near-field light intensity distribution showed good agreement with the experimental results. The method of particle enhanced laser irradiation allows the study of field enhancement effects as well as its potential applications for nanolithography.

P.5.15 CHARACTERISTICS OF POLYCRYSTALLINE SILICON THIN FILMS PREPARED BY PULSED ION-BEAM EVAPORATION. Sung-Choo Yang, Ali Fazli, Hisakuki Shimatsu, Weihua Jiang and Ryoichi Yasui, Extreme Energy-Density Research Institute, Nagoya University of Technology, Nagoya, Nishin, 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). Recently, we developed a novel technique for yielding high-quality silicon thin films, using a combination of pulsed ion-beam evaporation (PIBE) to produce high-quality silicon thin films. This technique is based on the use of a pulsed ion beam to deposit silicon on a substrate at high temperatures, thereby reducing the formation of defects in the silicon film. The polycrystalline silicon thin films prepared by this method have been characterized for their electrical and optical properties, and were found to be suitable for use in a variety of applications, including solar cells and microelectromechanical systems (MEMS). The results of these studies demonstrate the potential of this technique for the production of high-quality silicon thin films with applications in a wide range of fields. This technique also offers the potential for the production of high-quality silicon thin films with a wide range of applications, including solar cells and microelectromechanical systems (MEMS).
solar cells. If the pulsed proton beam irradiates solid targets, high-density ablation plasma can be produced due to short range of protons in targets. Using such the plasma, it has been found out to prepare thin films very efficiently, which was called as intense, pulsed, ion beam evaporation (IBE). After the first demonstration of the preparation of thin films of ZnS in 1988, various kinds of thin films have been successfully prepared by IBE, e.g., YBCO, ITGO, Bi2TiO3, BN, SiC, TiO2, SrO2, and AlN. One of the aims of this study is to prepare pol-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/h) have been achieved. The crystallinity of pol-Si film has been improved with increasing concentration of the ablation plasma. High crystallinity and the density of pol-Si thin films are increased by (-) ion voltage on the substrate. In this presentation, we will report the characteristics of pol-Si thin films prepared by using a high-density ablation plasma produced by IBE.

P.5.16

ELECTROCHEMICAL SYNTHESIS OF CARBON DIAMONDLIKE COVERS ON METALLIC SUBSTRATES. Vladimir Novikov, Larisa Kuznetsova Institute of Solid State and Semiconductor Physics, Minsk, BELARUS; Patrice Aubleine Lompes CNRS, St Martin d’Heres, FRANCE; Michel Meriaux, LEPAM/ENSEEG/CNRS, St Martin d’Heres, 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 permanganate, sodium formate and sodium borohydride. Nickel, titanium, zirconium and stainless steels were used as electrode materials. The electrolysis was carried out in the 250-300°C temperature range. A shifted sinusoidal alternating current of amplitude higher than 200 mA was applied to the electrodecell. 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 corrosion 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, while the films on pure substrate have 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, 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.

P.5.17

PREPARATION OF TiF 薄膜 B Y PULSED ION BEAM EVAPORATION P.5.17.


TiF6 is a hydrogen-storing alloy which can absorb hydrogen atoms as much as 1.8 wt% of the alloy. Because of the high reactivity of Ti with hydrogen, TiF6 and Crystalline TiF6 has 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 of ion plasma (1×1013/cm³) is formed. Thus, it was expected that the oxidation of the thin film TiF6 may be prevented because the number of oxygen atoms in the vacuum chamber (1×1013 particles) is too small to react with all the Ti and interstitial atoms in the high density plasma. In the present work, preparation of TiF6 thin films by IBE is performed. Thin films of TiF6 were prepared in a pulse ion beam generator (ETGO1-T). A pulsed ion beam of proton accelerated at 1 MV (peak) with a repetition of 70 kHz was focused on a TiF6 alloy target. Ti single crystal and SiO2 glass substrates were placed in front of the target. Phases in the thin films were identified by XRD (X-ray diffraction) and XRD results revealed that the thin films deposited on the SiO2 glass substrates consist of a TiF6 phase. Although the films also contain a small amount of TiF2, as a second phase, there are no TiO or Fe-O phases in the films. Crystallized TiF6 thin films without oxides were successfully obtained. On the other hand, when the deposition on the single crystal Si substrate consists of an amorphous TiF6 phase. The formation of a monoclinic 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.
Surface properties of carbon ion implanted (at doses ranging from 10^8 to 10^7 ions/cm² and accelerating voltages from 120 to 14keV) WC/10Co composite (WC grain size <488 nm) have been studied. Through Raman spectroscopy tests, it was found that surface hardness of the implanted (at the dose of 6 x 10^7 ions/cm² and accelerating voltage of 20keV) sample reached a maximum value of -25 GPa at the depth of ~125 nm into surface, compared to ~18 GPa (HKN6500g) of the virgin material. Auger electron spectroscopy (AES) analysis of the implanted sample indicated that a carbon-rich layer (a 120 nm thick) was formed in the subsurface. Glancing angle x-ray diffraction (GAXRD) analysis of the subsurface showed no evidence of the formation of new compounds and broadening of the peaks which is attributed mainly to the compressive stress (up to ~4 GPa) induced by the implantation process. Surface roughness measured by atomic force microscopy (AFM) of the implanted sample is around 3.5 nm. Effect of implanted ion dose, energy, and species on surface hardness, roughness, friction coefficient, and wear resistance of ultrahard WC/10Co composite will be presented.

P.5.22
HOMOEPIXTALAXIAL GROWTH ON THE Ge[100] AND THE Sb-TERMINATED Ge[100] SURFACE. Mia 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 Sb-terminated Ge[100] surface has been studied using scanning tunneling microscopy (STM) and other surface characterization techniques. When 0.12 ML of Ge was deposited on the Ge[100] surface at ~350 K, <110> oriented dimers dominated the surface with very few epitaxial dimer rows oriented across the substrate dimer row after deposition. The density of epitaxial dimer rows increased after 0.18 ML Ge deposition. At the same Ge coverage but at a higher growth temperature of 420 K, the <110> oriented dimers disappeared and were replaced by larger Ge epitaxial islands with a structure similar to that of the substrate. The "smooth" Sb-terminated surface with about 0.1 ML Sb dimer clusters was prepared by flashing an Sb multi-layer to 720 K. After 0.18 ML Ge deposition at 310 K, epitaxial Ge clusters were randomly distributed on the Sb-terminated surfaces. There was no appearance of <110> oriented Ge dimers that were found on the Ge[100] surface. Some small epitaxial dimers (<0.05 ML) were observed as the topmost white features. The surface morphology remained the same as the Sb-terminated surface, with either increased growth temperatures or Ge coverages. The morphology is basically dominated by Sb-Ge surface mixing. Based on our experimental results, the effect of Sb as a surfactant is discussed.

P.5.23
ENGINEERING THE Si[111] 7x7 SURFACE ENERGY USING. J.B. Mason, B. Yang, A.R. Wall, and M.G. Lagally, University of Wisconsin-Madison, Madison, WI.

The importance of strain in modifying the free energy of 2D and 3D nanostructures and their stability to surface, morphology, and structural defects has recently been more widely recognized. Modifications in the stress state of a structure can be introduced by the deposition of a heteroepitaxial film even at the monolayer scale. For example, deposition of Ge onto Si[111] can increase the transition temperature between the 7×7 and the ordered 1×1 states relative to that of clean Si[111]. We study this transition using Low-Energy Electron Microscopy (LEEEM). Earlier work [2], neglected to consider Ge adsorption at high temperature. We show that desorption significantly reduces the Ge surface concentration at high temperature. Tuning the temperature ramp rate and the initial Ge covering and correcting for the loss of Ge allows us to achieve a transition temperature up to 900°C. Quantitative arguments are presented to show how the 7×7 stabilizes on Si[111] with high modification of strain and bond energies. The surface energy is reduced by an additional 20 meV per 1x1 unit cell at a coverage of ~75 ML. [1] T. Ishikawa and I. Iino, Surf. Sci. 136, 267 (1984). [2] K. Kijima, Y. Tanaka, and K. Tokupangi, Surf. Sci. 122, 58 (1983). Supported by ONR and NSF.

P.5.24
PRECISE CONTROL OF CVD-ZrO2 FILM PROPERTIES BASED ON KINETIC INFORMATION. Koyamato Takashi, and Yukihiro Shimogaki, Department of Materials Engineering, University of Tokyo, Tokyo, Japan.

The shrinking of MOS (Metal-Oxide-Semiconductor) transistor enhances the performance of USLI devices. Gate dielectric scaling will require new insights into dielectric materials with lower leakage current by direct tunneling. Various kinds of high-k materials have been studied to replace conventional thermal oxide or gate dielectric. Among them, ZrO2 have attracted a lot of attention recently. We have investigated ZrO2-CVD reaction system using Zeeman-NMR spectroscopy. ZrO2 containing 3% Eu2O3 is used to study Zr:Eu2O3 reaction system. ZrO2 shows Zr:Eu2O3 reaction system. ZrO2 shows Zr:Eu2O3 reaction system. ZrO2 shows Zr:Eu2O3 reaction system. ZrO2 shows Zr:Eu2O3 reaction system. ZrO2 shows Zr:Eu2O3 reaction system.
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 cathode and the magnetic field strength are assumed to determine the dynamics of secondary electron. Compared to the small curvature magnetron, electrons easily escape from the large curvature magnetron. Therefore, the large curvature magnetron is found to be less efficient in confining secondary electrons and thus is expected to have a higher minimum chamber pressure. Also the strength of magnetic field and the configuration of magnets play an important role in determining the shape and properties of the film. The uniformity of sputtered thin film and the step coverage. This type of simulation turn out to be useful method in designing new magnetron cathode since it is capable to predict all the important characteristics of the process.

P5.28
Abstract Withdrawn.

P5.29
MOTION OF SAPPHIRE SURFACE STEPS. N. Hwangshian, C.B. Carter, Dept. of Chem, Engg, 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 field depends on the quality of the surface of the substrate. The quality of the surface is itself determined by the character and the behavior of steps and step-kinks, and the presence of impurities. Under conditions where the steps on the surface are mobile, several interesting interactions are possible. For example, steps can bunch and form new facets; this process can be influenced by the presence of foreign particles on the surface. In this paper the behavior of steps on sapphire under various conditions used to prepare the substrate and for subsequent growth will be discussed. The influence of impurities on the surface and their role on the step motion is investigated. Illustrations of extensive step bunching which results in the formation of 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

STRUCTURES AND DEVICES

Chair: Kathryn J. Walk and S. Mark Spearing

Wednesday Morning, November 28, 2001
Room 311 (Hynes)

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

Several fabrication routes are available to realize mechanical devices with structural elements that are microns to tens of microns in size. In particular, recent developments in surface micromachining (SM) and patterning techniques (LIGA) have resulted in complex machines with actuators and countershaping gears. Such machines include impacting and sliding surfaces in which friction and wear will determine the machines 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 of this size scale presents significant challenges, including modification of hidden surfaces, control of treatment thickness relative to gap dimensions, and the generation and trapping of third bodies. Further, understanding the behavior of surface treatments as pressure and velocity regimes relevant to microsystem operation requires the development of new tools for quantifying interface performance. A focus of our research is the development of special SM and LIGA structures in which we embed tribological contacts from which the friction forces may be extracted. Methods of quantifying static and dynamic friction in surface micromachined contacts will be shown, including measurements where the interface is parallel to the wafer surface (planar) and where the interface is perpendicular to the wafer surface (sidewall). Newly developed techniques for quantifying dynamic friction in LIGA contacts will be presented. Use of these approaches will be illustrated with several examples, including coupling spalls and selective tungsten to modify the frictional behavior in polycrystalline silicon contacts, and a diamondlike nanocomposite coating for LIGA nickel structures.

9:00 AM P6.2/B10.2
DIAMOND-LIKE NANOCOMPOSITE (DLN) COATINGS FOR LIGA MEMS: TRIBOLOGICAL BEHAVIOR AND COATINGS METHODOLOGY. Somuri Prasad, Todd 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 tribochemical (friction and wear) behavior remains somewhat undefined. In a number of Microsystems applications such as gear trains, comb drives and transmission linkages, tribological considerations, particularly amongst interfaces, are of paramount importance. The objective of this research is to device a novel coatings strategy that can be integrated into the mainstream LIGA technology to coat the sidewalls of intricate LIGA MEMS elements. As a first step in this direction, we applied a 100 nm thick diamond like nanocomposite (DLN) coating on a wafer containing LIGA MEMS elements by commercial plasma enhanced chemically vapor deposition (PECVD) technique. The MEMS elements were subsequently released from the wafer per standard LIGA process after backspattering to clear the coating on the wafer surface. Coverage of the DLN coating on the sidewalls was confirmed by X-TEM specimens from a DLN coated LIGA gear tooth. Tribological studies were conducted on plain test coatings using a ball-on-disk apparatus in different test environments. As compared with pure electrodeposited Ni, DLN coated Ni showed significant improvements in friction (0.04 versus 0.1-2), debris generation and stick-slip behavior.

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

9:15 AM P6.3/B10.3
CONFORMAL DEPOSITION OF AMORPHOUS HYDROCARBON BASED COATINGS ON METALLIC HIGH-ASPECT-RATIO MICRO-SCALE STRUCTURES (HARKS) 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 (HARKS) 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 HARKS substrates was studied as a function of the HARKS dimension and aspect ratio. Potential applications of surface engineered metallic HARKS will be discussed.

9:30 AM P6.4/B10.4
DEPOSITION OF LOW SURFACE ENERGY, WEAR-RESISTANT FILMS ON MEMS-LIGA DEVICES USING AN ENERGETIC PULSED PLASMA IMMERSION PROCESS. Kensei Shibazato, University of Wisconsin, Madison, WI; Alfredo Moradi, 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 general MEMS-LIGA parts. Film deposition was performed with the non-line-of-sight plasma immersion ion implantation and film deposition process operated in the low energy regime, using a mixture of acetylene and a fluorinated precursor gas. The film-substrate interface region was compositionally graded by adjustments in energy and deposition precursor contents. The film properties were observed, and improvements in conformity of the film to the contours of the devices were achieved by adjusting the plasma process parameters. Conformity 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 the SNL grant No. 16546.

9:45 AM P6.5/B10.5
Many MEMS devices involve rolling, sliding, or bending operations that are not well-suited for the mechanical properties of the base materials. In terms of mechanical and tribological properties, diamond clearly outperforms almost all materials. Additionally, diamond is not suitable for MEMS applications. We have recently demonstrated a novel ultrasonic diamond (UCD)-based MEMS technology based on an UCD coating technology developed at Argonne National Laboratory. This technology produces phase-pure diamond with extremely smooth surfaces (RMS roughness ~30 nm) and has shown excellent mechanical and tribological properties that are well-suited for MEMS applications. However, before these UCD-MEMS components are ready for integration into commercial MEMS devices, it is necessary to develop models for predicting 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 chamber (e.g., N₂, O₂, Ar). Our results have provided a complete understanding of the mechanical and tribological properties of 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 chamber (e.g., N₂, O₂, Ar). Our results have provided a complete understanding of the mechanical and tribological properties in various gas environments and under a wide range of test conditions.

Stiction between surfaces of moving thin film structures places a critical limit on the performance and reliability of mechanical devices. Thin film amorphous-Diamond (a-D) structures may be less susceptible to stiction problems than structures built with other materials, since a-D film surfaces are nearly hydrophilic 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 dehydrogen bake at 200-400°C under an 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 singly-clamped a-D cantilever beams electrostatically brought into contact with a ground plane. Two ground plane microscrews 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 formulation, one can extract the adhesion energy per unit area. We will discuss the effects of various surface treatments and humidity on the adhesion in these systems and compare the results to those obtained from poly-Si based devices. We are also investigating the number of contacts to failure and the effects of electrical current across the contact.

Stiction between surfaces of moving thin film structures places a critical limit on the performance and reliability of mechanical devices. Thin film amorphous-Diamond (a-D) structures may be less susceptible to stiction problems than structures built with other materials, since a-D film surfaces are nearly hydrophilic 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 dehydrogen bake at 200-400°C under an 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 singly-clamped a-D cantilever beams electrostatically brought into contact with a ground plane. Two ground plane microscrews 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 formulation, one can extract the adhesion energy per unit area. We will discuss the effects of various surface treatments and humidity on the adhesion in these systems and compare the results to those obtained from poly-Si based devices. We are also investigating the number of contacts to failure and the effects of electrical current across the contact.

Surface mechanical properties are important for understanding the behavior of tribological contacts, where changes in interfacial properties can result from surface treatments, contaminant films, or sliding processes. At small scales, from atomically thin surface films to clumps of wear particles, interfacial mechanics and dynamics play an important role in friction and wear. To address these problems, we are combining two approaches: 1) in situ macroscale tribological studies allowing visualization and chemisty of the burried interface and 2) “hybrid” nanoscale measurements, combining high spatial resolution and surface sensitive, quantitative mechanical property 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 bodies” found in the sliding interface. In this presentation, I discuss the issues of measuring and interpreting the mechanical response of ultrathin films and nanoscale structures. Combining these nanomechanical techniques with the in situ tribological studies yields a powerful approach to examine worn surfaces and interpret tribological response. For example, one can learn “how” third body films form on the stationary counterface, “what” are their composition and mechanical properties, and “why” they provide low friction and prevent wear. Such studies can provide a better understanding of the transformation and behavior of tribological interactions, 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 INITIO APPROACH TO SURFACE ENGINEERING. Louis G. Hector, Jr., Thomas A. Perry, General Motors R&D Center, Tribology and Surface Eng. Dept., Warren, MI; Donald J. Siegel, Univ. of Illinois, Dept. of Physics, Urbana, IL; James B. Aldrich, 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 plastic formation. Alloying agents, such as magnesium and manganese, along with sub-surface plastic deformation also enhance aluminum adhesion through mechanisms that are not fully understood at the present time. The challenge therefore remains to minimize aluminum adhesion by controlling the chemical and physical properties of the tool surface. For this reason, research on novel tool coating materials has increased rather dramatically over the past decade. Unfortunately, tool coating selection is based less upon the intrinsic or chemical component of adhesion, and more upon empirical methods. 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 energy of adhesion and examined the associated electronic structure of supercells with nominally flat aluminum and tool coating materials (with selected terminations) consisting of TiO2, Cr2O3, Cr, Ti, VC, VN, TaC, and W. The impact of aluminum alloying agents, slab stoichiometry, and magnetism (where appropriate) on the work of adhesion were considered in detail along with the nature and extent of adhesive transfer when the slabs were separated. Finally, we propose relationships between the work of adhesion and the surface energies of the interface slabs that can be used to provide insight into the selection of coating materials that reduce aluminum adhesion.

2:00 PM P7.2 FUNCTIONALLY GRADED CVD MULLITE COATINGS. Szemendra Bacs, Vincent Sun, 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 high temperature oxidation and corrosion. Mullite (3Al2O3·2SiO2) is an excellent candidate material for these applications due to its stable high temperature oxidation resistance atmosphere. A uniform and adherent mullite coating has been deposited at 950°C by chemical vapor deposition (CVD) on SiC substrates and fibers, using the AlCl3-SiCl4-CO2-H2 system. Using an extensive thermodynamic analysis of a guide for CVD coating system, the high Si content at the interface allowed excellent bonding with the Si3N4 substrate, while the high Al content of the outer coating surface in contact with the corrosive atmosphere accounted for the superior high-temperature oxidation resistance of the coatings. However, the typical coating microstructure consists of a thin layer of α-Al2O3 nanocrystallites in a viscous silica-rich phase at the coating-substrate interface. Above this layer, crystalline mullite grains formed with a columnar morphology. The nano-crystalline layer, whose thickness was controlled by adjusting the input AlCl3/SiCl4 ratio, was converted to equiaxed mullite grains after annealing at 1250°C without any loss of coating adherence. These mullite coatings exhibited excellent high temperature oxidation and hot corrosion resistance and were very effective in protecting the SiC substrates from corrosive atmospheres. The coatings also exhibited excellent adhesion during cyclic oxidation tests. A microstructural study 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 REFRUCTORY CERAMICS WITH COMBINED TWO LASER SURFACE PROCESSING. Dimitris Triantafyllidis, Univ. of Manchester Inst of Science and Technology, Dept of Mechanical Engineering, Manchester, UNITED KINGDOM; Johanan R. Bernstein, P. 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 linings in waste and other incinerators. The existence of porosity and material inhomogeneities can promote chemical degradation due to molten slag penetration, while impacting solid or liquid fuel feedstock can cause erosion/wear damage. Previous research has successfully used single laser energy sources to alter the surface properties of similar ceramics, with emphasis on sealing porosity and enhancing degradation resistance. However, this process has resulted in more solidification cracking at the surface due to large temperature gradients developed during processing. In the present, ongoing work, the surface of the refractory ceramic is modified by combining two laser energy sources to control the thermal gradients and cooling rates, with the objective of eliminating cracking formation. The surface morphologies and microstructures of the laser-treated areas are analyzed and the wear properties determined. This paper presents some initial results from the programme.

2:30 PM * P7.4 COATINGS AND SURFACE ENGINEERING FOR METAL CUTTING APPLICATIONS. Aaron Inskeep, 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 a suitable coating designed to work together. This concept will be illustrated by examples of cutting tool materials, trends in super-hard coated tools and recent developments in nanostructured films.

3:00 PM * P7.5 INDUSTRIAL PRACTICE OF CARBON-BASED COATINGS. O. Mueller, R. Herb, J. Kerner, M. Grohelle, Balzers Limited, Balzers, Liechtenstein.

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

4:00 PM P7.6 THERMOMECHANICAL BEHAVIOR OF Cu-DLC NANOCOMPOSITE FILMS. Vanshali 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 forming elements into the DLC structure produces a nanocomposite with 2-3 nm diameter.
n nanoparticles) offering the possibility to stabilize the film structure and enhance DLC properties. The present work focuses on the synthesis, characterization of structure and properties of Cr-containing amorphous films on trilobal 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 ± 2%. Mechanical and tribological properties were studied by nanoindentation 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 Hara, Hajime Sato, Tsuneo Suzuki, Hajime Inoue, Yoshinori Takahashi, Kiyoshi Yoda, Extreme Energy-Density Research Institute, Nagoya University of Technology, Nagoya, Nippon, JAPAN.

Chromium aluminum oxynitride (Cr-Al-N-O) films have been successfully prepared by pulsed laser deposition (PLD). The Cr-Al-N-O film, which is expected to exhibit high hardness and oxidation resistance, is promising as the coating material for high-speed cutting tools. Experiments were carried out by changing the surface area ratio of the target (\( S_T = (S_{AlN} / (S_{CrN} + S_{AlN})) \)) under a pressure of 1x10⁻⁶ Torr. The composition of the film prepared at the fluence of \( F = 0 \) J/cm² and \( S_T = 75 \% \) was determined to be Cr₄₂(Al,N)₂₃O₂₆(N,Al)₂₆ with a Rutherford backscattering spectroscopy (RBS) result indicating 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 oxygen atoms were incorporated from the residual gas in the chamber. The latter may be attributed to the residual oxygen being chemically absorbed on the film surface during deposition. The hardness of the Cr-Al-N-O film was found to be above 40 GPa, whereas Cr-N and Al-N films were incorporated from the residual gas in the chamber. The oxidation resistance of the Cr-Al-N-O film was found to be improved by fact that Cr₂O₃ and Al₂O₃ is formed on the film surface.

SESSION D8 POSTER SESSION
MECHANICAL, TRIBOLOGICAL, AND OTHER PROPERTIES
Chair: Wen-Jin Meng, Ashok Kumar, Yip-Wah Chung, Gary L. Dool, Yong-Tae Cheng and Stan Vetrók
Wednesday Evening, November 28, 2001
8:00 PM
Exhibition Hall D (Hynes)
PHASE ANALYSIS FOR SINGLE CRYSTALLINE SILICON SCHOTTKY CONTACT BY SPHERICAL DIAMOND TIP. Seong-Min Jeong, Han-Seog Oh, Sung-Bun Park, Hyun-Ho Kim, Hong-Lim Lee, Department of Ceramic Engineering, Yonsei University, Seoul, KOREA.

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

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

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

INVESTIGATION OF STRUCTURAL AND MECHANICAL PROPERTIES OF LAYER DEPOSITED MICROLAMINATE HARD COATINGS. Moinuddin Siddiqui and Ashok Kumar, Department of Electrical Engineering, University of South Alabama, Mobile, AL.

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

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

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

THE EFFECT OF PRE-OXIDATION ON THE OXIDATION BEHAVIOUR OF Ti-2Al-2.5Zr ALLOY AT 300°C IN AN ALKALINE STEAM. Xiao-tao Lu, X.-B. Xianglong Feng*, Zhiqiu Wang*, Guangming Zeng*, and Lihai Lin*, Key Laboratory for Radiochemistry Physics and Technology of Ministry of Education of China, Department of Physics, Sichuan University, Chengdu, PR CHINA; Department of Nuclear Engineering and Radiological Sciences, University of Michigan, Ann Arbor, MI.

The oxide scales on a Ti-2Al-2.5Zr alloy with and without pre-oxidation oxidized at 300°C in an alkaline steam for about 13000thh were studied by SEM, XRD, XPS and in-situ AES techniques. Some of the samples were subjected to 400°C denitified water steam at a pressure of 10MPa for 72 hours for pre-oxidation. The results showed that the oxide scales on the Ti-2Al-2.5Zr alloy were composed of TiO2, Ti2O3, Ti3O5, Al2O3, Al4O7 and TiF6. A comparison study has been carried out between the pre-oxidized and without pre-oxidized Ti-2Al-2.5Zr alloy to determine the influence of pre-oxidation upon the properties of oxidation resistance. The oxidation kinetics showed that the weight gain of the pre-oxidized samples was much lower than that of the controlled samples, which was consistent with the results by in-situ AES analysis. The AES results showed that the whole thickness of the pre-oxidized sample (about 35130Å) was thinner than that of the controlled one (about 8000Å), in contrast the pattern for the stable oxide scale was reversed, i.e. the pre-oxidized sample was much thicker. Thus pre-oxidation in an effective method to improve the oxidation resistance of Ti-2Al-2.5Zr.

THERMO-MECHANICAL EFFECTS OF CERAMIC THERMAL BARRIER COATINGS ON DIESEL ENGINE PISTON. Jose Machini, David E. Klett, Ajit D. Kellkar and Jeg Sankar, NSF Center for Advanced Materials and Smart Structures, North Carolina A&T State University, Greensboro, NC.

Coating the piston crown with ceramic thermal barrier coatings (surface engineering) can improve the thermal efficiency and reduce the NOx, CO and hydrocarbon emissions in direct injection diesel engines. Effect of Yttria Stabilized Zirconia (YSZ) thermal barrier coating (TBC) thickness on the piston surface was studied for Ricardo single cylinder diesel engine. The piston thermal boundary conditions were obtained from 1D engine thermodynamic cycle analysis. A 3D Finite Element Analysis using ANSYS was performed to evaluate the temperature distribution and heat transfer on the piston as a function of coating thickness. The paper will present the results of five different YSZ-TBC ranging from 8.5 to 20 mm. The transient thermal analysis was carried out followed by steady state temperature analysis. Simulation was performed at steady state during combustion, the main severe case. Analysis included piston stresses due to thermal and pressure loads, piston/connecting interfacial properties, engine performance and emissions. It was shown that coating thickness decreases heat transfer by 8.20% for 8.5 mm coating and coating thickness increases surface temperature by 21-53%. The paper will also discuss the use of this analytical route in understanding the surface engineered piston.

THRILOGY OF MATERIAL CONTACTS UNDER DYNAMIC LOADING, STUDIED BY ELECTRICAL RESISTANCE MEASUREMENT. Xiangcheng Luo, D.D.L. Chung, Composite Materials Research Laboratory, University at Buffalo, The State
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 composites, cement mortar and graphite, due to their relevance to fastening, concrete structures, electronic devices, and thermal management. Correlation was made between the contact resistivity and the occurrence of plastic deformation, oxidation, strain hardening, passive layer damage and local fracture. The interfacial structure was found to depend on the loading history.

**PS.12**

**MORPHOLOGICAL AND NANOTRIBOLOGICAL PROPERTIES OF DIAMOND LIKE THIN FILMS ERODED BY A NITROGEN PLASMA. R. Psili, S. Castaneda, F.L. Freire Jr., Dept. of Physics, Pontificia Universidad Catolica de Rio de Janeiro, Rio de Janeiro, BRAZIL.**

In this work we present a study of the morphological structure and nanotribological properties of hydrogenated amorphous carbon thin films (a-C:H) eroded by nitrogen plasma. The carbon films were deposited by rf plasma enhanced chemical vapor deposition (PECVD) onto Si substrates, using substrate siltions of -400 V and a methane pressure of 100 mtorr. After to 240 minutes of deposition, the samples 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 50 min. The films morphology and erosion were monitored using a field emission 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 N²⁺ ions plays a role on the final state of the films surface. As the energy of the impinging ions is increased the correlation length increases leading to changes in the films surface final state, from columnar to very smooth surfaces when the ion energy is changed from 100eV to 500eV. It is shown that the nitrogen incorporated on the films, during the erosion process, is located in the top layers of the film, i.e., first 20 Angstroms, and its amount is almost independent on the ion energy as revealed by AES 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 Si₃N₄ microscope tip. In our case, it is observed that after 50 μs 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. Vary Gogotsi, Tom Juliano, Drexel University, Department of Materials Engineering, Philadelphia, PA.**

Mechanical micromachining of silicon surfaces has been explored in this work. A single point diamond turning machine (SPDTM) was used to machine a surface of a 111 poly crystalline 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 photo-detectors and gap sensors working in each axis that push the resolution of the machine to about 2.5 nm. During machining, the pressure-induced metallization of silicon yields a ductile regime of mechanical micromachining on the wafer surface. Scratch tests in this ductile regime with three degrees-of-freedom have been performed at depths from a few nanometers up to about 3 μm with both sharp and spherical diamond tools. Greater depths will start to yield brittle fracture, and we have illustrated that the tool shape determines the precise value of the critical depth of cut. Multi-segment shapes have been successfully machined with overall dimensions of 1 by 20 μm. Depending on the cutting tool and depth of cut, material removal mechanisms were different and the amounts of ductile chips present were shown to change. It was found that a mixture of metastable silicon polymorphs and amorphous silicon covered the surface of the grooves after machining. These phases can, in turn, be transformed into cubic silicon by heating (such as by the authors), and can create any machined shape (like etching) limited only by the resolution of the tool shape itself. Possible applications include creating channels for micro-fluidic devices, or using the electrical properties of each phase to create electronic devices machined on the surface.

**PS.14**

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

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

**PS.15**

**STRESSES AND MECHANICAL EFFECTS OF OXIDE FILMS ON TUNGSTEN AND MOLYBDENUM SINGLE CRYSTALS. J.E. Talis, Dept. of Mechanical Engineering, Western Michigan University, Kalamazoo, MI; R. Gibian, Dept. of Materials Science & Engineering, Univ of Michigan, Ann Arbor, MI.**

Experimental results are reported on the effects of thin oxide films on the mechanical properties of tungsten and molybdenum single crystals oriented for single slip. Film thicknesses were in the range 40-400 nm and were deposited on 2-3 nm 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, metastable oxide systems exhibited surface film softening, i.e., at temperatures below approximately 0.15 of the alloy's melting temperature, the as-cast and molybdenum transformed 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 the be the expected for oxides formed by sputter and ionization deposition, respectively.

**PS.16**

**NANOSTRUCTURED ULTRATHIN FILMS OF SILICATE CLAY AND POLYELECTROLYTES: DEPOSITION PARAMETERS AND MECHANICAL PROPERTIES BY NANOINDENTATION. Rigoberto Avila-Calderon, Xianyou Fan, Department of Chemistry, University of Alabama at 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 such as 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 measurements. The self-assembled 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.
XPS and Rutherford Backscattering Spectroscopy (RBS) showed Cu diffusion upon one hour annealing of Cu/TiSn/Si stacks at 800°C. The diffusion of Cu in Si is obtained by the amount of diffused Cu through the TiSn film and the obtained Arrhenius relation is given by $D_\text{Cu} \sim \exp \left[ \frac{2.1 \pm 0.48 \text{ eV}}{kT} \right] \text{ cm}^2/\text{sec}$. The obtained results showed that CVD-grown TiSn material is a promising candidate that may be employed in a Cu diffusion barrier for sub-100 nm device generations.

Diamond coating was provided to improve the performance of WC-Co tools used in wood machining. Microcrystalline chemical vapor deposition was used to deposit diamond using a gas mixture with CH$_4$ and H$_2$ in the ratio 0.5:1.01 at a temperature of 900°C. The microcrystalline energy was set at 500W and a pressure of 35 Torr was maintained in the chamber. An essential factor that determines the life of polycrystalline diamond coated tools is poor film adhesion. To counter this problem, we have developed a process that includes etching away columns from surface regions, treatment with H$_2$ plasma and use of TiC/TiN intermediate layers. The TiC/TiN layers were deposited by reactive magnetron sputtering. These layers embed diamond crystals and improve adhesion, and in addition act as good diffusion barriers for Co. Various diamond coated tools have been characterized in the as-deposited conditions and after prescribed wear by machining wood stock using SEM and X-ray mapping. It was also found that the limited contact area with diamond on the cutting edge affects the adhesion of the coating. Improvement in contact area by providing a larger radius to the cutting edge is discussed.

Silicones have been widely investigated in the aerospace industry as adhesion promoters between metals and surface coatings. Here, the properties of the silicones themselves as functional surface coatings have been examined. Self-assembled monolayers (SAMs) of five different short chain silicones have been prepared on the oxide surface of aluminum silicon copper cast (ASC060) film deposited on silicon wafers, and on plates of bare and oxide clad 2024 aluminum. SAMs were prepared using both the simple dip coating and via vapor deposition at standard temperature and pressure. The formation of monolayers has been probed using contact angle microscopy, to observe changes in the surface wetting properties of the samples. Atomic force microscopy has been extensively used to characterize the topography of the surface and thus distinguish between monolayers and physically adsorbed species. The long term stability of the samples has been observed using contact angle microscopy and x-ray photoelectron microscopy when stored in an ambient environment. The corrosion resistance of the SAMs was evaluated using anodic impedance spectroscopy, with a 3.5% sodium chloride solution. It was seen that a single monolayer of silicone could provide at least 13 hours of corrosion resistance before the initial pitting event on the aluminum plate. In order to improve the adhesive properties of self-assembled monolayers, in which several layers of silicone molecules are bonded head to tail, have been investigated. Several chemical processes have been utilized to convert the SAM functional group to an alcohol, whereupon further silicone SAMs can be deposited. In this way it has been possible to build homo- and hetero-germous multilayers of silicones.

Metal matrix composites (MMCs) combine the properties of metal and ceramic or intermetallic materials. Common examples of metal
matrix composites are Cu-Al203, SiOx-Al, Al203, Al-B(CN)3, Ni-NiAs. Mechanical or thermal properties, such as strain-stress, thermal expansion 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 microscopic level. These techniques include atomic force microscope (AFM) and indentation techniques, based on Hertzian mechanics. However, up to now, there is no reliable quantitative method of measuring Young's modulus and Poisson's ratio of individual phases as well as properties at the interfaces. This presentation will focus on fundamental aspects of measuring of mechanical properties of metal matrix composites 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 Poisson's ratio of individual phases and their interfaces 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, SiOx-Al, Al203, Al-B(CN)3, Ni-NiAs 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-TNT AND TiC COMPOSITES FOR BIOMEDICAL APPLICATIONS.

Roger J. Narayan, Jerome J. Cuomo, Gary Poelting and Jagdish Narayan, Department of Materials Science of a fragment of the RNC, NC, and Wake Forest University, School of Medicine, Medical Center Blvd., Winston-Salem, NC.

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

PS. 25

PREPARATION AND CHARACTERISATION OF SELF-ASSEMBLED MONOLAYERS FOR THE REDUCTION OF ICE ADHESION ON OXIDE SURFACES.

A.G. Robinson, Q. Guo, Nanoscience Physics Research Laboratory, School of Physics and Astronomy, The University of Birmingham, UNITED KINGDOM; J.A. Pressey, School of Chemistry, The University of Birmingham, UNITED KINGDOM; D. Hammond, S. Harris, G.A. Johnson, Spectroscopy Research Centre, BAE Systems, Filton, Bristol, UNITED KINGDOM.

Prevention of the accretion of ice on surfaces is of great importance in several fields where structures are exposed to low temperatures. In particular icing of aircraft can dramatically affect flight characteristics and safety, whilst ice accretion on transmission line insulators can lead to icing and pylon collapse. This study has examined the effects of highly hydrophobic self-assembled monolayers (SAMs) on the adhesion of ice to oxide surfaces. Films of trichloro[1,1.2.2.3.2.1]heptadecane] were prepared using a simple dipping technique and from various precursors. The monolayers have been produced on the oxide surface of aluminum silicon copper oxide (AlSiCuO) films deposited on silicon wafers, on glass substrates, and on 2024 aluminum plate. Samples prepared under a variety of conditions have been characterized using contact angle microscopy, and atomic force microscopy. The SAMs are seen to substantially increase the contact angle on AlSiCuO, glass samples and 2024 aluminum plate. Films stored in ambient conditions have been examined using angle scattering, x-ray photoelectron spectroscopy, and shown to be stable with time. The effect of the SAMs on the adhesion of ice to the surfaces has been investigated using pristine strain fracture energy testing at -5°C. At this temperature ice on the unmodified aluminum samples survived a cohesive process (failure within the ice) or a mixed mode (cohesive and adhesive) process. The fracture mode of ice on the SAM treated samples was completely adhesive (failure at the ice/sample interface) and the pressure of nitrogen required to remove the ice was reduced by 50% which implies a large reduction of the work of adhesion of the interface process. Experiments were performed to depict that this reduction was repeatable, suggesting that SAM films are not significantly damaged by the removal of the ice.
reported.


PS.27
EFFECT OF Co SEED LAYERS ON THE MAGNETIC ANISOTROPY OF Au/Co METALLIC MULTILAYERS. M. Koyano, H. Yamaoka, K. Taniguchi, National Institute of Technology, 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 multilayers was studied by X-ray diffraction and reflection high-energy electron diffraction (RHEED), and compared to its effect on the magnetic anisotropy. The Au buffer layer grown on Al2O3 (0001) substrates display a large fraction of [111] twins, giving rise to a lack of lateral continuity in the film. The initial deposition of a few A of Co onto Al2O3 (0001) substrates prior to deposition of the Au buffer layer yielded [111] epitaxial films with no twins. The use of the Co seed layer results in a highly improved structural quality of Au/Co(111) multilayers. From the results of low-energy 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
MICROTENSURE OF COPPER-LOADED CARBON AEROGELS PREPARED BY AN ION EXCHANGE METHOD. Noriko Yoshimura, Masami Suzuki, Massachusetts Institute of Technology, Dept of Physics, Cambridge, MA; Joe S. Backer, Ted Baumam, Lawrence Livermore National Laboratory, Livermore, CA; Kazumi Kaneko, Chiba Univ, Dept of Chemistry, Chiba, JAPAN; Moritomo Endo, Dept of Electrical & Electronic Engineering, Nagano, JAPAN.

Copper-loaded organic aerogels were prepared by an ion exchange method of gels polymerized with a solution of 2,4-dialdehyde hydroquinone and formaldehyde. This sample was heat-treated at 1323 K in a nitrogen flow to obtain the carbon aerogel. After heat-treatment, the density of the sample increased from 26.5 to 48.5 g/cm^3. According to TEM observations, the sample before heat-treatment had a highly dense packing texture with a network of carbonaceous particles, 15-20 nm in diameter. Mesopores with almost the same, or often larger, size relative to these particles were found among the particles. It was not clear if any Cu-related compounds were present on the large enough to be seen by TEM. The carbonized sample also has a dense packing texture. Its particular structure shows less crystallinity and is much clearer than that of the non-carbonized sample, but the network of carbon particles seems more collapsed after carbonization. The carbon aerogel particles are 1-5.5 nm 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 range of 5-50 nm. The size, and chemical conditions of the Cu species, as well as their effect on the carbon aerogel texture, will be discussed in terms of their characterization using EELS, XRD, and molecular adsorption methods.

SESSION P9: MACRO-, MICRO-, AND NANO-
TRIBOLOGY II

Chairs: Ashok Kumar and Stan Veprek
Thursday Morning, November 29, 2001
Room 311 (Hynes)

8:30 AM P9.1
SUPERFLEXIBILITY AND WEARLESS SLIDING IN DIAMOND-LIKE CARBON FILMS. Ali Erdemir, 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. Systematic 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 at 10 to 10 m/s. 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 an important role in the tribological properties of these films. Based on these studies, a mechanistic model is proposed to explain the superior friction and wear properties of the new DLC films.

9:00 AM P9.2
PLASMA DEPOSITION OF AморPHOUS CARBON FILMS FROM CH4 AT HIGHLY DILUTED IN Ar. Luiz Gustavo Jacobson, Fernando Lázaro Freire Jr., Departamento de Física, Pontifícia Universidade Católica do Rio de Janeiro, Rio de Janeiro, BRAZIL.

Recently, strong indications pointed that C2 species, instead of CH4 radicals, are the building blocks of n-C:H films when CH4 is highly diluted in argon. In this work, we systematically study the deposition of n-C:H 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 flux of 50 scm and a fixed selfbias voltage of +350 V. The CH4 partial pressure ranged from 1 to 100%. The effect of the residence time of the plasma species was investigated by varying the residence time of the plasma species was investigated using a fixed total pressure of 5 to 50 scm and the total pressure for a fixed CH4 partial pressure of 5%. The deposition rate decreased by a factor of ~1.1 as the CH4 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 CH4 partial pressure increases, the fraction of hydrogen bonded to carbon increases, while the total hydrogen content remains constant. The internal stress was determined by measuring the substrate curvature. The behavior of the composition, density and stress are correlated and explained by means of the ion bombardment during film growth.


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

Continued miniaturization of the device dimensions and the related need to interconnect an increasing number of devices on a chip have led to building multilevel interconnection on planarized levels. In chemical mechanical planarization (CMP) very thin materials (< 5 µm) have to be removed very precisely while maintaining the precise characteristics of remaining materials. Because CMP cannot be controlled at the slurry/interface, slurry, pads and film surface play a critical role in the successful implementation of this process. Surface roughness, elastic and viscoelastic properties, thickness and pore sizes of pad play an important role in this process. The film surface properties along with the mechanical properties also affect the planarization accuracy, removal rate and roughness. We have studied the CMP process of oxide on different polyurethane pads with colloidal silica slurries at different conditions. The friction coefficient and acoustic emission signal was monitored during process. Surfaces of the pads were investigated before and after polishing using scanning electron microscopy (SEM). The oxide film surfaces were characterized using both SEM and atomic force microscopy. The removal rate was calculated by the initial and final thicknesses of the oxide film, measured by Ellipsometer. The validity of Preston equation was also verified.

9:30 AM P9.4
MOLECULAR DYNAMICS SIMULATIONS OF CMP OF n-SiO2. Evgenii Chigrin 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-SiO2. Specifically, the simulations involve n-SiO2 slurries of various n-SiO2 nanoparticles, these films internal stresses and adhesion forces. 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 an important role in the tribological properties of these films. Based on these studies, a mechanistic model is proposed to explain the superior friction and wear properties of the new DLC films.
Recent advancement of the silicon technology requests the ultimate integration technique for the development of new devices. Especially, the global planarization technique of the silicon wafer is strongly demanded for new device development. Recently, the chemical mechanical polishing (CMP) process has gained much attention as a key technology to realize the planarization of the silicon wafer. The CMP is expected to solve all problems related to the roughness of the silicon surface such as the aspect ratio, focus depth, and so on. Although a lot of experimental results related to the CMP processes have been accumulated, the detailed chemical and mechanical mechanism of the CMP process has not been clarified on atomic and electronic level. Recently, computational chemistry has been applied to a lot of silicon technology, however no simulation study on the CMP processes has been performed, to the best of our knowledge, because of the lack of the software which can simulate the CMP processes. First-principles molecular dynamics method cannot simulate the CMP processes since it requests huge calculation time. Hence, in order to solve the above problem, we developed a new accelerated quantum chemical molecular dynamics program, based on our tight-binding theory. It is more than 5000 times faster than the first-principles molecular dynamics program. In this program, the shear process on the silicon wafer can be simulated by sliding the polishing particles, considering the electron transfer and chemical reactions. We successfully applied our accelerated quantum chemical molecular dynamics program to various CMP processes as well as the electronic and atomistic dynamics of the CMP processes were well elucidated.

10:00 AM P9.6

STOICHIOMETRIC TiC AND Ti-Si-C FILMS DEPOSITED BY MAGNETRON SPUTTER/PULSED LASER DEPOSITION. Jose J. Nainaprampl, Systran Federal Inc., Dayton, OH; James E. Kozmowski and A.R. Plam, University of New Hampshire, Durham, NH.

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 stoichiometric 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: a pure Ti target, a Ti-12% Si target, and a Ti-25% Si targets. The hardness of the deposited films ranged from 10 to 28 GPa. The friction and wear properties were evaluated using a ball-on-disk method in an atmosphere of ambient air containing 50% r/h. Friction values in the range of 0.1-0.3 were obtained, and the films exhibited a very long wear life. X-ray diffraction and transmission electron microscopy were used to evaluate film structure. In most cases, the films with super-stoichiometric levels of carbon were found to have either a nano-crystalline or amorphous structure.

10:15 AM P9.7

IONIZING RADIATION EFFECTS ON INTERFACES IN CARBON NANOTUBE-POLYMER COMPOSITES. Julie P. Harman, Patricia Anne O. Quisener, Lori Adorno, LeNora Clayton, John DiAngelo, Department of Chemistry, University of South Florida, Tampa, FL; Arun K. Sikder, Ashok Kumar, Center for Microelectronics Research, University of South Florida, Tampa, FL; Alan M. Cassell, Ecleret 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 1.28 X 106 rad/hour in an air environment. Both irradiated and non-irradiated samples were compared. Glass transition temperatures were characterized by differential scanning calorimetry. Dynamic mechanical analysis and dielectric analysis evidenced changes in relaxations induced by irradiation. Irradiated composites exhibited radiation induced chemical changes in 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 imports insight into the nature of chemical reactions in these materials induced by ionizing radiation.