SYMPOSIUM T
Surface Engineering—Fundamentals and Applications

November 30 - December 2, 2004

Chairs

James E. Krzanowski  
Dept of Mechanical Engr & Matls Science  
University of New Hampshire  
Kingsbury Hall  
Durham, NH 3824  
603-862-2315

Joerg Patscheider  
Lab for Surfaces, Coatings, & Magnetism  
EMPA  
Ueberlandstr. 129  
Duebendorf, CH-8600 Switzerland  
41-1-823-4365

Soumendra N. Basu  
Dept. of Manufacturing Engineering  
Boston University  
15 St. Mary’s St.  
Brookline, MA 2446  
617-353-6728

Yury Gogotsi  
Dept of Matls Science & Engineering  
Drexel Univ & A.J. Drexel Nanotechn Inst  
3141 Chestnut St.  
Philadelphia, PA 19104  
215-895-6446

Symposium Support
Balzers AG
†Renishaw Inc.
†2004 Fall Exhibitor

Proceedings to be published in both
book form and online
(see ONLINE PUBLICATIONS at www.mrs.org)
as volume 843
of the Materials Research Society
Symposium Proceedings Series.

* Invited paper

Hard coatings deposited by plasma-assisted vapor deposition are widely used in tool wear. The presently applied transition metal nitride coatings show limited hardness and high friction against steels, which restricts their applicability with reduced or without coolants. Tool temperatures for machining operations may be extremely high, differing ranges from low temperature to above 1000°C for dry cutting. This work summarizes recent developments on applying nano-structured design concepts to optimize hardness and tribological properties at application temperatures. Concepts for improved hardness at high temperature include compositional modulations formed during film growth with a B-rich tissue phase in TiB2-based coatings, reduction of the amount of grain boundary phase in nano-composite TiN-TiB2 coatings and age hardening, which is demonstrated for the Ti1-xAlxN system. These approaches are suitable to balance or even overcome the hardness loss by the unavoidable stress recovery in hard coatings grown under ion irradiation in the temperature range between 500 and 1000°C. The second part of this work deals with concepts for low-friction coatings for different temperature ranges. lubrication at low-temperature is provided by Cl- alloyed TiN coatings, where low-friction coefficients result from the Cl-induced formation of rutile layers on top of the carbon rich Cr/Co/CH, where graphitization of the a-C:H phase is responsible for low friction coefficients. Approaches for lubricant phases at high temperatures (i.e. above 600°C) are based on the formation of Magneli phase oxides, in particular of VOx, due to oxidation of VN in Ti1-xAlxN superlattices or V in V- alloyed Ti1-xAlxN/VN coatings. Using these concepts, friction coefficients of 0.2-0.4 against steel can be obtained for temperatures of 700°C, where lubrication is achieved by melting of the VOx phase. Another high-temperature low-friction concept is the application of thin top layers based on intermetallic phases on hard coatings. In particular, the Al2O3 phase is stable up to 850°C without oxidation, which shows a pink color and yields friction coefficients of 0.45 at 700°C. These nano-structured designs approaches allow the utilization of functional properties facilitating the development of next generations hard coatings.


Originated from the tooling industry, PVD (Physical Vapor Deposition) coating development focused on increasing the wear resistance. Nowadays, a steady increase in market is evolving by coating machine parts. The requirements that have to be met due to the needs of the new market segment focus on tribological behavior. This makes, that the properties of wear resistance is shifted towards properties like friction coefficient, wetting behavior and the response of coatings towards dynamic loads. For many tribological applications, coatings are exposed to severe alternating loads, which is usually left out in common test methods. The approach of common coating test methods is based on a static behavior of deposited coatings. The impact tester is a testing device with a novel approach to dynamic load behavior of both bulk and coated materials. In this paper, the effect of the coatings microstructure on the impact toughness was investigated. A change in microstructure was provoked by changing deposition parameters like self bias and aluminum content. In a second stage these coatings were tested with respect to their response to high alternating loads. For this purpose both load and number of impacts were varied.

Interface Studies in the System TiN-Si3N4. Joerg Patscheider1, Niklas Hellgren2,3, Rick Haasch4, Ivan Petrov2, Kirsten Bobzin and Michel Maes; PVD, Material Science Institute, Aachen, Germany.


Originated from the tooling industry, PVD (Physical Vapor Deposition) coating development focused on increasing the wear resistance. Nowadays, a steady increase in market is evolving by coating machine parts. The requirements that have to be met due to the needs of the new market segment focus on tribological behavior. This makes, that the properties of wear resistance is shifted towards properties like friction coefficient, wetting behavior and the response of coatings towards dynamic loads. For many tribological applications, coatings are exposed to severe alternating loads, which is usually left out in common test methods. The approach of common coating test methods is based on a static behavior of deposited coatings. The impact tester is a testing device with a novel approach to dynamic load behavior of both bulk and coated materials. In this paper, the effect of the coatings microstructure on the impact toughness was investigated. A change in microstructure was provoked by changing deposition parameters like self bias and aluminum content. In a second stage these coatings were tested with respect to their response to high alternating loads. For this purpose both load and number of impacts were varied.
Ceramic thermal and environmental barrier coatings (T/EBCs) will demonstrate a high specific surface area (1768 m²/g) with pores less than 5 nm. Such highly porous membranes fall in the category of nanofiltration membrane and can be used in filtration of pharmaceutical products, treatment of water, and molecular sieves. Nanoporous coating on B4C can be used in sorption and filtration applications.

Very low friction coatings are very important especially in dry friction applications and boundary lubrication in engine oils. Such a drastic reduction in friction is very crucial in many industrial applications, especially in automotive powertrain systems. For example, it is expected that the fuel consumption is reduced by 5 percent if superlow friction would occur in severe sliding parts in engine. In MEMS, where friction is very important part of energy loss, very low friction is also needed. Ultralow friction refers to friction coefficient below 0.1. Superlow is below 0.01. It is noticed that friction coefficient below 0.001 is hardly measurable in practical cases. Ultralow friction in dry condition can be easily attained by molybdenum disulphide (MoS₂) coatings. However, the environment conditions are very stringent to reach the superlow level. For example, superlow friction of MoS₂ and DLC coatings are only possible in ultrahigh vacuum conditions or in presence of inert gases like nitrogen. In the case of pure MoS₂ (molybdenite) coatings, superlow friction has been achieved experimentally by Hirano in 1991 and verified in 1993 by high resolution TEM observation of wear fragments when sliding pure molybdenite (MoS₂) in an analytical UHV tribometer. Under boundary lubrication, it is supposed much more difficult to reach ultralow friction than in ultrahigh vacuum. This may be due to the detrimental effect of oxygen gas dissolved in the base oil on interface compounds. Actually, superlow friction has not yet been attained under boundary lubrication conditions. Recently, it was observed that friction of hydrogen-free DLC (ta-C) in presence of some ester additive in a poly-alphaolefin base can generate friction coefficient of about 0.02 without measurable wear. In the case of MoS₂, superlow friction is due
to crystal orientations effects and the formation of uncommensurate sliding surfaces. In the case of DLCs, mechanisms of low friction may be broken down by associating them with low chemisorption and the effect of hydrogen is important in vacuum tribochemistry of a-C:H. Boundary lubrication with ta-C in presence of ester (glycerol monooleate for example) is attributed to hydrolysis of graphic surfaces and formation of OH-terminated surfaces. In the case of COF-102 surfaces, this mechanism has been suggested by ToF-SIMS analyses. The next challenge will be to reach superlow friction under boundary lubrication.

2:00 PM T2.2
Ultralow Friction in Boundary Lubrication of Carbon-Based Materials. Maria Isabel De Barros Bouchet, Jean-Michel Martin, Thierry Le-Mogne and Beatrice Vacher, Laboratoire de Tribologie et Dynamique des Systèmes, Ecole Centrale de Lyon, Ecully, France.


2:15 PM T2.3
Pre-sliding tangential deflections can govern the friction of MEMS devices. Alex D. Corwin1, Mark D. Street2, Robert W. Carpick2,3,4 and W. R. Ashurst3,4 and W. R. Ashurst, 1Department of Energy, BES-Materials Sciences, under Contracts DE-AC02-04CH11231 of the US Department of Energy, BES-Materials Sciences, under Contracts DE-AC02-04CH11231. Part of this work was also supported by the US Department of Energy, BES-Materials Sciences, under Contracts DE-AC02-04CH11231. While good solid lubricants such as graphite and Teflon as standard microelectromechanical systems (MEMS) applications. However, when micro-scale structural materials come into contact, their response may be dominated by frictional effects and therefore rubbing surfaces are often avoided in MEMS. Conversely, we can take advantage of this friction to achieve high-performance actuation mechanisms [1]. The active surfaces have developed features large force (several mN), large travel range (+-100 nm) and precise positional control (40 nm steps), and is now called the "nanotactor". We can also employ the nanotractor to obtain the PSTD are greatly reduced. This behavior may qualitatively be captured some of the behavior of pre-sliding tangential deflections, and suggest some possible microscopic interpretations. Acknowledgment: Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. [1] M. P. de Boer, D. L. Luck, W. R. Ashurst, A. D. Corwin, J. A. Walraven and J. M. Redmond, High-performance surface-micromachined inchworm actuator. J. Microelectromech. Syst. 13 (1), 63 (2004).

2:30 PM T2.4
Surface Chemistry and Nanotribology of Nanostructured Carbon Thin Films for MEMS and NEMS Applications. Anirudha V. Sumant1,2, David S. Grierson3, Jennifer E. Gerbi3, James Birrell1, John A. Carlisle4, Orlando H. Auisci1, Thomas A. Friedmann1, John P. Sullivan5, Greg M. Swain6 and Robert W. Carpick2,3,4, Engineering Physics, University of Wisconsin at Madison, Madison, Wisconsin; 2Materials Science Division, Argonne National Laboratory, Argonne, Illinois; 3Sandia National Laboratory, Albuquerque, New Mexico; 4Department of Chemistry, Michigan State University, East Lansing, Michigan.

Fundamental understanding of the chemistry and bonding configuration of materials at or near surfaces, particularly at tribological interfaces, is absolutely essential to build reliable MEMS and NEMS devices that involve rolling and/or sliding contacts. Ultrananocrystalline diamond (UNCD) and tetrahedral amorphous carbon (ta-C) thin films have exceptional physical, chemical and tribological properties at the nanoscale, notably those of single crystal diamond, and are promising materials for high performance MEMS and NEMS devices. However, little is known about the surface chemistry of these materials, and how it changes with different processing conditions. In this work we present a comprehensive study of surface chemistry and nanotribology for undoped, nitrogen-doped, and boron-doped ultrananocrystalline diamond (UNCD), and for as-deposited, furnace-annealed, and laser-annealed ta-C. We present a methodology for studying the tribologically relevant interface, namely, the underside of the films as revealed by etching the substrate. We characterize the surface chemistry, bonding configuration and nanotribological properties of these materials by using a combination of synchrotron-based near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and atomic force microscopy (AFM). We show that there are subtle and correlated changes in the surface chemistry, the ratio of sp2 and sp3 bonded carbon, the local and long-range order, and the nanoscale friction and adhesion as these materials undergo different doping and processing conditions. We will discuss specific methods to improve the nanoscale tribological properties of these materials, in particular, the use of a post-growth hydrogen plasma treatment, which dramatically reduces nanoscale friction and adhesion for anodised UNCD. Part of this work was funded by Sandia National Laboratory and supported by the US Department of Energy, BES-Materials Sciences, under Contracts DE-FG02-02ER46016 and W-13-105-ENG-38.

2:45 PM T2.5
Tribological behavior of MAX phases at temperatures up to 500 °C. Sarojit Gupta1,2, ZhengMing Sun3,4, Michel W. Barsoum1,2, Palanisamy Cheni-Wei Li5,2, Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania; 4Honeywell, Morrisville, New Jersey; 5National Institute of Advanced Industrial Science and Technology (AIST), Nagoya, Japan.

While good solid lubricants such as graphite and Teflon as standard materials for low temperature applications, these materials are of no use in systems with low friction and low wear at temperatures in the 400-600 °C range are lacking. In this paper we show that select members of a new class of solids, namely the M_{n+1}AX_{n} phases (M: early transition metal, A: group A element, X: C and/or N, n=1-3), that can be best described as polycrystalline nanolaminates show great promise in contact with superalloys. In this paper we show that generally the friction coefficients, µ's, of many of these MAX phases-of which there are more than 50 - against superalloys are around 0.5 at room temperature. We also show that the µ's are reduced, in some cases to < 0.3, at higher temperatures. In contrast to the data of friction coefficients, the wear resistances varied greatly from compound to compound. Among the compounds tested in this work. C_{3}AlN, Ti_{3}AlCN, and Ti_{5}AIC_{2} were found to demonstrate the best tribological properties at 500 °C. For example, the µ of C_{3}AlN was measured to be 0.7 at room temperature and 0.5 at T > 300 °C. The wear rate was 2.10^{-7} mg/cm²·s, a value that decreased with further
testing. Further material processing and doping led to even lower \( \mu \)'s and lower wear rates over the 25-500 °C temperature range. SEM and EDAX analysis of the samples and the microstructure revealed that the good tribological behavior can be attributed to the formation of multi-element triboxides.

3:30 PM T2.6

Carbon-based materials and coatings have attracted an overwhelming interest in recent years for a wide range of applications ranging in size from nano/micro-scale devices (such as NEMS/MEMS) to meso-scale machines. This is mainly because of the very unique and unusual properties that various carbon structures can offer for intended applications. For example, disordered or amorphous carbon films combine hardness with high thermal conductivity that can be ideal for sliding bearing applications; while crystalline diamond and nano-structured carbon films offer a range of mechanical, electrical and thermal properties that make them an attractive choice in many different applications. The purpose of this paper is to provide an overview of the very unique friction and wear properties that various carbon structures can provide and to describe fundamental mechanisms that control such properties in various test environments. The origin of superhardness in carbon-based materials and coatings will also be covered and some of the present and future applications for these coatings will be discussed.

4:00 PM T2.7
X-ray Studies of Near-frictionless Carbon Films. Sikhi Mehta1,2, Sujoy Roy3, Jacqueline Anne Johnson1, John Woodford1, Alexander Zinoviev4, Zahir Islam5, Ali Erdemir1 and Shamlal S. Singha6; 1Energy Technology Division, Argonne National Laboratory, Argonne, Illinois; 2Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois; 3Physics, UCSD, San Diego, California; 4Materials Science, Argonne National Laboratory, Argonne, Illinois; 5Ultrasonic polishing and surface scratching with fine diamond powder have been done to enhance the nucleation density and growth rate before the deposition. Patterned growth of NCD films have been achieved by selective nucleation. The surface morphology was investigated using scanning electron microscopy (SEM), the bonding purity and structure information were obtained from Raman Spectroscopy, Near Edge X-ray Absorption Spectroscopy (NEXAS) and X-ray diffraction (XRD). The toughness of the films was measured by atomic force microscopy (AFM). Mechanical and tribological properties important in MEMS applications were investigated using nanoindentation and pin-on-disc methods. Correlations of the quality of the NCD films estimated using different characterization techniques would be discussed with the film deposition parameters. The effect of Nitrogen doping on the mechanical and electrical properties of NCD has also been investigated. Diamond is the ultimate biocompatible material. The electronic properties of NCD can be modified by engineering its surface chemistry which may make NCD an interesting bio-interfacing material. The NCD film can interface between biomimetic lipid layers containing membrane and protein which can be used as a sensor for selective absorption of analyte. This approach results in a highly stable and sensitive NCD based biosensor.

4:15 PM T2.8
Synthesis and Characterization of Nanocrystalline Diamond Film and Its Biomedical Applications. Zheng Xu1,2, Arun K. Sidke1, Arun Kumar2 and Ashok Kumar1,2; 1Nanomaterials and Nanomanufacturing Research Center, University of South Florida, Tampa, Florida; 2Department of Mechanical Engineering, University of South Florida, Tampa, Florida.

Due to its unique chemical, physical, mechanical and electrical properties, nanocrystalline diamond (NCD) is considered for a wide variety of microelectronic, biomedical, and MEMS (micromechanical systems) applications. The fabrication of NCD films by chemical vapor deposition (CVD) method is of great interest because of its coating ability of pure and conformal NCD film. The chemical vapor deposition (CVD) method is the most important of these processes because of its ability to deposit a wide range of materials directly onto a variety of substrates.

4:20 PM T2.9
Atomic Level Studies of Kinetic Friction and Its Velocity Dependence at Aluminum and Alumina Interfaces. Qing Zhang1, Tahir Cagin2, Yue Qi2, Louis G. Hector2 and William A. Goddard3; 1MSC, Caltech, Pasadena, California; 2GM Research & Development Center, General Motors, Warren, Michigan.

The kinetic friction behavior of Al/AI (flat and rough), Al2O3/Al2O3 (commensurate and incommensurate) interfaces have been studied by molecular dynamics simulations. In this study, we have employed a transferable reactive force fields for metal and its oxide. It is found that the commensurate Al2O3/Al2O3 interface has higher friction than incommensurate Al2O3/Al2O3 interface. For both interfaces, at low velocities, kinetic friction exhibits Coulomb friction (independent of velocity), whereas at high-speed range, the velocity dependence follows a viscous relation. For Al/AI flat interface, only viscous friction is observed. Roughness on the surface leads to the increase of friction and velocity dependent frictional parameters.

4:30 PM T2.10
Subcritical CO2 Assisted Polymer Surface Engineering at Low Temperatures. Yong Yang and Ly James Lee; Chemical and Biomolecular Department, The Ohio State University, Columbus, Ohio.

Polymer-based Micro/Nano Electro Mechanical Systems (MEMS/NEMS) have attracted a great deal of interest from industries and academia. The common polymer processing methods involve either organic solvents or temperatures above the glass transition temperature (Tg), which is undesirable, particularly for biomedical applications. On the basis of different properties near polymer surfaces from those in the bulk, subcritical supercritical fluids (particularly carbon dioxide, CO2) into polymer processing at the micro/nanoscales and produce these micro/nano-sized devices at low temperatures. In this study, polymer surface dynamics under CO2 were addressed using atomic force microscopy (AFM) and neutron reflectivity (NR). A novel AFM approach was developed to evaluate the effect of CO2 on the polymer surface. Monodispersed nanoparticles were deposited onto the polymer surfaces (rms < 1 nm) of polymers including polystyrene (PS) and poly(DL-lactide-co-glycolide) (PLGA), and the system was annealed at the pre-specified temperatures and CO2 pressures. The embedding of nanoparticles in the proximity of the surface was measured using AFM, and thus the surface Tg profile could be determined. It was found that there is a rubbery layer of up to a hundred nanometers thick at the surfaces where the Tg is lower than that in the bulk. The thickness of the rubbery layer can be controlled by tuning either temperatures, or CO2 pressures, or both, which makes it possible to engineer polymer surfaces at low temperatures. Meanwhile, NR is utilized to measure CO2 enhanced chain mobility at the polymer surfaces below the polymer Tg. The results indicated that even low concentrated CO2 greatly enhanced polymer chain mobility below the Tg of the CO2 plasticized polymers. With the knowledge of polymer surface dynamics under CO2, we demonstrated polymer surface interaction by using CO2 while retaining the micro/nanostructures. NR studies also revealed that the chain mobility decreased when the interaction between polymer chains and the substrate was strong. By taking advantage of this phenomenon, the effect of the substrate on the nanoparticles, serving as the substrate, were added into polymers to reinforce the nano-sized polymer features, which is usually weak mechanically. The research results were successfully applied to fabricate, assemble, and functionalize well-defined three-dimensional (3D) biodegradable polymeric scaffolds for tissue engineering. These scaffolds have a uniform and well-defined geometry and structure, which provide powerful tools to understand the effects of scaffold architecture on tissue growth and to better understand the
Amorphous carbon has been irradiated by a nitrogen ion beam and changes in surface morphology, composition and tribological properties due to surface nitridation have been studied. The nitrogen ion beam energy was varied from 0.1 to 2.0 keV under the constant ion current density. Surface morphology was observed with atomic force microscopy (AFM). Composition and chemical bonding states near the surface were analyzed by X-ray photoelectron spectroscopy (XPS). Tribological properties were studied by a ball on disk testing. AFM observations reveal that the surface of the amorphous carbon specimens becomes rough after the nitrogen ion beam irradiation and the friction coefficient of amorphous carbon after irradiation by 1.5 keV nitrogen ions approaches to that of graphite.

Surface Nitridation of Amorphous Carbon by Nitrogen Ion Beam Irradiation, Chihiro Iwanska, Masami Aono, Nobusuki Kitsazawa and Yoshishita Watanabe, MSE, National Defense Academy, Yokosuka, Japan.

The ability to selectively etch diamond on a fine scale has become an important requirement in producing new types of micro-technical and electronic devices. This work has examined for the first time the use of implantation-induced damage with CT+, ST+, or SN+ ions as a means of increasing the etch rate of diamond during subsequent reactive ion etching. CT+, ST+, and SN+ ions were implanted in order to form a nitrogen-rich layer of diamond that was then etched in a plasma of chlorine at a power of 500W. Raman spectroscopy has shown that the proportion of non-diamond or sp²-bonded carbon increased with ion dose in the range 5 x 10¹⁵ - 5 x 10¹⁷ ions/cm². Photoluminescence measurements of the ST+ implanted diamond have indicated a rising concentration of sp³-bonded carbon located within the grains with increase in the implant dose. For implantation with ST+ or SN+ ions, a complete amorphization near to the surface was evident at a dose of 5 x 10¹⁷ ions/cm². We have examined the reactive ion etch (RIE) rate of the films as a function of the implant species and dose. The etching experiments were performed in plasmas of CF₄/O₂ and CHF₃/O₂ which have previously produced a smooth surface on diamond at moderate etch rate [1]. For a given ion, the etch rate was directly proportional to the concentration of non-diamond carbon as controlled by implant dose or the equivalent implantation-induced disorder. For a given implant dose, the etch rate was again proportional to the concentration of non-diamond carbon as controlled by ion mass or the level of implantation-induced disorder. [1] P.W. Leech et al., J. Mater. Sci. 36, 3453-3459, (2001).
T3.5 Fabrication of Surface Nitridation Mask on GaAs Substrate for Nano-Lithography, Kazuhiro Tanaka, Yo Yamada, T. Kondo, Tatsuki Maruyama, and Shigei Narita, 1,2 Meijo Univ. 21st Century COE Program, Nagoya, Nagoya, Japan; 2Dept. of Materials Science & Engineering, Meijo University, Nagoya, Japan.

Combination of STM lithography and selective-area growth allows us to design a nano structured optical and electronic devices. In order to realize such a system, we have chosen an ultra-high-vacuumed process containing scanning tunnel microscopy (STM) lithography and molecular beam epitaxy (MBE). To take full advantages of STM lithography, it is important to develop the applicable mask. In this study, we focus on the nitridation of the GaAs (001) surfaces in RF-MBE chamber for making the mask material with minimal surface damage and low process temperature. After chemical etching with solution of NH₄OH: H₂O₂: H₂O = 4:1:20, GaAs (001) substrate was heated up to 580°C in a MBE chamber to remove the native oxide. Then, the substrate was nitrogen ion bombarded, changing the RF power between 200-400W, N₂ flow rate between 1.2-0.6 SCCM and substrate temperature between 300-500°C which was set, and the nitridation time for 15-60 min. Numerous nano particles were observed on the surfaces by using atomic force microscopy. The formation of nano particles on the surface, which is closely related to the degradation of the RMS roughness of surface, is controlled by the temperature change. The higher substrate temperature was, the higher RMS roughness made. For example, when the nitridation was done at 500°C for 60 min, it made rougher surface with RMS roughness of 4.5nm, which was brought by the formation of large particles whose diameter was as large as 200 nm. On the other hand, when the substrate was nitridated at 300°C for 60 min, it was made relatively flat surface with RMS roughness of 0.5nm. Considering that As evaporation and migration of Ga surface atoms was accelerated by high substrate temperature of 500°C and consequently the formation of nano particles, the formation process of those particles was considered to be closely related to As evaporation and Ga migration.

T3.6 Abstract Withdrawn

T3.7 Characterization of Nanocrystalline Surface Layer Induced by Shot Peening and their Fatigue Strength, Hideo Mano,1,2 Satoru Kondo1, Akihito Matsumura1 and Toru Iruma1.1 Togo Seisakuyko Corporation, Aichi-gun, Aichi, Japan; 2Nagoya University, Nagoya-shi, Aichi, Japan.

It could be produced nanocrystalline layer in the surface of carbon steel under shot peening processing. This nanocrystalline surface layer is higher hardness than matrix phase. Therefore, this nanocrystalline layer is expected as the new surface hardening processing method. But, there is little information about the fatigue strength of this nanocrystalline surface layer. In this study, coil springs whose surface had been shot peened were produced. And the surface of a spring was examined using a micro Vickers hardness meter, FE-SEM, and TEM, and a residual stress distribution and surface roughness were measured. Moreover, the fatigue examination was done by using the coil springs. The coil springs were made from oil tempered steel wire, its chemical compositions contain (mass%) 0.6C, 1.4Si, 0.7Mn and 0.7Cr. It was compressive coil spring. Two kinds of springs with which shot peening conditions are different were produced. The spring (spring A) of Category A is a spring with a surface nanocrystalline layer, and Category B (spring B) is a spring without the nanocrystalline layer. The shot conditions of a spring A were made into two-step peening. The projection material of the 1st step shot is a 0.22mm steel cut wire, and projection speed is about 100 m/s. The nanocrystalline layer is made by this peening process. And second step peening used cut steel wire of 0.6mm, projection speed is about 75m/s. Result of observation spring A, The dislocation cell structure having 100% of average crystal particle diameter was observed by the layer directly under the surface. This layer was called nanocrystalline surface layer. Thickness of this layer was 2.5μm. micro Vickers hardness of 2.5μm was about 1000HV. A and spring B have same shape, residual stress distribution and surface roughness. Only one difference is that a spring A has nanocrystalline layer in the surface. Fatigue test carried out spring fatigue test machine at a frequency of 1600 cycles/min until 187 cycles. This test method was close to the actual working condition of valve springs. Results of the fatigue test, Fatigue limit of springs A was am±e=600±535MPa at 107 cycles. And, springs B was am±e=600±400MPa. Otherwise, this nanocrystalline surface layer improved fatigue strength 3%.


Interface coatings on fibers are important in ceramic matrix composites. In addition to providing toughness, the interface coating must also protect the reinforcing ceramic fibers from corrosive degradation. Interfacial coatings of silicon carbide fibers. The double interface coating comprised of combinations of nitride and oxide coatings. Among the nitrides, boron nitride and titanium nitride were utilized. These nitrides were deposited by CVD. The metal oxides were also used in oxide and nitride coating, which were applied on top of the nitride coatings by MOCVD. The composition and phase of the treated fibers were determined by XRD. The surface coating microstructures were observed by SEM. Auger spectroscopy was used to study the coating composition.

T3.12 Mechanical and Contact Damage Behaviors with Thermal Fatigue in Thermal Barrier Coatings. Hong-Jun Kang, Seung-Woon Kim, Seong-Hwan Park, Seong-Seo Lee, Yeon-Gil Jung, Jung-Chel Chang and Ungyu Paik; 1 Ceramic Science and Engineering, Changwon National University, Changwon, Kyungnam, South Korea; 2 Powder Generation Lab, Korea Electric Power Research Institute, Daegu, South Korea; 3 Ceramic Engineering, Hanyang University, Seoul, South Korea.

The effects of thermal fatigue conditions on mechanical and contact damage behaviors were studied in thermal barrier coatings (TBCs) used to increase the thermal efficiency of gas turbines and diesel engines are investigated. Three kinds of TBCs with different thickness in bonding layer are prepared by two different methods of APS and HVOF, respectively, and of which static and cyclic thermal fatigue are conducted at temperatures of 980° and 1100°C with holding times of 10 and 100 hr and number of cycles of 10 ~ 100 in each temperature. The thickness of thermal growth oxidation (TGO) layer is observed according to fabrication method, bonding layer thickness, fatigue conditions. Mechanical properties of hardness and elastic modulus in each condition are measured by nano-indentation. The contact damage behaviors depending on fatigue condition, bonding layer thickness, and thermal fatigue method are confirmed on the TBCs surface by Hertzian contact tests. The TGO thickness is mainly dependent on temperature tested. The mechanical properties of the TBCs are increased due to the re-sintering of coating layer during thermal fatigue tests, which causes crack or delamination. The contact damage behaviors are affected by thermal fatigue conditions and fabrication method, independent of bonding layer thickness. Effects of bonding layer thickness, the TGO thickness, and fabrication method on mechanical properties, contact damage behavior, TGO layer formation in the TBCs are discussed extensively.

T3.13 Fracture Investigation of Alumina (Al2O3) Thin Films Developed using Pulsed Laser Deposition (PLD) for Bioapplication. Xinya Wang, 1,2 Sudheer Nerrlis 1, Cindy Water1,2, Sergey Yarmolenko2, Dhamanjay Kumar1,2 and Jag Sankar1,2; 1 Mechanical Engineering, North Carolina A&T State University, Greensboro, North Carolina; 2 Center for Advanced Materials and Smart Structures, North Carolina A&T State University, Greensboro, North Carolina.

One of the important property requirements for alumina (Al2O3) to be used as the dental restoration is its fracture property. Al2O3 thin film grown on Si (100) and Al203 substrates using KrF excimer laser to produce a new crown structure in this investigation. Three substrate temperatures of 400°C, 600°C and 800°C are used for PLD process. The mechanical properties such as hardness, elastic modulus, especially fracture toughness which vary with increasing temperature are investigated. Al2O3 thin films are investigated using nanoindentor and Vickers indenter. The film thickness was known to decrease with an increase in substrate temperature and the hardness and the elastic modulus of the films were known to increase with an increase in substrate temperature based on the previous investigation. The crack morphology and fracture toughness of the films are investigated. The relationship between the substrate temperature and the film fracture property is discussed.


Inspired by the water-repellent behavior of the micro- and nano-structured plant surfaces, superhydrophobic materials, with a water contact angle larger than 150 degree, have received a lot of research attentions recently. It has been suggested that contamination, oxidation and current conduction can be inhibited on superhydrophobic surfaces, and the flow resistance in the microfluidic channels can also be reduced using super water-repellent materials. In order to prepare superhydrophobic materials, we have developed two simple approaches for fabricating tunable superhydrophobic surfaces using nanosphere lithography and plasma etching. In the first case, the polystyrene nanospheres were employed to create well-ordered rough surfaces covered by gold and alkylthiols. Using oxygen plasma treatment, the topmost surface area can be modified systematically, as the result the water contact angle on such surfaces can be tuned from 132 to 170 degree. The water contact angles measured on these surfaces can be modeled by the Cassie’s formulation without any adjustable parameter. In the second approach, thin films of Teflon were spin-coated on the substrate surfaces and treated by oxygen plasma. Superhydrophobic surfaces with water contact angle up to 170 degree were obtained by this approach. If the TFO glasses were used as the substrates, the hydrophobicity of the surface can be tuned by applying DC voltage. Water contact angle can be adjusted from 150 degree to 40 degree.

T3.15 Photochemical Adhesion of Fused Silica Glass Lens by Silicone Oil. Takayuki Funatsu, Masanori Kobayashi and Masatada Murahara; Department of Electrical Engineering, Tokai University, Hiratsuka, Japan.

The optical system that is pervious to ultraviolet light of 200nm and under in the wavelength has been developed by putting one silica glass another with the silicone oil photo-oxidized in oxygen atmosphere. In general, balsam, unsaturated polyester resins and UV hardening agent are used as adhesives for lenses and optical materials. These adhesives are transparent when exposed to visible light, but cannot transmit light of 300nm and under. In high polymers, these adhesives absorb UV rays of 250nm and below. Today, like the excimer laser as a typical example, the applications of the optical materials for UV rays are getting wider. An optical contact method is the only way to satisfy these conditions. It, however, requires a high precision roughness to use the intermolecular force that is called air contact. Moreover, the optical contact method is so weak in slight vibration that its field of use is limited. Thus, the new, strong adhesion method has been developed for the optical materials to transmit U-V rays. Quartz has siloxane bonds, while silicone oil (dimethyl siloxane) is composed of siloxane bonds of the main chain and methyl groups of the side chain. Therefore, the organic silicone oil has been photo-oxidized by irradiation with UV light to change into inorganic glass. That is, the silicone oil was poured into the thin gap between two pieces of silica glass in oxygen atmosphere and was irradiated with the Xe2 excimer lamp while heating at temperature above 150 degrees centigrade. Consequently, the silicone of the silicone oil was linked with the O atoms that had been absorbed on the glass surface to form SiO2. The UV and IR spectrum analysis was conducted on the silicone oil before and after laser irradiation. The result revealed that the transmittance of the 190nm wavelength conversely became high. The UV transmittance of the silicone oil was 20~25% before the lamp irradiation; which improved to 90.6% after the irradiation for 60 minutes. Furthermore,
the tensile strength of the bonded sample was measured. It confirmed that the adhesive strength of the silicone oil was enhanced from 0 kgf/cm² before-irradiation to 60 kgf/cm² after-irradiation.

T3.16

The photochemical reaction process in substituting the functional groups on the surface of fluorocarbon [FEF] by irradiating the Xe₂ excimer lamp on the water and FEP placed on the attenuated total reflectance [ATR] prism has been measured at actual time: the water dissociation was at the surface of the FEP, the chemical reaction being occurred on the sample surface and its interface sequentially by irradiating UV rays on the reaction solution and the sample that are placed in the ATR prism. This makes it possible to determine the dissociation of a reaction solution, its reaction products and substitution of functional groups on the sample surface. In the new method, the sample and the reaction solution are photo-chemically brought into reaction in the air, which enables to measure the reaction process of modifying into hydrophilic at real time. Water or formic acid was used as a reaction solution in order to modify the FEP surface into hydrophilic. Firstly, the solution was dropped on the FTIR-ATR prism made of germanium and covered with the FEP. Then, the Xe₂ excimer lamp was vertically irradiated to the FEP and the solution as well. With the irradiation, the solution was photo-dissociated to produce H atom and OH radical. The -H bond of the FEP surface was photo-chemically decomposed at the same time into C and F atoms; The F atom was pulled out by the H atom and the dangling bond of C was linked with the OH radical. Namely, the hydrophilic group was substituted on the surface of the FEP sample. The surface reaction brought by the UV irradiation has been evaluated to clarify the mechanism of its photochemical surface modification. The ATR-FTIR analysis was carried out to investigate the process of the photochemical reaction. In case of formic acid, the absorption peaks of the -C=O in the region of 1720 cm⁻¹ and the -COOH in the region of 1710 cm⁻¹ decreased respectively by photo-dissociation, but that of the OH in the region of 3600 cm⁻¹ increased. The results indicated that the C-O and -COOH have turned to the -OH. Furthermore, the contact angle with the water was measured. When comparing to the non-treatment sample of which contact angle was 110 degrees, the contact angle of the sample modified with the Xe₂ lamp irradiation for 15 minutes became 36 degrees, and that of the sample modified with formic acid and the lamp irradiation for 25 minutes further improved to 17 degrees. As a result, the hydrophilic groups were produced more in formic acid than in water.

T3.17
Comparison of -OH and -NH₂ Functional Group Substitution on PTFE Surface with V-UV Photon Irradiation for Protein Adsorption by Masatoshi Hiratstuka, Yujiro Koheyashii, Yutaka Sato and Masatake Murahara, Electrical Engineering, Tokai Univ., Hiratsuka, Kanagawa, Japan.

Poly-tetrafluoroethylene [PTFE] presents few rejections in a living body but has low tissue affinity. Then, the soft tissue implant material that has not only high biocompatibility but also superb bondability has been developed by photo-chemically substituting the hydrophilic of -OH or -NH₂ groups on the PTFE surface with V-UV photon irradiation. In general, the protein is at first adsorbed on the plastic surface when the plastic is implanted in a living body, where the fibroblast and tissue cell adhere to form the fibrous tissue. It is, therefore, essential to improve the biocompatibility. Especially, the biocompatibility depends on the molecular structure of the material surface regardless of the bulk characteristics, so the PTFE has low tissue affinity due to its water repellency. Thus, we have photo-chemically modified the PTFE surface to be hydrophilic by the V-UV photon irradiation. In our previous study, we have found that B, Al and H atoms are effective for the defluorination of PTFE. It was also clarified that no reaction occurs in the presence of H atom as a defluorination agent. In this study, using water or ammonia gas as the reaction agents, the OH or NH₂ radicals were photo-chemically substituted on the PTFE surface to modify into hydrophilic: the Xe₂ excimer lamp was irradiated on the PTFE surface in the presence of the OH groups or in ammonia gas ambiance to replace with the NH₂ groups. Infrared spectroscopy analysis (FT-IR) was carried out to confirm the substitution of the functional groups on the PTFE surface before and after treatment. The hydrophilic functional group substitution using the water as a reaction agent, the OH absorption strength was observed in the region of 3300 cm⁻¹; in case of NH₂ group substitution using the ammonia gas as reaction gas, the NH₂ absorption strength was appeared in the region of 3200-3300 cm⁻¹. Then, the contact angle with water was measured. To compare the non-treatment sample of which contact angle was 110 degrees, the contact angle of the sample became 36 degrees when treated with water and 10-minute Xe₂ lamp irradiation and 90 degrees when treated with ammonia gas and 20-minute Xe₂ irradiation. The protein adsorption of the sample before and after treatment was also evaluated by scanning electron microscope [SEM] and XPS analysis, by using bovine serum albumin [BSA] and fibrin [FB] solution as a protein index in biocompatibility test. From the results, it has been clarified that the protein adsorption increased with the increase in the hydrophilic groups substitution density. The OH-substituted sample adsorbed the fibrin more than the NH₂-substituted sample; the amount of the albumin and fibrin sticking increased 2.3 times larger than that of the non-treatment sample.

T3.18
Photochemical Deposition of Transparent Low Refractive Index SiO₂ Topcoat for Laser Head at Room Temperature by Yuki Sato. Yuki Sato and Masatake Murahara, Electrical Engineering, Tokai Univ., Hiratsuka, Kanagawa, Japan.

A transparent, low refractive index SiO₂ film was photo-chemically laminated on a glass slab laser head by the Xe₂ excimer lamp in the atmosphere of NF3 and O₂ mixed gas at room temperature; which made it possible to inhibit the decrease in the laser output power caused by the evanescent wave leakage. The evanescent waves arise on the interface between cooling water and glass head when the lights reflect perfectly from the front surface, of which leads to the decrease in the laser output power. To inhibit the decrease, we have tried to laminate the thin protective coat of 2-micron meter refractive index, the contact surface with the cooling water and glass head. For a protective coat formation, there are a vacuum deposition method as a dry process and a spin coating method as a wet process. The former requires the temperature of 500 degrees centigrade and above; therefore, the cost becomes non低廉 but the thermal denaturation of the substrate cannot be avoided. The latter cannot attain a good adhesion to the substrate due to its low density of the topcoat. For this reason, a new method to form a hard protective coat at room temperature was developed. We, therefore, demonstrated a photochemical method to laminate the SiO₂ film on the glass substrate using the Xe₂ excimer lamp at room temperature. A glass substrate and Si wafer were placed in the reaction chamber, which was filled with NF3 and O₂ gases. Irradiating the Xe₂ excimer lamp, the mixed gas was photo-dissociated to produce F₂ and NO. The F₂ etched the Si wafer to generate SiF₄, which was adsorbed on the sample surface. The adsorbed SiF₄ and the NO were oxidized to grow a SiO₂ film on the other side of the substrate. As a result, the transparent SiO₂ film of 260nm thickness was laminated on the non-heated substrate by the lamp irradiation for one hour. The hardness of the film before annealing was 3 by Mohs' Scale of Hardness, and its hardness improved to 5 after annealing at 500 degrees for one hour. The refractive index of the film was 1.42, being lower than the index of silica glass that is 1.46. Furthermore, the transmittance in the visible region increased by 2% with its antirefection coating. In conclusion, the SiO₂ film that is antireflective, that is insensitive to water and heat, protects from cooling water and is not heat-denatured has been laminated on the optical material. This new technology contributes to improvement in the output power of glass slab laser.

T3.19
Copper Pattern Formation on Fluorocarbon Film by Single Shot of ArF Laser by Takashi Itoh, Tatsuya Nishimura and Masatake Murahara, Electrical Engineering, Tokai Univ., Hiratsuka, Japan.

The copper nuclei have been photo-chemically patterned on the fluorocarbon film surface in copper sulfate atmosphere via the reticle with a single shot of the ArF laser. It was demonstrated that it required more than 3,000 shots of the ArF laser to substitute the Cu atoms on the fluorocarbon surface. Fluorocarbon has excellent properties such as heat resistance, chemical resistance, water or oil repellency, high electrical insulation and low dielectric constant of 2.1. Polytetrafluoroethylene (PTFE), for this reason, is regarded as promising as a printed wiring board material in a high-frequency band. However, the fluorocarbon is chemically stable; which makes it difficult to bond to copper substrate. Generally, a copper film is formed on the fluorocarbon surface by electroless plating with palladium (Pd) or platinum (Pt) as a catalyst core. Or the copper foil is bonded to the fluorocarbon surface with epoxy adhesives. In these methods, however, the surface is high-rent because of pretreatment and laser irradiation. In the case of GMP laser irradiation, and the ArF laser. Firstly, the sample surface was irradiated by the

Silicone oil was photo-chemically oxidized to change into SiO2 on the crystal by using an ArF excimer laser; the protective moisture proof film has been developed for a nonlinear optical crystal that is deliquescent. The nonlinear optical crystals such as CuLiB$_2$O$_6$ (CLBO) and KH$_2$PO$_4$ (KDP) are deliquescent, which causes their surfaces to be cloudy by absorbing moisture in the air. In general, the crystal is placed in a cell, which is heated to control the temperature and pressure of the atmosphere. We, therefore, investigated the growth of the SiO2 film directly on the crystal so as to be moisture proof. The vacuum vapor deposition and sputtering methods are generally used for making the optical thin films. They require heat, and the difference between the crystal and the film in thermal expansion rate cause cracking. Thus, remarking the silicone oil that has siloxane bonds in composition like quartz, we developed the new film formation method to inhibit cracking by irradiating the ArF laser on the silicone oil to be photo-oxidized in the air. Firstly, dimethylsiloxane silicone oil (-O-Si(CH$_3$)$_2$-O-)$_n$ was poured on the substrate and coated by a spinner for making the silicone oil thin layer. Then, the ArF excimer laser was vertically irradiated on the sample in oxygen atmosphere. The oxygen molecule was excited in the laser to generate a high active O atom; at the same time, the Si-CH$_3$ bond of the silicone oil was photo-dissociated and the dangling bond of Si was linked with the active O atom to form a SiO2 film on the crystal surface. The UV and IR spectrum analysis was carried out on the silicone oil with and without the laser irradiation. The results revealed that as the laser shot increased, the -CH$_3$ absorption strength decreased but the UV transmittance of the film increased. The highest UV transmittance of the treated silicone oil, 94.2%, was achieved at the laser fluence of 80 mJ/cm$^2$ and the shot number of 20,000 in the fourth harmonic generation region of 260nm. To compare with that of the non-treatment sample, the UV transmittance of the treated silicone oil increased by 95%. The film thickness was 1.9µm. In short, the film formed by the new technology can be used as a protective coating for a nonlinear optical crystal that has the moisture resistance and the UV permeability.


Pulsed laser deposition technique is known to be desirable for low temperature epitaxial growth of oxide films. We have recently found the selective homoepitaxial growth of sapphire (α-Al2O3) thin films at low temperatures (200K) assisted by appropriate electron beam irradiation during the pulsed laser deposition in UVH (called laser Molecular Beam Epitaxy : MBE). The novel growth manner in laser MBE with KrF excimer laser (248nm, 20ns) is such that only in the electron-beam irradiated region, Al2O3 films grow epitaxially and amorphous Al2O3 films are grown in the non-irradiated region. Thus, we could attain the electron-beam induced in-plane patterning of sapphire substrate at low temperatures. For in-plane patterning of functional ceramic thin films, NiO buffer layer for AIN epitaxial growth at room temperature was deposited on the in-plane patterned sapphire substrate. Then, AIN was deposited on the selective epitaxially grown NiO buffer layer. As a result, the AIN thin film could be grown epitaxially on the NiO buffer layer at room temperature while amorphous AIN film was grown on the polycrystalline NiO buffer layer. On the other hand, by wet-etching the in-plane patterned sapphire substrate, an amorphous part can be removed selectively, resulting in the in-plane patterns on sapphire microcrystals. The present in-plane microwalls of sapphire might be useful for micro-flow chemical chips. The present electron-beam induced low-temperature process is expected to have the possible application to the fabrication of photonic crystal, optical waveguides and MEMS.

**T3.22** Effect of High-Speed Deformation on Phase Stability at Unusually Jointed Surface: High-Flow Epitaxy Growth. Emily D. Shatuck, Teichi Ando, Peter Y. Wong and Charnaboo C. Dounandiss; 1 Mechanical, Industrial and Manufacturing Engineering, Northeastern University, Boston, Massachusetts; 2 Mechanical Engineering, Tufts University, Medford, Massachusetts; 3 Mechanical and Manufacturing Engineering, University of Cyprus, Nicosia, Cyprus.

High-speed deformation of crystalline solids by ultrasonic metal welding leads to the formation of high concentration of excess vacancies. The energy associated with these defects greatly alters the phase stability in materials at the deformed interface and surfaces. This phenomenon can be exploited in new fabrication technologies to produce coatings and bulk meta-stable intermetallics at lower temperatures than used in traditional processes. Experimental results showed unexpected evidence of (1) enhanced solid-state diffusion (µm diffusion zone) and local melting in ultrasonically welded Al-Zn foils at 513 K (a corresponding melting depression of 150 K) and (2) transformation of bcc-δ phase into γ phase in Cu-Zn (dendritic cartridge brass) alloy that was ultrasonically deformed on the surface at room temperature. These results were analyzed using a new thermodynamic model and a new interdiffusion model. The thermodynamic model predicts stable alloy phases obtained through high-speed deformation while accounting for the free energy of excess vacancies and solid-liquid states. In the interdiffusion model which uses EDS profiles, it is assumed that the diffusivities and excess vacancies are directly proportional to each other. Both models predict an excess vacancy fraction of 0.67 at the joined surfaces of Al-Zn foils. The experimental observation and the theoretical calculation revealed that the high vacancy concentrations are responsible for the phase transformation in Cu-Zn alloy at room temperature. These findings indicate that high-speed deformation at low temperatures (<0.5 Tm) can assist phase transformation from stable phases to meta-stable phases which typically are attained either at high temperatures or rapid quenching from liquid state. This method opens a new approach to manufacture engineered coatings such as high temperature intermetallics (NiAl or TiAl) or metallic glass (ZrCu or ZrNi) at low temperatures. Additionally, the low-processing temperature and no-vacuum requirement makes this method suitable for coating temperature sensitive microelectronic and MEMS components.
The effect of the glass-forming coating on the fatigue behavior of the 316L stainless steel was investigated. The Zr-3Cu-13Al-Ni (atomic percent) coating was deposited onto the uncoated steel by the magnetron sputtering, followed by subsequent annealing. The application of the glass-forming coating gave rise to significant increases in both the fatigue life and the fatigue limit, in comparison with the uncoated steel. Depending on the maximum stress applied to the steel, the fatigue life can be increased by 20 times, and the fatigue limit can be elevated by 30%. High compressive residual stresses were introduced when depositing the glass-forming coating onto the steel. The residual stresses could not only improve the fatigue behavior but also have a significant influence on the cracking behavior. The residual stresses were determined by the curvature measurement. The measured stresses were compared with the predictions using the analytical model of the progressive-coating deformation. The results showed that the coating remained well adhered to the steel even after the severe plastic deformation of the coating-substrate system. The surface-roughness measurements also indicated the improvement of the surface conditions due to the glass-forming coating. The improved fatigue behavior may be related to the fracture behavior. The fractographic results indicated that the fatigue-fracture process of the coated steel system was dominated by crack nucleation at the surface of the glass-forming coating. The excellent adherence of the coating to the steel, the improved surface condition, together with the high compressive residual stresses, were the main reasons for the improvement of the fatigue behavior of the coated steel system.

Acknowledgement: The present work is supported by (1) the Department of Materials Science and Engineering, The University of Tennessee, (2) the National Science Foundation (NSF) Integrative Graduate Education and Research Training (IGERT) Program (DGE-0203415), (3) the NSF Combined Research and Curriculum Development (CRCD) Program (DGE-0082901), and (4) the National Science Council of the Republic of China in Taiwan (NSC92-2216-E-015-004).


Natural gas reforming has been regarded as an alternative to hydrogen generation technologies that are not well developed or not economically viable. Efficient and clean conversion of natural gas to hydrogen would be a significant advancement towards a hydrogen-based economy. Recent progress in the field of catalysis has made natural gas reforming even more attractive by use of advanced catalysts. Nanostructured materials have the potential of reducing the requirement of high temperature operation of natural gas reformers. When combined with a plasma-assisted process, the synergy between the catalyst structure and the delivery of energy in the form of ionization and reaction can make the process even more promising and, less stringent. However, this type of process is still in the development stages, and a better understanding of the fundamental interactions between the catalyst surface and the plasma is still needed. The IMPACT facility at Argonne National Laboratory was used to study plasma-surface interactions for a variety of applications, ranging from plasma/wall interactions in nuclear fusion reactors to evaluation of next-generation lithography optical components performance under plasma exposure conditions. The capability to diagnose surfaces with in-situ metrology techniques such as ISS, AES, XPS are total erosion measurements during treatment of the sample allows the study of interactions relevant to plasma-assisted catalysis. A study was performed on the interaction between a methane beam plasma and a nanostructured catalyst for methane full oxidation. The relevant surface processes leading to the oxidation are studied, especially the role of ions and free radicals in the plasma. The effect of variables such as plasma temperature and environment conditions was also explored. Degradation of the catalyst due to the plasma bombardment was assessed by fully characterizing the nanostructure before and after operation.

T3.26 Structural, Mechanical and Tribological Properties of TiN and CrN Films Deposited by Reactive Pulsed Laser Deposition Technique, Phumij Ratanu-Aya and Samanrat Panyathanabut and James Krzanowski; 1Department of Physics, University of L'Aquila and INFN-CASTI Regional Laboratory, Aquila, Abruzzo, Italy; 2Department of Mechanical Engineering, University of New Hampshire, Durham, New Hampshire.

Nitride thin films have gained much interest due to their potential applications in different areas of silicon device technology, namely as diffusion barrier in encapsulation schemes, for identifying and cleaning contacts, and gate electrodes in field-effect transistors. In the present investigation, TiN and CrN films have been deposited by reactive pulsed laser deposition technique using Ti and Cr targets at 10 mTorr background pressure of N2. Si (111) and AISI 4030C steel substrates were used for the present study. Films were deposited at different temperatures in the range of 200°C to 600°C. X-ray Diffraction (XRD) reveals that the films were highly oriented with (100) planes deposited at substrate temperature of 500°C. However, films deposited at 400°C and 600°C have shown randomly oriented diffraction planes. Films deposited at all temperatures have shown preferential growth of TiN (111), whereas CrN is polycrystalline at 200°C and (111) preferential growth at higher substrate temperature. The deposited films exhibited densely packed grain, with smooth and uniform structures. In both cases, the residual stresses were determined by the curvature measurement. The measured stresses were compared with the predictions using the analytical model of the progressive-coating deformation. The results showed that the coating remained well adhered to the steel even after the severe plastic deformation of the coating-substrate system. The surface-roughness measurements indicated the improvement of the surface conditions due to the glass-forming coating. The improved fatigue behavior may be related to the fracture behavior. The fractographic results indicated that the fatigue-fracture process of the coated steel system was dominated by crack nucleation. The excellent adherence of the coating to the steel, the improved surface condition, together with the high compressive residual stresses, were the main reasons for the improvement of the fatigue behavior of the coated steel system.

Acknowledgement: The present work is supported by (1) the Department of Materials Science and Engineering, The University of Tennessee, (2) the National Science Foundation (NSF) Integrative Graduate Education and Research Training (IGERT) Program (DGE-0203415), (3) the NSF Combined Research and Curriculum Development (CRCD) Program (DGE-0082901), and (4) the National Science Council of the Republic of China in Taiwan (NSC92-2216-E-015-004).

T3.27 The Use of Closely Spaced Vickers Indentation to Predict Erosion of Polycrystalline TiAl. Adolfo Junior Franco and Steve George Roberts; Matematica e Fisica, Universidade Catolica de Goias, Goiania, Goiania, Brazil.

A wear map was created based on closely spaced quasi-static indentation loads arrays (square grids of 9 indents) produced by pyramidal diamond indenters (Vickers indentation) on each specimen (at room temperature) performed on polycrystalline AlTi203, mean grain size G=1, 3.8 and 14.1 µm. This was to simulate the observed erosion mechanism for crack linking from multiple impacts. For a given load a critical indentation spacing to produce damage was determined for each specimen. SEM micrographs of the worn area (G=14µm) due to 9 indentation were analysed. The wear maps based on closely spaced arrays of quasi-static indentation may thus be a guide for predicting the wear resistance of brittle materials and for producing an improved model.

T3.28 Formation of High-Resistivity Silver-Silicon Dioxide Composite Thin Films Using Sputter Deposition, Ann Marie Shover, Nicholas S. Dallas and James M.E. Harper; Physics, University of New Hampshire, Durham, New Hampshire.

Composite Ag-SiO2 thin films were deposited to examine the stability of high resistivity at high temperatures and the role of SiO2 volume fraction over a wide range of composition, consistent with a tunneling conductivity mechanism. In order to obtain a broad composition range, these films were deposited on a stainless steel substrate placed above the SiO2 sputtering sources. This configuration allowed coverings ranging from 5 to 60% SiO2 to be deposited on the same sample. Resistance measurements were made using a four-point probe and a profilometer was used to measure thickness. A model was developed to predict the thickness and composition as a function of position. The model calculations were verified with composition measurements using Rutherford Backscattering Spectroscopy in addition to calibrations of deposition rates from the separate sources. These results demonstrate that high-resistivity thin films can be reliably grown using Ag-SiO2 composites.

T3.29 TRANSFERRED TO T4.4

T3.30 TRANSFERRED TO T6.8/R10.8


Although glass materials surface-controlled at a nanoscale have the potential to provide different functionalities of nano-electronics, some attempts have been made to investigate nanoscale behavior of glass at high temperatures. Softening behavior and viscous flow resulting from the supercooling state, which is characteristic of glass materials, are expected to be utilized for construction of novel nano-structures.
as well as for soldering the nano-elements. Here we report nanoscale surface control techniques based on softening and viscous flow behavior of oxide glasses at high temperatures. The oxide glasses ultra-thin films were deposited at room temperature by pulsed laser deposition method onto the ultrasmooth sapphire substrates with 0.2 nm-high atomic steps. These sapphire substrates were obtained by annealing in air at 1350°C (Appl. Phys. Lett. Vol. 67, (1995) 2966). The glass thin films (about 3 mm thick) annealed over glass transition temperature exhibited the nano-stepped (ultrasmooth) surface structure reflecting the sapphire substrate surface. By scanning an atomic force microscope (AFM) tip on the as-deposited glass film in a contact mode and then thermal annealing the film, we could pattern the nano-stepped glass surface in a nanoscale. Moreover, we applied the thermal softening behavior of this ultra-thin film glasses for development of flattening processes of thin film surfaces. The surfaces of transparent conducting oxide (TCO) films coated with the ultra-thin film glasses were ultrasmooth even after thermal crystallization of amorphous phase. The over-coated glass films were thought to suppress the thermal softening caused by the crystallization of the amorphous TCO films. This technique is expected to fabricate the ultrasmooth surfaces of crystallized films. On the other hand, bulk glass surfaces were also subjected to high temperature nanoprint lithography using our original oxide nanopatterned molds with nanochannel arrays. Mechanical strength and chemical property of nano-patterned glass surfaces were characterized by nano-indentation or contact angle measurement.

T3.32

A nullite coating process has been conducted to form an electrical insulating layer on the surface of the silicon carbide whiskers for whiskers formation by a deposition and hydrolysis. The phase, structure, morphology and electrical insulating property of the coated silicon carbide whiskers has been investigated by using x-ray diffraction, scanning electron microscopy and electrical measurement. The study indicates that a multi-layer coating layer can form after heat treating the precursor coating at high temperature. The formed nullite coating significantly increases the electrical resistance of the coated silicon carbide whiskers. Details of the study will be addressed in the presentation. Acknowledgements This work is supported by NAVY under the contract No.: N00178-04-C-3658

T3.33
Adhesion Improvement of CVD Diamond Coatings on WC-Co Substrates for Machining Applications. Michael J. Lukitch1, Leonid Lev1, Zhengong Xu1,2 and Ashok Kumar1,2,3.

1GM Research & Development Center, Warren, Michigan; 2Department of Mechanical Engineering, University of South Florida, Tampa, Florida; 3Nanomaterials & Nanomanufacturing Research Center, University of South Florida, Tampa, Florida.

In order to improve the performance of WC-Co cutting tools, high quality polycrystalline diamond coatings have been coated using microwave plasma enhanced chemical vapor deposition (MPECVD) method. The adhesion of the diamond films deposited on the Co-containing substrates by the CVD process was very poor. Various interlayers between the WC substrate and diamond coating have been applied. Investigation showed that interlayers functioned effectively as a diffusion barrier inhibiting the Co migration from the insert interior to the surface. The substrates with interlayers were treated to improve the nucleation and adhesion. Polycrystalline diamond films have been continuously synthesized from hydrogen and methane gas mixture in a temperature of 750-850°C for 6 hours. Rockwell indention tests have been performed to evaluate the adhesion of diamond on the substrate. The results indicate that inserts with treated interlayers have stronger adhesion compared to the samples without interlayers. Scanning electron microscopy (SEM) has been used to study the surface morphology. Residual stress was measured using Nanoindent and X-ray diffraction methods.

T3.34
New Process Development for Low Temperature Deposition using Metal-Organic Plasma CVD. Seok-Jae Son1,2, Jens Mahrolz2, K.-T. Ric3 and Kyung-Woo Yi3, 1School of Materials Science and Engineering, Seoul National University, Seoul, South Korea, 2ITOPW, TU Braunschweig, Braunschweig, Germany.

TiCN layer as a lower layer and DLC or Sr-DLC layer as a top were deposited on an 106Cr6 and WC by using dimethylaminoformonat(or diethylaminoformonat), hydrogen and nitrogen with the bipolar DC-pulse Metal-Organic Plasma CVD process. The layer thus obtained had high hardness and a low friction coefficient. But up to recently the Plasma CVD and Plasma MOCVD processes in low temperature have been carried out mostly with equipments having a diameter less than 400 mm and a height less than 1000 mm. In order to fulfill the increased requirement of industry, the larger equipment, for example 1500 mm in diameter and 2100mm in height, has to be applied. But there are few related reports about scale-up of Plasma CVD process. To make use of large equipment, uniform coating of the specimens has to be guaranteed and nearly homogeneous streaming must be considered. The component coating is required to satisfy the uniform quality of specimens. And to satisfy this, appropriate gas CVD and Plasma MOCVD processes is used, to calculate the optimum flow patterns and streamlines for uniform coating of specimens and determine those in advance. And the comparison between the result of numerical simulation and the experiment on a laboratory scale is followed by simulation. For the optimum chamber design, further optimization of the streaming profile will be achieved by adaptation of proper gas inlets and gas outlet system and determination of the expected number of nozzle. The effects of process parameters such as temperature, pressure, gas ratios and plasma effect on the properties of the deposited layer are investigated and detailed results on the streamlines and gas distribution near the tappets are presented for the statistical analysis. The uniformity of the streamline is depends on the gas outlet system.

T3.35
Corrosion Resistance of Boronized Steel, Roumiana S. Petrova and Naruemon Sawattanont; Physics, NJIT, Newark, New Jersey.

Boronizing is a thermo-chemical treatment by forming boride phases (FeB and Fe2B) on the surface as the coating. It is known as the surface modification to improve the mechanical, erosion and corrosion properties of metals and alloys. The experimental boronized steels were compared with powder boronizing method at 860°C for 4 hrs in the inert atmosphere. The thickness of the boride coating on the experimental steel surface varies by the types of steels. The corrosion resistance of the boronized coating was determined in 5%, 10% and 15% of Hydrochloric acid (HCl), Sulfuric acid (H2SO4) and Nitric acid (HNO3). Optical microscopy, X-ray diffraction, SEM was used to investigate the microstructure, phase composition, and oxides formed on the steel surface. The comparison experiments showed the excellent corrosion resistance of boronized steels over unboronized steels. This characteristic feature can prevent or delay the catastrophic of metals and alloys in the severe environments.

T3.36
High-Speed Processing with Reactive Cluster Ion Beams. Tosho Seki and Jiro Matsumoto; Quantum Science and Engineering Center, Kyoto University, Kyoto, Japan.

Cluster ion beam process has high potential for material processing in nano-technology, such as photonic crystal and MEMS. In order to fabricate the devices, it is needed to etch targets with high-speed, low-damage, and ultra-smooth processes. A cluster ion beam is a cluster of the few to several thousands atoms. When many atoms constituting a cluster ion bombarded a local area, high-density energy deposition and multiple-collision processes are realized. Because of the interactions, cluster ion beam processes can produce high rate sputtering with low damage in comparison with monomer ion beam processes. Moreover, cluster ion beam etching can smooth both bottom surface and sidewall. Especially, it is expected that the extreme high rate sputtering can be realized using reactive cluster ion beams. Reactive cluster ion beams, such as SF6, CF4, CH3F, and CH2F2, were generated and their cluster size distributions were measured using Time-of-Flight (TOF) method. Si substrates were irradiated with the reactive cluster ions at the acceleration energy of 3-6 keV. Each sputtering yield was increased with acceleration energy and was about 1000 times higher than that of Ar monomer ions. The sputtering yield of SF6 cluster ions was about 1000 atoms/cluster at 6 keV. With this beam, 12 inch diameter wafers can be milled in a minute at 1 mA of beam current. The TOF measurement showed that the size of SF6 cluster ions was about 500 molecules and the number of fluorine atoms in a SF6 cluster ions was about 8000. If the sputtered product was SiF4, the yield has to be less than 0.1% of the SF6. These results indicate that the reactive cluster ions etch targets not only chemically, but also physically. This high-speed processing with reactive cluster ion beam can be applied to fabricate nanomaterials. This work is supported by Ministry of Economy, Trade and Industry (METI) and New Energy and Industrial Technology Development Organization (NEDO).

T3.37
A Study of Surface Segregation Energies of Copper by Means of X-ray Photoelectron Spectroscopy, Nail Chamsudinov, Amarante Bottger and Wim Smets; Department of Materials Science and Technology, TU Delft, Delft, the Netherlands.
Experimental values for segregation energies or surface energies are difficult to obtain. Surface (segregation) energies of metals can be correlated to hardness measured by the presence of a surface in an X-ray photoelectron spectroscopy (XPS) experiment. For industrially important 3-d transition metals this proved to be difficult because of the large core-hole lifetime broadening of their photoelectron peaks. In this study it was shown that eventually a marked increase in the apparent hardness enhancement was measured when nanocomposite films were developed and discussed.

As the dimensions of materials are reduced to the nanometer scale, the stabilization of pseudomorphic crystal structures that differ from their bulk equilibrium phases can occur. The pseudomorphic growth is well documented in multilayered thin film and related nanostructured materials, which provide a substantially larger bulk modulus and greater hardness than the average of the constituent materials. In this paper we show that similar mechanisms can operate in nanocomposites when the mean grain size is below 10 nm. For this purpose, a series of TiAl N films with x values up to 0.7 were deposited onto WC-Co substrates using arc PVD, and were investigated to describe mechanical properties in terms of microstructure. Chemical composition by RBS together with HRTEM, XRD, and SAD analysis showed that for the Al content below x = 0.4 a solid solution single-phase film is formed, while for x values beyond 0.5 mixed structures made of fcc-TiN and wurtzite AIN, or nanocomposites of fcc-TiN and TiAlN are found, depending on deposition conditions. Hardness of solid solution films was found to increase almost linearly with the Al content, while two opposite behaviours were distinguished for higher values of Al. Hardness rapidly decreased according to the rule of mixture as soon as solid solution phase began to separate into TiN and AIN growing in their natural structures with misfit dislocation at the interface to relieve the strain. In contrast, further hardness enhancement was measured when nanocomposite films that showed coherent interfaces were formed due to pseudomorphic stabilization of fcc-AIN on fcc-TiN crystallites. In this paper different hardening mechanisms operating in solid solution and nanocomposite films will be developed and discussed.

T3.38 Pseudomorphic stabilization on crystal structure and mechanical properties of nanocomposite Ti-Al-N thin films. Ayat Karimi, Themistoklis Vasco and Antonio Escudero Santana. Basic science, EPFL, Lausanne, Switzerland.


Because of its high mobility and compatibility with plastic substrates, pentacene has been the subject of much study in the area of organic and organic electronics. The growth of pentacene on chemically modified surfaces has received much attention in an effort to improve the performance of organic thin-film transistors, but there remains little understanding of how the chemistry of the functionalizing layer affects pentacene nucleation and growth. We have used low energy electron microscopy, low energy electron diffraction, and photoelectron spectroscopy to study the growth of pentacene on several chemically modified surfaces. Cyclooctadecene, which on Si(001) forms an ordered array of exposed CoC double bonds, and cycloocta-1,5-diene, which leaves only saturated C=C bonds exposed, have both been studied as interfacial layers for pentacene growth. Functionalization with these molecules enables pentacene nucleation to begin almost immediately (as opposed to a ‘dead layer’ that occurs when growing on clean Si(001)) and leads to very large pentacene grains (as large as 0.2 mm in diameter) with their crystal axes oriented with respect to the underlying lattice. We will present details of our experimental results and discuss their implications for the formation of highly ordered interfaces between organic and inorganic crystals, as well as for the design of high performance organic and molecular devices.

T3.40 Tribological Aspects of Aluminum Nitride-Titanium Nitride Thin Composite Films. Cindy Waters1, Xinyu Wang1, Sergey Yarmolenko1, Dhananjay Kumar2 and Jaq Sanjiv1. 1Mechanical Engineering, NCA&T State University, Greensboro, North Carolina; 2North Carolina A&T State University, Greensboro, North Carolina.

Physical properties, and the friction and wear are important issues in small-scale applications, it is therefore essential that the materials used are good micromechanical and tribological materials. Adhesion, friction, toughness and wear properties of AlN-TiN thin composite films is being investigated in this study. The multilayered structures are generated using Pulsed Laser Deposition (PLD). The plausibility and functionality of the adhesion between the coating and the underlying substrate in addition to its resistance to cracking. The magnitude of the critical load during a scratch test is related to the adhesion of the substrate to the coating. In a test a spherical indenter with a tip radius of 5 μm is used for measurements and is drawn across the surface of a coating under an increasing load. The magnitude of the critical load will be studied for various films from a monolayer TiN film to different AlN-TiN films and compared to their relative frictional behavior and their wear properties. Despite the adhesion, the critical load depends on several other parameters including the friction coefficient. Friction and wear properties were measured using an accelerated ball-on-flat tribometer. The critical characteristic load is shown to depend on the number of layers and the relative AlN-TiN thickness. The fracture toughness showed a weak dependence on the layer characteristics.
Both tensile and compressive intrinsic stresses are known to occur during the growth of polycrystalline films and coatings. A number of mechanisms have been proposed to describe the mechanisms that produce these stresses. However, experimental evidence from various systems demonstrates that these models do not accurately describe key effects. For example, investigations with AlN grown by MBE demonstrate the increasing the growth rate leads to significant intrinsic tensile stress. Existing models also fail to accurately predict the grain size effects that we have observed. To explain these effects, we propose a kinetic model that describes the competition between three key phenomena: growth, stress relaxation due to grain boundary formation, and compressive stress creation due to adatom insertion at grain boundaries. Finite element modeling was also used to consider surface roughness effects. These models provide a reasonably accurate description of intrinsic stress data in AlN and in several other high performance coatings that we have investigated. Stress gradients that are produced during film growth are also an important consideration in many systems, and our kinetic model suggests several strategies for controlling these gradients. For example, varying the deposition conditions can be used to either minimize gradients, or to produce alternating regions where compressive and tensile stresses offset each other. In addition to controlling the residual stress in a coating, these approaches can also be used to produce free-standing films where unwanted curvature can cause significant problems.

8:45 AM T4.3
Stress Evolution in Chemically Vapor Deposited Nanocrystalline Diamond Films. Hao Li, Abhishek Kothari and Brian W. Sheldon; Engineering Division, Brown University, Providence, Rhode Island.

Nanocrystalline diamond films were grown on silicon substrates by microwave plasma enhanced chemical vapor deposition (MPCVD) with hydrogen and argon as the diluents. Intrinsic and intergranular stresses were investigated using wafer curvature. The intrinsic stress is tensile and increases with longer deposition time and with higher hydrogen concentrations. A detailed analysis of the stress evolution and the stress gradients indicates that diffusion into the film affects stress evolution. High resolution transmission electron microscope images (HRTEM) and selected area electron diffraction patterns (SAED) confirm that the films consist of nano-size diamond grains with very thin grain boundaries. The intrinsic tensile stresses might be affected by changes in chemical bonding, particularly at grain boundaries. The effect of hydrogen plasma annealing was also investigated. These results show that the pure hydrogen plasma can significantly increase the tensile stress. These plasma anneals produce virtually no stress change in larger grained diamond films. Thus, it appears that the relatively high density of grain boundaries makes it possible to engineer residual stresses in nanocrystalline diamond films. Based on the combined data from as-grown and plasma annealed films, it appears that SP²/r-bonding at grain boundaries can be modified to produce significant variations in the residual stress in these films. The hydrogen plasma treatments were performed using a series of hydrogen gradients. This approach was used to fabricate free-standing nanocrystalline diamond films that do not exhibit bending due to stress gradients. Thus, this technique has the potential to improve the viability of nanocrystalline diamond films in MEMS.

9:00 AM T4.4
Measurement of Intrinsic Strength, and Intrinsic and Total Fracture Energies of Metal/Ceramic Interfaces, Steel/E-glass Joints, and Solder Joints in Electronic Packages. Vijay Gupta, Mechanical and Aerospace Engineering, UCLA, Los Angeles, California.

The intrinsic strength (σ₁), intrinsic fracture energy (Go), and the total or the overall fracture energy (Ge) are parameters typically used to characterize the interfacial fracture process. The intrinsic strength and the intrinsic fracture energy are related via the interface structure and chemistry and hence either one of them can be regarded as the fundamental parameter characterizing interface fracture on the atomic scale. The overall fracture energy is the sum of Go and the plastic dissipative work (Gp). Gp depends on the loading and geometry of the structure, the total fracture energy is not a fundamental property of the interface. A relationship between these parameters is of importance to design and predict interface failure from a fundamental standpoint. Experimental procedures to measure the above parameters will be discussed. The interface strength is measured by using a novel laser spallation experiments, which uses a laser-induced stress wave to separate the interface, while the intrinsic and total fracture energies are measured using a double pendulum impact experiment performed at ambient and cryogenic temperatures, respectively. In the first part of the talk, relationships between Gc and Go, and between σ₁ and Go, for interfaces between sputtered-deposited polyimide and stainless steel and a polyimide adhesive are discussed. The relationship among these parameters for the same system have never
been accomplished before. The intrinsic toughness and strength were modified by changing the orientation of the sapphire surface and its damage tolerance was varied between three silicon carbide (ambient and cryogenic) and the thickness (1-3 mm) of the ductile Ta layer. In the second part of the talk, the above relationship is obtained for the steel/E-glass composite joints that are chemically bonded using silane layers. The degrading effect of moisture on the fracture energy of the joint is also measured. A silane chemistry is freestanding and board-mounted chip-scale packages. The technique is functional group, which was developed at Vanderbilt University, to investigate the SM and SE effects at the micro- and nano-meter length scales. Recently, we have investigated these effects in NiTi and other materials. These studies provide new insights into the mechanisms of SM and SE effects at multiple length scales and illustrate the possibilities of using shape memory alloys and thin films for novel tribological and MEMS applications. We provide some examples, including methods for making self-healing tribological surfaces and durable interfaces, as well as a strategy for reducing friction and enhancing wear resistance by engineering the ratio of hardness to elastic modulus using shape memory alloys and multilayered constitutive materials. We are evaluating tetrahedral amorphous-carbon (ta-C) as a material for use in MEMS and sensor applications due to its advantageous mechanical properties when compared to polysilicon. We have used two as the structural layer in the fabrication of many devices (e.g., electrostatic comb-drive actuators, nanomechanical resonators, and microelectronic test specimens). To control average stress and strain gradients we have used two approaches—post-deposition annealing and laser annealing. Thicker layers are deposited by a sequence of deposition and annealing steps to prevent film delamination due to buildup of stress-induced interfacial shear forces. In general, we find that in both approaches the average stress values in our films can be easily reduced to near zero stress (±10 MPa). Harder to control are the strain gradients that result in out-of-plane curvature of released structures, although we have made structures with radii of curvature >1 μm. One reason for this difficulty is that strain-gradients are difficult to deduce in monolithic thin films requiring that actual devices be fabricated to make accurate measurements. In addition, the nature of the film deposition process and the layering approach to thick films suggests that the strain gradients are not uniform throughout the thickness of the film. One possible way to accurately assess strain gradients is to measure the stress during etch-back of the deposited film. We have implemented an in situ optical stress measurement technique on a commercial etch tool to characterize strain-gradients in ta-C thin films. Within this system, we can simultaneously measure the etch rate and wafer curvature and thus deduce the strain gradient as a function of film thickness. We find very high gradients in laser annealed films, and more modest gradients in laser present correlations between the deposition and annealing parameters on the measured strain gradients and strategies for reducing their presence to prevent out-of-plane bending in released structures. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.
analysis gives a strong hint that the reconstructed wafer surface is (111)-oriented, in contrast to the (100)-orientation of the underlying wafer substrate. The absence of whisker growth on the new surface is evident. The stressed region in the surface engineered silicon wafer can be controlled by the process parameters. The presented methods might be important for various applications in semiconductor technology. For example, the H-plasma exposure could be done in industrial technology. For example, the H-plasma exposure could be done in industrial technology.

11:30 AM T4.10

Substrate materials for flexible devices are multi-layer composite structures. On top of a base polymer functional layers such as permeation barriers, hard coats and conductive layers are applied. In flexible microelectronic devices and flexible displays, high performance functional layers are required. Flexible displays require a transparent well-conducting electrode material, such as Indium Tin Oxide (ITO). In OLED displays, transparent (inorganic) hermetic barrier coatings are necessary. Thin functional inorganic layers (30-500 nm) are applied on top of a polymer substrate. Due to the thermal mismatch between polymer and layer the functional inorganic layer is compressive loaded at ambient conditions. Bending of the (flexible) substrate during manufacturing or application results in additional compressive load. A characteristic failure mode, occurring on compressive loaded thin layers, is buckling failure. The interface between adjacent layers fails locally, and the thin top layer bends outward. The buckles have a characteristic width and height. These sizes might be used in the analysis of the plastic deformation of the substrate, profile microscopy and profile measurements. Using the measured curvature of the sample between an estimate of the stresses and strains can be derived using Stoney’s formula. With high stage microscopy the failed sample is heated and the bending is suppressed at a specific temperature. From profile measurements on the buckle two length parameters are compared along the buckle and the base length. The three techniques give different estimates of the compressive strain. To resolve these inconsistencies, a finite element model is used to analyze the characteristic shape of a simple buckling profile as a function of compressive strain and the adhesion quality. From the calculations 3D-graphs are composed, where the buckle height and the adhesion energy are represented as a function of buckle length and compressive strain. These graphs are used to determine the compressive strain and the adhesion quality from the experimentally determined buckle width and buckle height. The analysis shows that the thermal mismatch between a polymer substrate and the substrate is more important than the plastic deformation in the substrate seriously affects the dimension of the buckle. Due to the deformation of coating and substrate, the height of the buckle is significantly larger than expected from the compressive strain in the original layer. When this deformation is taken into account appropriately, the height and width of a buckle can be used to determine the compressive strain in the layer and the adhesion energy of the failed interface.

11:45 AM T4.10
Raman Scattering of the Local Bonding Structure in Nano and Micro Machined β-Si3N4 and 4H-SiC, Jennifer Bunning,1 Mengling Liang,1 John A. Patten,2 Leah Bergman,1 Xiuang-Bai Chen,1 Jae-il Jung,1 George M. Pharr3 and Robert J. Nemchak1,1North Carolina State University, Raleigh, North Carolina; 2Western Michigan University, Kalamazoo, Michigan; 3University of Idaho, Moscow, Idaho.

During the machining process, very high pressures can be achieved at the contact interface between the machining tool and the surface of the material. If the induced pressures exceed the hardness of the material, transformation can occur through a series of phases. Upon releasing the pressure, the material can again be transformed to a new phase. The Raman technique is employed as a nondestructive structure sensitive probe to investigate the vibrational properties of machined β-Si3N4 and 4H-SiC and provides evidence of bonding structures. In these materials, the short absorption depth of UV light allows for accurate analysis of the surfaces and the transparency to visible light allows for analysis of the bulk material. The studies reveal that the surface of machined β-Si3N4 and the chips that result from the machining are transformed to an amorphous phase for a range of cuts extending from nm to μm depths. Wavelength dependence analysis provides information on the depth of the amorphous zone. The study on 4H-SiC included measurements of machined basal plane surfaces and edges of (0001) planes and a new havemachined wafer edges, the structure is found to change when machined on the (0110), (1120), etc. face (i.e. when the machining contact interface is parallel (0001) surface). To aid in understanding these structural changes, as they relate to plastic deformation, studies have been conducted on indentation made on the (0001) surface. Biaxial stress measurements indicate that the plasticity can cause shear stresses, which can drive phase transformations at lower pressures than would occur if subjected to hydrostatic stresses.

1:30 PM T5.1

Ion bombardment during deposition may simultaneously affect thin films’ topology, composition and crystallinity. In the case of nanoscopic etching one might produce periodic ripples that depend on the angle of ion incidence and surface temperature. When applied during deposition, ion bombardment can produce in-plane crystallite orientation in some materials for specific angles of incidence. In addition, ion bombardment changes the composition of the component thin films according to the local angles of ion incidence and ion/atom ratios. Therefore, these mechanisms may be linked under certain deposition conditions to generate novel topographically patterned materials with locally controlled composition and texture. Examples will be given that include metal alloys, oxides and nitrides, and recommendations for specific nanoscale structures will be given.

2:00 PM T5.2
The erosion of material surfaces produced by electrical discharges plays an important role in the degradation of many electrical devices, such as electrical contacts, switches or spark plugs. A discharge energy heats the material and can even cause melting or vaporization. The microscopic erosion mechanisms at metallic surfaces which lead to local material removal and to the local microstructure modifications are qualitatively and quantitatively analysed. For this purpose single discharge experiments at high pressure were done. Characterization techniques include white light interferometry for topography measurement, focus ion beam for crater cross sections preparation and scanning and transmission electron microscopy for imaging. Connecting the detailed experimental investigations with finite element method simulations, it could be proven that the mass loss by crater formation depends substantially on the melting enthalpy of the materials but additionally on the viscosity and the surface tension of the micrometer large melting pool. Due to the high temperatures generated by the plasma and also in certain high temperature applications, formation of oxide scales is an important process that may influence the discharge characteristics and erosion mechanisms. These effects are discussed on results in pre-oxidized samples and on those modified on electrodes which are externally heated. It was shown, that in certain systems, i.e. intermetallic compounds, the surface can be additionally stabilized by controlling the protecting oxide coatings.

D. Petersen2 and Donald W. Petersen1; 1Sandia National Laboratories, Albuquerque, New Mexico; 2University of California, San Diego, California; 3University of Alabama, Birmingham, Alabama.

This paper deals with the surface engineering of Ti-6Al-4V and Co-Cr-Mo in order to improve both their tribological performance, and, in the case of Ti-6Al-4V, to enhance its biocompatibility for potential in-body applications such as hip and knee implants. The method consists of applying a 1 μm thick sputtered coating, and then exposing the protected material to multiple ion shots from an intense focused ion beam. The 200ns ion pulse produces fast melt and cool cycles (109K/sec), leading to melting and mixing of the coating and some amount of the substrate, depending upon the beam fluence. In the case of Ti-6Al-4V, the coating process varied from high to medium and medium to low, and in the case of Co-Cr-Mo, we are investigating several candidate layers, both metallic and non-metallic. The fluences range from low enough to only partially melt the coating, to high enough to cause surface ablation. The microscopic erosion mechanisms at metallic surfaces which lead to local material removal and to the local microstructure modifications are qualitatively and quantitatively analysed. For this purpose single discharge experiments at high pressure were done. Characterization techniques include white light interferometry for topography measurement, focus ion beam for crater cross sections preparation and scanning and transmission electron microscopy for imaging. Connecting the detailed experimental investigations with finite element method simulations, it could be proven that the mass loss by crater formation depends substantially on the melting enthalpy of the materials but additionally on the viscosity and the surface tension of the micrometer large melting pool. Due to the high temperatures generated by the plasma and also in certain high temperature applications, formation of oxide scales is an important process that may influence the discharge characteristics and erosion mechanisms. These effects are discussed on results in pre-oxidized samples and on those modified on electrodes which are externally heated. It was shown, that in certain systems, i.e. intermetallic compounds, the surface can be additionally stabilized by controlling the protecting oxide coatings.

3:00 PM T5.4

The erosion of material surfaces produced by electrical discharges plays an important role in the degradation of many electrical devices, such as electrical contacts, switches or spark plugs. A discharge produces an extreme and concentrated flow of energy onto the surface of the material. The energy is supplied by resistance heating on the electron emitting area and by the impinging of plasma ions. This energy heats the material and can even cause melting or vaporization. Furthermore, the plasma pressure may cause an even greater removal of material by the emission of droplets of molten material. In this way craters are formed in the surface of the material. In this contribution the microscopic erosion mechanisms at metallic surfaces which lead to the local material removal and to the local microstructure modifications are qualitatively and quantitatively analysed. For this purpose single discharge experiments at high pressure were done. Characterization techniques include white light interferometry for topography measurement, focus ion beam for crater cross sections preparation and scanning and transmission electron microscopy for imaging. Connecting the detailed experimental investigations with finite element method simulations, it could be proven that the mass loss by crater formation depends substantially on the melting enthalpy of the materials but additionally on the viscosity and the surface tension of the micrometer large melting pool. Due to the high temperatures generated by the plasma and also in certain high temperature applications, formation of oxide scales is an important process that may influence the discharge characteristics and erosion mechanisms. These effects are discussed on results in pre-oxidized samples and on those modified on electrodes which are externally heated. It was shown, that in certain systems, i.e. intermetallic compounds, the surface can be additionally stabilized by controlling the protecting oxide coatings.

4:30 PM T5.5
Low Damage Smoothing of Magnetic Materials using Oblique Irradiation of Gas Cluster Ion Beam: Shigeru Kakuta,1 Shinji Sasaki,2 Kenji Sasa,2 Toshiro Seki,1 and Jiro Matsuo1,1 Storage Technology Research Center, Hitachi, Ltd., Yokohama, Japan; 2Collaborative Research Center of Nano-scale Machining with Advanced Quantum Beam Technology, Kyoto, Japan; 3Quantum Science and Engineering Center, Kyoto University, Kyoto, Japan.

As increasing areal density of hard disk drives (HDDs), the flying height of magnetic recording head have been been decreasing. To achieve small flying height, smoothing technique with low damage to magnetic materials extremely essential, since the surface roughness and damaged surface layer decreases sensitivity of the sensor. Gas cluster ion beam (GCIB) can provide low damage smoothing processes for various materials with very low damage. Therefore, the GCIB is expected as one of novel processes for magnetic recording heads. Properties of magnetic materials, however, are extremely sensitive to their composition. Because the GCIB is manufacturing process of magnetic devices, morphological, magnetic and other types of damages resulting from the irradiation should be evaluated. To obtain ultra-smooth surface, oblique irradiation, well known as low damage process using heavier ion beam, have been introduced to the GCIB process. In this paper, 50 nm thick NiFe films deposited on Si wafers by Ar sputtering were used as a magnetic material. Incident angle measured from the surface normal was varied from 0° to 47°. In this paper, irradiation damages such as NiFe composition ratio change and surface oxidation have been investigated by secondary ion mass spectroscopy (SIMS). Depth profiles of Ni, Fe, and O were obtained through SIMS measurement. Surface morphology of NiFe irradiated NiFe films was investigated by atomic force microscopy (AFM) and scanning electron microscopy (SEM). From the results of AFM and SEM observation, it was found that the surface morphology of GCIB irradiated NiFe films drastically varied with incident angle. After GCIB irradiation with an acceleration voltage of 20 kV, the averaged surface roughness (Ra) increased as the incident angle increasing from 0 to 47°. At an incident angle of 47°, a ripple pattern was formed. At larger incident angle (>47°), the averaged surface roughness decreased with the incident angle. At an incident angle of 87°, a quite smooth surface was obtained (Ra=0.3 nm). It was found that the oblique irradiation of GCIB was also effective for increasing thickness of composition ratio changed layer and oxide layer. At normal GCIB irradiation with an acceleration voltage of 20 kV and a dose of 1x10^15 ions/cm^2, the thicknesses of composition ratio changed layer and oxide layer increased, respectively, by 3 and 5 nm compared to pre-GCIB films. Both thicknesses decreased with increasing the incident angle. These decreases were attributed to decrease of vertical ion bombardment energy. At GCIB irradiation with incident angle of 87°, the thicknesses of composition ratio changed layer and oxide layer were the same as the pre-GCIB films. Consequently, ultra-smooth (Ra=0.3nm) and low damage processing of NiFe films was demonstrated with oblique GCIB irradiation at a large incident angle.

5:00 PM T5.6
Molecular Dynamics Study of Sputtering Process by Reactive Cluster Impacts: Yasukata Aoki and Jiro Matsuo, Quantum Science and Engineering Center, Kyoto University, Kyoto, Japan.

For the last decade, the surface modification processes utilizing the GCIB can be generated not only from rare-gas materials such as Ar but also from reactive materials such as SF6, CF4, etc. The use of reactive gas cluster is expected to enlarge the application and potential of GCIB process in nano-scale surface modification processes. The characteristics of GCIB process is that high energy cluster ions impacts on the target surface, large number of collisions occurs simultaneously, which causes local heating, large motion of and chemical excitation of the surface atoms. However, the mechanism of the impact process of cluster and target surface is still unknown. In this study, the evolution of surface structure and sputtering with sequential fluorine cluster impact was examined using molecular dynamics simulation. For example, when an F cluster with 6eV of total incident energy (=10eV/F atom), a crater-like structure with many F atoms absorbed is formed on the target surface. After such impact, the cluster rearranges to a mixture of a crater-like structure and atomic layer.
Laser Induced Hierarchical Nano-Composites in Metallic Multi-Films: Limits of Intermetallic Formation and Penetration Depth. Claus Daniel and Frank Muecklich; Materials Science, Functional Materials, Saarland University, Saarbruecken, Germany.

Due to the corresponding intermetallic compounds, Ni/Al multi-layered thin film systems are important to protect the mechanical and chemical impact on the bulk component. The mechanical properties of these tough intermetallic compounds, NiAl, can be further improved by combining with other stiff phases. Pulsed laser interference irradiation of Ni-Al-thin multi-films can produce periodical defect structure and periodical formation of intermetallics. The thickness of individual layers in a multi-film and therefore the vertical layer period is very important for the type and the amount of formation of intermetallics and by the way for the chemical and mechanical properties. In this study, the vertical layer period ranges from 3 nm up to 50 nm. It is shown that PVD-produced films down to a few nm-period show individual metallic layers without any intermetallic formation. The morphological structure of such multi-films can be studied by TEM target-preparation by FIB to be possible up to 20 nm period. For larger layer periods the amount of intermetallics is negligible. The irradiation density is relatively independent from the layer period to be around 100 nm for a ns-laser pulse.

A Nitration Procedure to Improve the Interfacial Quality of Ultrathin Hafnium Oxide Films. Ping Chen and Tonya M. Klein; Chemical Engineering, University of Alabama, Tuscaloosa, Alabama.

HfO₂ has generated attention in recent times as a new gate material due to the corresponding intermetallic compounds, Ni/Al. The morphology of such thin multi-films is studied. The intermetallic formation of intermetallics by the interference pattern of two coherent Nd:YAG-nm-laser pulses is studied by TEM target-preparation by FIB to be possible up to 20 nm period. For larger layer periods the amount of intermetallics is negligible. The irradiation density is relatively independent from the layer period to be around 100 nm for a ns-laser pulse.

This revealed no difference in the mechanical response of the films from that of pure Si despite the varying Ge concentrations. However, under the indentation conditions used, the penetration depth was of the order of 50% of the film thickness and the effect of the underlying Si substrate cannot be neglected. To avoid this uncertainty low-load indentation was carried out in a Hysitron (Ubi) nanoindenter using a Berkovich indenter with an effective radius of 70 nm. This resulted in a maximum penetration depth of 30 nm when loaded to 300 μN. The measured mechanical properties remained very similar to that of Si, even at indentation depths of less than one fifth of the film thickness. Conventional transmission electron microscopy images and thickness measurements confirm the films undergo phase transformations during indentation similar to that previously observed in pure Si.

Interestingly, however, some subtle differences in the mechanical response of the SiGe films were observed when compared to the pure bulk Si, with the scatter of the mechanical property data increasing with Ge content. To investigate this further, AFM imaging of the SiGe films revealed a change in the morphology of the surfaces with increasing Ge content. The films containing the highest percentage of Ge were observed to have the highest surface roughness. This is thought to correspond to the density of misfit dislocations caused as a result of the lattice mismatch between the SiGe layers and the Si substrate.

Many machining operations, including scribing, edge grinding, dicing and ductile regime turning of silicon wafers, lead to pressure-induced phase transformations. These transformations produce a layer of amorphous silicon or metastable phases on the wafer surface which need to be removed by subsequent polishing or etching. Characterizing the effect of localized contact pressure on phase transformations in silicon and other materials through depth-sensing indentation has been shown to be very useful in recent years. While load and displacement are measured in real time, a wealth of information regarding material response under different loading conditions can be gathered. The rate the indenter tip is unloaded and the maximum applied load on the sample have been proven to affect the response of silicon to sharp indentation, but no such study exists for spherical indentation. In this work, a statistical analysis of over 1900 indentations made with a 13.5 μm nominal radius sapphire indentor on a single-crystal silicon wafer over a range of loads (25-700 mN) and loading/unloading rates (1-30 mN/s) is presented. The location of the displacement discontinuities on loading and unloading ("pop-in" and "pop-out" events), likely due to pressure-induced phase transformations, is noted as well as pressures at which they occur. Similar to Berkovich indentation, increase in maximum applied load and decrease in unloading rate are seen to raise the average pressure that phase transformations occur on unloading. Multiple occurrences of pop-in and pop-out events are reported for the first time. Raman micro-spectroscopy shows a higher intensity of metastable silicon phases at comparably deeper depths under the interface of the typical imprintation, while sharper stress are present. A stability range for Si₁₋ₓS𝑖ₓ, Si₁₋ₓS𝑖ₓ, Si₁₋ₓS𝑖ₓ, and a-Si is found and compared with previous results for Berkovich indentation. Indentation with spherical indenters allows patterning of the wafer surface with new phases of silicon without cracking, which is almost unavoidable in the case of sharp indenters.
Si phase during indentation. Results have provided a better understanding of the various modes of deformation and raised some interesting questions relating to amorphous-to-crystalline phase transformations under indentation loading. Discontinuities on both loading and unloading (so-called pop-in and pop-out events), which are associated with phase transformations in c-Si were observed in the annealed (relaxed) as well as in the as-received samples but not in Si. These discontinuities correlated well with the observed onset of a phase transformation. After nanoindentation, the samples were additionally examined using a range of ex-situ techniques including Raman microspectroscopy and cross-sectional transmission electron microscopy to study the end phases (crystalline and amorphous).

9:15 AM T6.4/R10.4
Cross Sectional TEM Studies of Indenter Angle Effects on Indentation-Induced Phase Transformations in Si and Ge. Songqin Wen1, James Bentley1, Jae-il Jang1,2 and George M. Pharr1,2,1,2 Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee, 2Metal & Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

It is well known that Si and Ge transform to a metastable state under pressure and that other crystalline and amorphous phases can form. A greater amount of transformed metallic silicon AFM and SEM have been used to measure the groove shape and study the chips generated in nanoindentation. This will show that during indentation, the loads investigated, correlate with the generation of the metallic silicon during simulated machining.

9:45 AM T6.6/R10.6
Abstract Withdrawn

10:30 AM T6.7/R10.7

In majority of mechanical applications of materials, their surface experiences a contact with another material and takes the external load before the bulk of the material is influenced. In some cases, surface interactions influence the bulk (e.g., propagation of cracks, dislocations or point defects from the surface in depth). In many cases, only the outermost surface layer is affected by the surface contact with no detectable changes in the bulk of the material. We are primarily concerned in this review with that kind of interactions. The thickness of the surface layer affected by the external mechanical forces ranges from nanometers to micrometers. Thus, in our case, the definition of "surface" is different from the one used by surface scientists. We need to introduce an engineering definition of the surface as the outermost layer of the material that can be influenced by physical and/or chemical interaction with other surfaces and/or the environment. During contact interactions, a harder object can leave imprints on the material surface. In particular, when a hard indenter (e.g., diamond) touches the surface of another hard material (certainly not that of semiconductors), very high pressures (up to one megabar) can be achieved under the indenter because the contact area in the beginning of the penetration of the indenter in material is small. These pressures can exceed the phase transformation pressure for many materials. Understanding and appreciation of this fact can help to understand the mechanisms of wear, friction and erosion. High shear stresses and flexibility of contact loading conditions allow one to drive phase transformations that cannot occur under hydrostatic stresses, or would occur at much higher pressures and temperatures. We will describe phase transformations and amorphization that occur in many semiconductors under contact loading such as indentation with hard indenters or scratching, grinding, milling, etc. Contact loading is one of the most common mechanical impacts that materials experience during processing or application. Examples are cutting, polishing, indentation, tensile, wear, friction and erosion. This kind of loading has a very significant nonhydrostatic component of stress that may lead to dramatic changes in the materials structure, such as amorphization and phase transformation. Simultaneously, processes of plastic deformation, fracture and interactions with the environment and counterbody can occur. The latter have been described in numerous publications, but the processes of phase transformations at the sharp contact were investigated only during past decade and the data obtained have never been summarized. This problem is at the interface between at least three scientific fields: namely, materials science, mechanics and solid state physics. Thus, an interdisciplinary approach will be used to describe how and why a nonhydrostatic (shear) stress in the two-body contact drive phase transformations in materials.

11:00 AM T6.8/R10.8

Impregnated hard multilayered coating rod in a 9.5 mm 1018 steel bars were studied used microhardness and nanoscratch techniques. Constant and ramped load nano scratch tests were done using a MTS Nano Indenter XP system. The dependence of the residual wear depth, profile height and friction coefficient on load are compared in constant and ramped load test conditions. The impregnated hard coatings show less permanent damage, lower friction coefficients and lower pileup heights than untreated steel under the same load conditions.

11:15 AM T6.9/R10.9
Micro-Raman Mapping and Analysis of Indentation-Induced Phase Transformations in Germanium, Jae-il Jang1,2, M.J. Lancs, Songqin Wen1 and G. M. Pharr1,2,1 The University of Tennessee, Knoxville, Tennessee; 2Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Through a number of theoretical studies and diamond anvil cell experiments over the past four decades, it is now well accepted that...
germanium transforms under pressure from the normal diamond cubic phase (Ge-I) to the metallic bet-phi phase (Ge-II) at about 10 - 11 GPa and re-transforms to Ge-III (st12 structure) or Ge-IV (hct structure) during release of the pressure. Since these transformations are broadly analogous to those occurring in silicon, one might expect the indentation-induced phase transformations in these two materials to be approximately the same. However, the number of experimental studies that have examined indentation behavior of Ge is relatively small. This study was undertaken to answer several key unresolved questions. Nanoindentation experiments were performed on Ge-I (100) Ge single crystals in a series of triangular pyramidal indenters with different tip angles, including the common Berkovich and cube-corner indenters. Although, in contrast to Si, none of the indentation load-displacement curves indicated pop-out or other unusual shape changes, micro-Raman microscopy in conjunction with scanning electron microscopy provided positive evidence that phase transformations involving amorphous and crystalline phases do indeed occur. In addition, the observations suggest that the size and concentration of the retarding effect for the transformations progress and affect deformation during nanoin indentation. * This research was sponsored by the National Science Foundation under grant number DMR-0208552, and by the Division of Materials Sciences and Engineering (ShAndE User Center), U. S. Department of Energy, under Contract DE-AC05-00OR22725 with UT-Battelle, LLC.


The mechanical properties of surfaces can be dramatically affected by a dispersion of fine precipitates such as those produced by ion implantation, insoluble species. We previously formed nanometer-size precipitates of hard oxides (Al2O3) in implanted Ni and produced surface layers with yield strengths as high as 5 GPa (Follstaedt et al., Mat. Trans. A, 2003). Here we examine the strengthening that can be achieved with small bubbles, which are shearable precipitates, formed by implanting hydrogen under severe conditions to study the effects of varying bubble size and concentration. This treatment could be used to engineer hard surface layers, and the results are also of interest for understanding the effects of He build-up due to tritium decay in metal tritide films used in neutron tubes. In Ni implanted with 5 at % He to a depth of 600-700 nm at room temperature, cross-section TEM shows a dispersion of He bubbles with diameters of 1 nm or smaller. Using nanoindentation combined with detailed finite element modeling to separate layer properties from the substrate, the bubble-containing layer is found to have a yield strength of 2.4 GPa, nearly 7 times that of the underlying Ni. This pronounced strengthening is ascribed to the retardation of dislocation glide by the bubbles, an effect originating from the combined influence of image forces, gas pressure, and step energies associated with dislocation cutting. Initial estimates indicate that the retarding effect for the small bubbles approaches that necessary to prevent passage of the dislocation core. As an assumption of Orowan hardening gives a flow stress of 2 GPa, comparable to what is observed. We have numerically solved the continuum strain equations for dislocations moving in a three-dimensional periodic array of pressurized bubbles, and are using this model to interpret the observed mechanical behavior at a more quantitative level. When the same He concentration is implanted at 500°C, the bubbles are much larger at 5 nm in diameter and the hardness of the layer is 40% lower, though still substantially higher than untreated Ni. The bubble layers also show signs of abrupt yielding in shear at depths of 100 nm during the indentation; notably, the shear stresses at failure are relatively modest (1.3 GPa) when compared to Ni containing Al2O3 precipitates, which show even higher stresses without failure. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy’s National Nuclear Security Administration under Contract DE-AC04-94AL85000.


Hardness depends on the strength of bonding in solids. Therefore, it depends on the type of bonding: covalent, metallic, ionic, or dispersion. The micro-mechanism of the deformation that occurs during indentation (or scratching) involves either the motion of glide dislocations or a phase transformation (twinning is taken to be a mono-molecular phase transformation), or both. In pure simple metals, the mobilities of individual dislocations on the primary glide systems are indefinitely large since the bonding is non-local. A result of the non-local bonding is that the energies of the cores of the dislocations are independent of their positions so no static forces resist their motion. In this case, their motion is limited only by electron and/or phonon viscosity. Therefore, the deformation associated with indentation is only resisted by strain-hardening (dislocation dipoles), and not the need for defect annihilation. However, in covalent crystals the behavior is quite different because the bonding is localized. In them, dislocation motion (via the motion of localized kinks) requires the expenditure of valence (bonding) electrons into conduction (anti-bonding) states. The energy required is that of the minimum band gap. But a kink has an associated volume. Therefore, the overall deformation process depends on the energy-gap density. For the homopolar (Group IV) crystals, as well as the covalent III-V crystals, this observed experimentally. The situation is somewhat more complex for the hetero-polar III-V crystals because ionic charge centers play a role in them. Band gaps are related to polarizabilities, and are expected to shear moduli so there are some additional links between hardnesses and electronic properties that are discussed.
performed by using Raman spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and x-ray diffraction (XRD). Pin-on-disc tribological tests were performed and the results were compared to tribological properties of CDC and untreated Si.

2:00 PM T7.3
Synthesis and characterization of carbon nitride thin film with evidence of nanodomains. Shaiful Azam Md. Chowdhury and Michael T. Laugier; Physics, University of Limerick, Limerick, Ireland.

We have reported the synthesis of carbon nitride thin films with evidence of formation of carbon nanodomes over a range of substrate temperature from 50 oC to 550 oC. An RF magnetron sputtering system was used for depositing carbon nitride films. The size of the nanodomes can be controlled by deposition temperature and increases from 40-80 nm at room temperature to 200-400 nm at high temperature (550 oC). Microstructural characterization was performed by AFM and TEM. Electrical characterization shows that these films have conductive behaviour with a resistivity depending on the size of the nanodomains. Resistivity value of 20 milliohm-cm was found for nanodomes of size 40-80 nm falling to 6 milliohm-cm for nanodomes of size 200-400 nm. Nanoindentation results show that the hardness and Young's modulus of these films are in the range from 9-22 GPa and 100-168 GPa respectively and these values decrease as the size of the nanodomes increases. XRD results confirm that a crystalline graphic carbon nitride structure has formed.

2:15 PM T7.4
Electron Microscopy Analysis on the Worn Surface of a High-Chromium White Iron During Dry Sliding Contact. Arrollo de Bodelia-Jacuende and Mark W. Rainforth; 1 Instituto de Investigaciones Metalurgicas, Universidad Michoacana de San Nicolas de Hidalgo, Morelia, Michoacan, Mexico; 2Department of Engineering Materials, The University of Sheffield, Sheffield, United Kingdom.

A series of microstructural phenomena within a thickness of material (tribolayer) below the worn surface, have been developed during dry sliding wear of a high-chromium cast iron against a hardened M2 steel counterface. The overall wear behavior of the alloy is determined by such a tribolayer. From the present work, a scanning and transmission electron microscopy analysis has been undertaken on the different features developing at different distances below the worn surface, during wear sliding tests of a 17%Cr white iron, whose microstructure is composed by about 25% eutectic Fe-Cr carbides in an austenitic matrix. The coating was shown to be plastic for the load range applied (42-228 N/pin). The observed phenomena is an increase in the dislocation density, plastic deformation by twinning followed by severe shear banding along with carbides fracture, a mechanical mixture composed by iron oxide and carbide particles produced from large carbides comminuting, and finally a flat iron oxide layer. Wear debris was apparently created from the oxide film detaching from the outermost surface where equivalent strain is maximum. No evidence of stress whitening or martensite was observed from the present work, which has been reported for some austenitic materials. The implications of the microstructural evolution are discussed in terms of the wear theories and behavior of metals at high strain levels.

2:30 PM T7.5

Wafer level monolithic three-dimensional (3D) integration is an emerging technology to realize enhanced performance and functionality with reduced form-factor and manufacturing cost. The foreseeable drivers for the technology will be memory stacks, such as Sn, posi...
continuous stiffness measurement technique in terms of hardness and elastic modulus, which varied between 15-25 GPa and 190-200 GPa, respectively. The mechanical response of the CrN was found to be affected by various factors related to the structure and the morphology. More specific, it was found that the preferred orientation is a dominant factor that affects the nanomechanical properties.

When the grains are grown along well defined crystallographic directions ([111] or [100]) the hardness and elastic modulus values are maximized, while they reduced in the case of coatings exhibiting a mixed growth orientation (both [111] and [100]). Moreover, internal stresses and density are also related to the nanocrystallite hardness and modulus, since the presence of internal stresses reduces the induced plastic deformation for a given load, while the densification of the coatings leads to a more compact structure, which is deformed more difficult under certain loading conditions. Both of them lead to the increase of the hardness and elastic modulus. All the above are discussed in terms of the kinetics and thermodynamics during growth taking into account the ion solid interactions induced by Vb. In addition, these results are compared with reports concerning balanced-MS grown TiN films under various Vb [1]. In the latter case the hardness was found to increase with both density and fraction of grains grown along [100] orientation, while the measured hardness for the films, which exhibit well-defined [111] crystallographic structure was the minimal. This can be attributed to the lower density and compressive internal stresses of the coatings grown with balanced MS at low Vb, compared to the corresponding values at the same Vb in the case of the coatings grown in unbalanced configuration due to the more intense ion bombardment of the growing film. [1] P. Patsalas, C. Chakidissis, S. Logothetidis, Surf. Coat. Technol. 125, 335 (2000).

4:00 PM T7.9
Ultrahard Diamond/a-C Nanocomposite Films. Maria G. Fyta and Pantelis C. Kelires; Physics, University of Crete, Heraklion, Crete, Greece.

Nanostructured amorphous carbon (a-C) is a hybrid form of carbon in which nanocrystallites are embedded in an a-C matrix. It has attracted considerable attention because it offers the possibility to tailor the mechanical and electronic properties of a-C. Among its various forms, diamond nanocomposite films are particularly attractive for their diamondlike properties, including high hardness. Still, many of their structural characteristics, especially in the interfacial regions, and their relative stability with respect to the density of the a-C matrix remain poorly understood. We present here theoretical work based on tight-binding molecular dynamics and Monte Carlo simulations which shed light on several issues of nanodiamond films. We examined their structure, stability as a function of temperature and size of nanocrystallites, stress state, and hardness. The key findings are: (a) Nanodiamonds are stable only in dense, highly coordinated a-C matrices. (b) Relaxed nanocomposite films can possess negligible intrinsic stress. This implies conditions for excellent substrate adhesion. (c) The elastic moduli are consistently and considerably higher than those of pure a-C films, making the diamond nanocomposite films suitable for ultrahard mechanical coatings. For example, the bulk modulus exceeds, in some cases, the value of 360 GPa (Young's modulus 820 GPa). This is, according to our calculations, the modulus of "amorphous diamond", the hypothetical fully tetrahedral a-C network. We are currently examining the fracture strength of this material.

4:15 PM T7.10
Metalizable Polymer Thin Films using Supercritical Fluids. Tadanori Koga, John Jerome, Miriam Rafailovich and Jonathan Sokolov; SUNY at Stony Brook, Stony Brook, New York.

Polymer metallization is very important in the industrial fields for improvement of polymer surface properties, including wear, conductivity and appearance[1]. One problem is, however, that they often react with difficulty and, as a result, many polymer/metal components exhibit poor adhesion properties. This could be a serious problem when the films are heated to temperatures above their glass transition temperatures (or melting point); instability at the interface (dewetting) will occur, and the film properties will severely deteriorate. Here we show that supercritical carbon dioxide (scCO₂) can improve the adhesion of the polymer/metal interface significantly. Spun-cast polystyrene (PS) and poly(methyl methacrylate) (PMMA) thin films on Si wafers were used for this study. The film thicknesses of both polymer films were prepared in the range from 10 nm to 150 nm. We first exposed the films to scCO₂ in the P-T range corresponding to the density fluctuation ridge where the excess swelling of both polymer thin films occurred[2]. Chromium (Cr) layer with the film thickness of about 40 nm was then deposited onto the polymer films by using E-beam Evaporator. X-ray reflectivity measurements showed that the interfacial width between the Cr and polymer layers increased a factor of 2 compared to that without exposure to scCO₂. The correlation between interfacial width and adhesion strength will be also discussed. [1] Pireaux, J.; Kowalczyk, S. P. in Metalization of Polymers, ACS Symposium Series; Sacher, E., Ed.; American Chemical Society: Washington, DC, 1990. [2] Koga, T. et al. Macromolecules 2003, 36, 5236.

4:30 PM T7.11
Surface Modification of Polymeric Nanocomposite Thin Films using Supercritical Fluids. Tadanori Koga, Chunhui Li, Yuan Sun, Miriam Rafailovich and Jonathan Sokolov; SUNY at Stony Brook, Stony Brook, New York.

We report on an efficient and environmentally friendly means to modify surface properties of polymer thin films supported for nanoparticles. Ultrathin polystyrene (PS) films ranging from 10 to 100 nm, in which inorganic nanoparticles were embedded, were exposed to supercritical carbon dioxide (scCO₂) at the density fluctuation ridge in the pressure-temperature phase diagram where the anomalous excess swelling was induced[1,2]. The swollen structures were then preserved by quickly evaporating CO₂. X-ray reflectivity results showed that most of the nanoparticles segregated at the polymer/air interface regardless of a choice of nanoparticles. The correlation between the surface segregation of gold, C₀ₓ and clay nanoparticles and the physical properties such as conductivity and glass transition temperature will be discussed. [1] Koga, T. et al., Phys. Rev. Lett. 2002, 89, 155506. [2] Koga, T. et al., Macromolecules 2003, 36, 5236.