

SYMPOSIUM T

Surface Engineering—Fundamentals and Applications

November 30 - December 2, 2004

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* Invited paper

8:30 AM *T1.1

Self-adaptive nano-structured hard coatings for wear protection. Christian Mitterer, Department of Physical Metallurgy and Materials Testing, University of Leoben, Leoben, Austria.

Hard coatings deposited by plasma-assisted vapor deposition are widely used to reduce 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 different ranging from low temperatures for deep drawing 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 Ti_{1-x}Al_xN 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 coating in humid air, and CrC/a-C:H, 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 V₂O₅, due to oxidation of VN in Ti_{1-x}Al_xN/VN superlattices or V in V-alloyed Ti_{1-x-y}Al_xV_yN 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 V₂O₅ phase. Another high-temperature low-friction approach is the application of thin top layers based on intermetallic phases on hard coatings. In particular, the Al₂Au phase is stable up to 850°C without oxidation, shows a pink color and yields friction coefficients of 0.45 at 700°C. These nanoscale design approaches allow the utilization of functional properties facilitating the development of next generations hard coatings.

9:00 AM T1.2

Investigations of the Effect of PVD (Cr,Al)N Coatings Micro Structure on Impact Toughness. Erich Lugscheider, Otto Knotek, 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 steadily increasing market is evolving by coating machine parts. The requirements that have to be met due to the needs of this new market segment focus on tribological behavior. This means, that the focus 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.

9:15 AM T1.3

Interface Studies in the System TiN-Si₃N₄. Joerg Patscheider^{1,2}, Niklas Hellgren^{3,2}, Rick Haasch², Ivan Petrov² and Joe E. Greene²; ¹Surfaces, Coatings & Magnetism, EMPA, Duebendorf, Switzerland; ²FS-MRL, University of Illinois, Urbana-Champaign, Illinois; ³Intel Corp., Portland, Oregon.

Nanocomposites of TiN/Si₃N₄ show superhardness when deposited under appropriate conditions. Apart from the crystallite size, the sharp interfaces between the crystalline TiN and the amorphous Si₃N₄ as well as the structural quality of the amorphous phase are decisive for the performance of these materials. Due to their three-dimensional nature there is no analytical technique available to probe the chemical nature of these interfaces. To overcome these

limitations model interfaces were synthesized on single-crystalline TiN under clean conditions with several monolayers of Si₃N₄ and other materials relevant for the system TiN-Si₃N₄. The thickness was chosen to be close to the typical values for hardness-enhanced nanocomposites and to be transparent for photoelectrons from the base material. In situ analyses with XPS were performed in order to analyze the influence of these overlayers on the bonding characteristics. The results indicate that the bonding characteristics observed in nanocomposite TiN/Si₃N₄ can be explained by the different chemistry at the interface. The implications on the macroscopic properties and practical applications will be discussed.

9:30 AM T1.4

Functionally Gradient Diamondlike Carbon Nanocomposites. Roger Jagdish Narayan, Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.

Diamondlike carbon thin films exhibit poor adhesion to metals because of internal compressive stress within the diamondlike carbon film and poor interfacial bonding between the diamondlike carbon film and the substrate. A novel multicomponent single target pulsed laser deposition process was developed to create diamondlike carbon-metal nanocomposite films. We developed functionally gradient diamondlike carbon-metal nanocomposite films by varying the metal concentration as a function of distance from the film-substrate interface. Z-contrast transmission electron microscopy imaging of the diamondlike carbon-metal nanocomposite films reveals that metals that do not form carbides (e.g., silver) form 2-10 nm self-assembled nanoparticle arrays within the DLC matrix. Metals that form carbides (e.g., titanium) form alternating metal carbide layers within the DLC matrix. The size of silver nanoparticles and the thickness of titanium layers were varied as a function of distance from the substrate-film interface. Linear tribometer measurements made on these samples have demonstrated that DLC-metal nanocomposite films possess exceptional wear resistance. These DLC-metal nanocomposite thin films have multiple biomedical and tribological applications.

9:45 AM T1.5

Hard PVD Coatings for Austenitic Stainless Steel Machining: New Developments. Jose Luis Endrino, Joerg Neuhaus, Axel Wachter and Christoph Gey; SBU Tools, Balzers AG, Balzers, Liechtenstein.

The machinability of austenitic stainless steels is, in general, considered to be a difficult process. This is due in great part to the high plasticity and tendency to work-harden of the workpiece which normally results in extreme conditions imposed on cutting edges as well as adhesive wear. Additionally, austenitic stainless steels have much lower thermal conductivities in comparison to plain carbon and tool steels; this inflicts high thermal loads within the chip-tool contact zone which can significantly increase the wear rate. The complex machining of austenitic stainless steels can be, in part, relieved by use of a hard coating with low thermal conductivity and an adequate coating surface quality. This can lead to a low friction coefficient between the parts and an improved chip evacuation process. In this study, the wear mechanism during milling processes of cemented carbide tools coated with diverse widely industrially used coatings such as TiN, TiCN, TiAlN, AlTiN, and AlCrN is introduced. The mechanical properties of the coatings employed in this study were investigated at high temperatures. An effort was made to interpret the influence of coatings' hardness, friction and thermal conductivity at high temperatures in relationship to the observed tool wear. Also, in some cases, the surfaces of the coated tools were enhanced by post-treatment processes. The pre- and post-treated surfaces were then compared by means of scanning electron microscopy (SEM) and atomic force microscopy (AFM) in order to try to provide insightful information about the configuration of optimized microstructured surfaces leading to reduced tool wear.

10:30 AM *T1.6

Nanocomposite DLC coatings: structure and properties. Jeff T. De Hosson¹, Yutao Pei¹, Daminiao Galvan¹ and Albano Cavaleiro²; ¹Applied Physics, University of Groningen, Groningen, Netherlands; ²University of Coimbra, Coimbra, Portugal.

This contribution deals with fundamental and applied concepts in nano-structured coatings, in particular focusing on the characterization with high-resolution (transmission) electron microscopy. Nanocomposite coatings consisting of TiC nanoparticles embedded in an amorphous carbon (a-C) matrix are able to combine high fracture toughness and wear resistance with a low friction coefficient. Coatings currently employed for such applications are based on a hydrogenated a-C matrix. However, if a hydrogen-free a-C matrix could be made, an improvement in thermal stability of the nanocomposite coating would be expected, together with a decrease in the sliding coefficient of friction in a humid environment. Both balanced and unbalanced magnetron-sputtering systems were used to

deposit nc-TiC/a-C nanocomposite coatings with hydrogen-free DLC matrix. The contents of Ti and C in the coatings were varied in the whole range of interest (5-45 at.%Ti) by changing the configuration of the targets. Different levels of applied bias and deposition pressure were used to control the coatings nanostructure. Nanoindentations and tribological tests determined that the coatings exhibit hardness (H) of 5-36 GPa, Young's modulus (E) of 55-335 GPa, an H/E ratio of 0.07 - 0.15 and a friction coefficient of 0.06. The size and distribution of the nanoparticles were determined with High-Resolution (HR) and Energy-Filtered (EF) Transmission Electron Microscopy (TEM); their size varies between 2 and 20 nm diameter and particle clustering was observed. Electron microscopy was further employed to determine the chemistry of the a-C matrix (sp³/sp² ratio), through Electron Energy Loss Spectroscopy (EELS). It was demonstrated that both TiC particle size and a-C chemistry could be directly controlled by change of deposition parameters such as applied bias and deposition pressure. The chemical composition of the coatings was determined through EMPA and XPS, and was employed to determine the coatings particles volume fraction (VF). A rule of mixture (ROM) approach can explain the variation of Young's modulus (E) as a function of particles VF. A model was developed to include the variation in geometry of the nanocomposite as a function of particle size and VF. This model also allows for the explanation of toughening effects, as detected from the observation of crack propagation at the edges of cube-corner indentations in various coatings.

11:00 AM T1.7

Carbide Derived Carbon Coating on Boron Carbide.

Ranjan K. Dash, Gleb Yushin, Adrian Gurga and Yury G. Gogotsi; Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania.

Carbide derived carbons (CDCs) represent a new class of microporous carbons produced by selective removal of metal atoms from carbides. In this work, CDC coatings were synthesized on a sintered B₄C ceramic by selective etching of boron with chlorine gas for 4, 8, 12, and 16 hours at 800C. Measurements of the thickness of the carbon coating formed on B₄C suggest a linear chlorination kinetics and formation of an interconnected network of pores in CDC. Raman spectroscopy and depth-sensing indentation studies were performed across the CDC-B₄C interface. Nanoindentation studies showed that the elastic modulus and hardness change sharply at the interface, suggesting a sudden change in the material structure. Furthermore, with an increased distance from the interface the elastic modulus of carbon became constant. Results of the Raman analysis were in agreement with indentation tests and showed bands of both boron carbide and carbon at the interface and only the D and G-bands of graphitic carbon in the CDC away from the interface. A completely converted sample of B₄C synthesized at 800C for 24 hours demonstrated a high specific surface area (1768 m²/g) with pores less than 5 nm. Such highly porous membrane falls 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.

11:15 AM *T1.8

Thermal and Environmental Barrier Coatings for Advanced Turbine Engine Applications. Dongming Zhu and Robert A. Miller; NASA Glenn Research Center, Cleveland, Ohio.

Ceramic thermal and environmental barrier coatings (T/EBCs) will play a crucial role in advanced gas turbine engine systems because of their ability to significantly increase engine operating temperatures and reduce cooling requirements, thus help achieve engine low emission and high efficiency goals. Under the NASA Ultra-Efficient Engine Technology (UEET) program, advanced T/EBCs are being developed for the low emission SiC/SiC ceramic matrix composite (CMC) combustor applications by extending the CMC liner and vane temperature capability to 1650C (3000F) in oxidizing and water vapor containing combustion environments. Advanced low conductivity thermal barrier coatings (TBCs) are also being developed for metallic turbine airfoil and combustor applications, providing the component temperature capability up to 1650C (3000F). The advanced T/EBC system is required to have increased phase stability, lower lattice and radiation thermal conductivity, and improved sintering, erosion and thermal stress resistance, and water vapor stability under the engine high-heat-flux and thermal cycling conditions. Advanced high heat-flux testing approaches have been established for the coating developments. The simulated combustion water-vapor environment is also being incorporated into the heat-flux test capabilities for evaluating T/EBC performance at very high temperatures under thermal cycling conditions. In this paper, ceramic coating development considerations and requirements for both the ceramic and metallic components will be described for engine high temperature and high-heat-flux applications. The performance and durability of several ZrO₂ or HfO₂/mullite and mullite/BSAS model coating systems were

investigated. The underlying coating failure mechanisms and life prediction approaches will be discussed based on the simulated engine tests and fracture mechanics modeling results. Further coating performance and life improvements will be expected by utilizing advanced coating architecture design, composition optimization, in conjunction with more sophisticated modeling and design tools.

11:45 AM T1.9

Effect of Surface Geometry on Stress Generation in Thermal Barrier Coatings during Plasma Spray Deposition. Guosheng Ye and Soumendhra N. Basu; Department of Manufacturing Engineering, Boston University, Brookline, Massachusetts.

Low thermal conductivity and extended service lifetimes are two key requirements for plasma sprayed thermal barrier coatings (TBCs). Microcracks formed during the plasma spray deposition process play a critical role in determining the coating thermal conductivity and elastic modulus, both of which affect the performance and lifetimes of TBCs. A fully coupled thermo-mechanical finite element model was used to study the buildup of stresses during splat solidification, and to understand the effect of deposition conditions on crack formation during plasma spray deposition. Through the simulation, the locations and magnitudes of maximum stresses were identified, where crack formation would presumably initiate. Two normal stress components were considered, S₁₁, oriented in the coating plane, which leads to vertical cracks; and S₂₂, oriented normal to the coating plane, which leads to horizontal cracks. A parametric study was carried out with two temperature variables (splat temperature T_{splat} and substrate temperature T_{sub}) and three geometric variables (splat thickness t, surface roughness amplitude A, and wavelength λ). It was found that the maximum S₁₁, which leads to the vertical cracks, occurs at the top of the splat and the maximum S₂₂, which leads to the horizontal cracks, occurs at the bottom of the splat, both at surface roughness valleys. It was found that subsequent splats increased the magnitude of S₂₂ and decreased the magnitude of S₁₁ in the original splat. The model showed that both S₁₁ and S₂₂ scaled with the temperature difference between the superheated splat and the substrate. The simulation further showed that the stresses scale with the three geometric parameters, and two independent geometric ratios were defined; ζ (defined as t/λ) and ψ (defined as A/λ). 2-D maps of maximum S₁₁ and S₂₂ under different combinations of ζ and ψ were constructed. The mappings showed that only roughness features on the scale of splat thickness were important in providing locations of maximum stress concentration.

SESSION T2: Tribological and Wear Resistant Surfaces and Coatings

Chairs: Jeff De Hosson and Ashok Kumar
Tuesday Afternoon, November 30, 2004
Room 203 (Hynes)

1:30 PM *T2.1

Ultralow and Superlow Friction Coatings. Jean Michel Martin, Ecole centrale de Lyon, Ecully, France.

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 films and hydrogenated DLC 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 attributed to specific friction-induced crystal orientations mechanisms in the contact area. Particularly rotational movement of MoS₂ sheets around the c-axis is responsible of sliding between uncommensurate crystal surfaces. The effect has been predicted theoretically 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 surprisingly 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, we 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 different and is generally associated with tribochemical reactions and the effect of hydrogen is important in vacuum tribometry of a-C:H. Boundary lubrication with ta-C in presence of ester (glycerol monooleate for example) is attributed to hydroxylation of graphitic species and the formation of OH-terminated surfaces. The data have been obtained 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 Systemes, Ecole Centrale de Lyon, Ecully, France.

Fuel economy and reduction of harmful elements in lubricants are becoming important issues in the automotive industry. An approach to respond to these requirements is the potential use of low friction coatings on engine components exposed to specific boundary lubrication conditions. Superlow friction stands for friction coefficient below 0.01 and ultralow friction is below 0.1. Superlow friction was experimentally observed for the first time with molybdenite coatings in UHV [1]. Diamond-like-carbon (DLC) coatings present a wide range of tribological behaviours, including superlow friction coefficient in ultra-high vacuum and inert gas environmental conditions [2]. The engine oil environment that provides different lubrication conditions must lead to such low friction levels with carbon-based materials in the near future in order to meet the economical requirements. In this work, friction and wear properties of DLC coatings under boundary lubrication conditions are investigated. Hydrogenated DLC coatings (a-C:H) can be better lubricated than non-hydrogenated DLC (ta-C) in presence of friction-modifier additive MoDTC thanks to the formation of MoS₂ lamellar sheets [3]. In contrast, the antiwear additive ZDDP does not significantly affect the wear behaviour of DLC coatings. On the other hand, ta-C coatings give lower friction in presence of some ester additives blended to synthetic oils like Glycerol Mono-Oleate (GMO), a well-known friction modifier already used in many engine oils. Friction level below 0.04 has been recently attained with proper combinations of DLC material/additive tribological systems [4]. Superlow friction under boundary lubrication might be not far to be reached. [1] J.M. Martin, C. Donnet, Th Le Mogne and Th Epicier, "Superlubricity of Molybdenum disulphide" Physical Review B48 N 14, p. 10583, (1993). [2] C. Donnet, M. Belin, J.C. Auger, J.M. Martin, A. Grill and V. Patel, Tribochemistry of diamond-like carbon coatings in various environments, Surface and Coatings Technology, 68/69, pp. 626-631, (1994). [3] M. I. De Barros, J.M. Martin, T. Le Mogne and B. Vacher, Mechanisms of boundary lubrication with carbon coatings, ECI Conf. On Boundary Lubrication (2003), Copper Mountain, Colorado, USA. Tribology International (2004 in press). [4] M. I. De Barros, J.M. Martin and T. Le Mogne, Ultra-low friction of DLC lubricated with ester containing oils, 30th Leeds-Lyon Symposium, (2003), Lyon.

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, William R. Ashurst³ and Maarten P. de Boer¹; ¹Reliability Physics Dept. 1762, Sandia National Labs, Albuquerque, New Mexico; ²Engineering Physics, University of Wisconsin Madison, Madison, Wisconsin; ³Chemical Engineering, Auburn University, Auburn, Alabama.

Surface micromachining fabrication techniques are used to construct a wide range of microactuators for microelectromechanical (MEMS) applications. However, when micron-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 characteristics at the microscale [1]. The actuator we have developed features large force (several mN), large travel range (+100 μ m) and precise positional control (40 nm steps), and is now called the "nanotractor". We can also employ the nanotractor to obtain detailed information on friction of contacting MEMS surfaces. Of particular interest here, we have found that before the static friction event occurs, pre-sliding tangential deflections (PSTD) of up to 200 nanometers are measured. This is very large relative to positioning requirements in applications such as optical MEMS and it is necessary to characterize it in more detail. Therefore, we have developed an optical metrology that allows us to measure tangential displacements with 1 nm resolution. The PSTD appear to be a manifestation of discrete asperity-asperity interactions which can be resolved by this metrology. Furthermore, results indicate a strong dependence on surface treatment. For an eight-carbon chain monolayer coating we see substantial PSTD. However, for an eighteen-carbon chain monolayer, the PSTD are greatly reduced. This behavior may qualitatively be related to a larger difference in the dynamic versus static coefficient of

friction in the eight-carbon monolayer than the eighteen-carbon monolayer. We also present a simple phenomenological model that captures some of the behavior of pre-sliding tangential deflections, and suggest some possible microscopic interpretations.

Acknowledgment: 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. [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, David S. Grierson¹, Jennifer E. Gerbi², James Birrell², John A. Carlisle², Orlando H. Auciello², Thomas A. Friedmann³, John P. Sullivan³, Greg M. Swain⁴ and Robert W. Carpick¹; ¹Engineering 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 macroscale, nearly equivalent to 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 report the first 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 undoped UNCD. Part of this work was funded by Sandia. 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. Part of this work was also supported by the US Department of Energy, BES-Materials Sciences, under Contracts DE-FG02-02ER46016 and W-13-109-ENG-38.

2:45 PM T2.5

Tribological behavior of MAX phases at temperatures up to 500 °C. Surojit Gupta¹, ZhengMing Sun^{1,3}, Michel W. Barsoum¹, T.

Palanisamy² and Chien-Wei Li²; ¹Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania; ²Honeywell, Morristown, New Jersey; ³National Institute of Advanced Industrial Science and Technology (AIST), Nagoya, Japan.

While good solid lubricants such as graphite and Teflon as standard coating materials for low temperature low friction applications exist, 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, Cr₂AlC, Ti₂AlCN, and Ti₃AlC₂ were found to demonstrate the best tribological properties at 500 °C. For example, the μ of Cr₂AlC was measured to be 0.7 at room temperature and 0.5 at T > 300 °C. The wear rate was 2x10⁻⁵ mg/cm²-s; a value that decreased with further

testing. Further material processing and doping led to even lower μ 's and lower wear rates over the 25-500 °C temperature range. SEM and EDAX analysis of the samples and the superalloy counter-discs revealed that the good tribological behavior can be attributed to the formation of multielement trioxides.

3:30 PM *T2.6

Tribology of Disordered and Nano-structured Carbon Films.

Ali Erdemir¹, Energy Technology Division, Argonne National Laboratory, Argonne, Illinois; ²Argonne National Laboratory, Argonne, Illinois.

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 superlow friction with superhardness 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 can make a huge positive impact in machining, microelectronics, and biomedical 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 superlubricity 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.

Nikhil Mehta^{1,5}, Sujoy Roy³, Jacqueline Anne Johnson¹, John Woodford¹, Alexander Zinovev⁴, Zahir Islam², Ali Erdemir¹ and Sunhil Sinha³; ¹Energy Technology, 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; ⁵Materials Science, Auburn University, Auburn, Alabama.

Carbon-based coatings exhibit many attractive properties that make them good candidates for a wide range of engineering applications. Tribological studies of the films revealed a close correlation between the chemistry of the hydrocarbon source gases and the friction and wear coefficients of the diamond-like carbon films. Those films grown in source gases with higher hydrogen-to-carbon ratios had much lower friction and wear coefficients than did films derived from source gases with lower hydrogen-to-carbon ratios. The mechanism for this low friction is as yet not properly understood. Ongoing structural characterization of the films at Argonne National Laboratory is gradually revealing this mechanism. Recent studies have included XPS, NEXAFS and X-ray reflectivity. XPS has given the surface chemical composition; NEXAFS has categorized the films in terms of sp²:sp³ ratio for different ratios of hydrogen-to-carbon (both deuterated and hydrogenated) in the source gases; and x-ray reflectivity has given a comprehensive depth profile. These results will be presented and correlated to give further insight into near-frictionless carbon films.

4:15 PM T2.8

Synthesis and Characterization of Nanocrystalline Diamond Film and Its Biomedical Applications.

Zhenqing Xu^{1,2}, Arun K. Sikder¹, Arun Kumar¹ and Ashok Kumar^{1,2}; 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 (microelectromechanical 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. In this paper, NCD films were deposited on the silicon (100) substrates from a gaseous mixture of Argon, Methane and Hydrogen by using MPCVD (microwave plasma-assisted chemical vapor deposition) method. The NCD films were successfully grown at substrate temperature around 750 °C using a high Ar concentration (95 vol%). Up to 20 vol% Nitrogen has been added to dope the NCD. The pressure inside the chamber was also found an important parameter to affect the formation and quality of nanodiamond. Ultrasonic polishing and surface scratching with fine diamond powder (0.5 μ m) were employed to enhance the nucleation density and growth rate before the deposition. Patterning 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 roughness 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-disk 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 electrochemical properties of NCD can be modified by altering 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 particle target analyte. This approach results in a highly stable and sensitive NCD based biosensor.

4:30 PM T2.9

Atomic Level Studies of Kinetic Friction and its Velocity Dependence at Aluminum and Alumina Interfaces.

Qing Zhang¹, Tahir Cagin¹, Yue Qi², Louis G. Hector² and William A. Goddard¹; ¹MSC, Caltech, Pasadena, California; ²GM Research & Development Center, General Motors, Warren, Michigan.

The kinetic friction behavior of Al/Al (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 lower velocities, kinetic friction exhibits Coulomb friction (almost independent of velocity), whereas at high-speed range, the velocity dependence follows a viscous relation. For Al/Al flat interface, only viscous friction is observed. Roughness on the surface leads to the increase of friction and change of velocity dependence. Simulation results reveal that at low sliding speed, the kinetic friction is from the shearing of the sliding slab caused by the interfacial potential along the sliding direction, which is the origin of Coulomb friction.

4:45 PM T2.10

Subcritical CO₂ Assisted Polymer Surface Engineering at Low Temperatures.

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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 (T_g), which is undesirable, particularly for biomedical applications. On the basis of different properties near polymer surfaces from those in the bulk, we introduce subcritical fluids (particularly carbon dioxide, CO₂) into polymer processing at the micro/nanoscales to produce and assemble 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 T_g. Monodispersed nanoparticles were deposited onto the smooth surfaces (rms < 1nm) 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 T_g 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 T_g 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 bulk T_g. The results indicated that even low concentrated CO₂ greatly enhanced polymer chain mobility below the T_g of the CO₂ plasticized polymers. With the knowledge of polymer surface dynamics under CO₂, we demonstrated polymer interfacial bonding at low temperatures and low CO₂ pressures (350C and 100 psi for PLGA) 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 confinement effect of polymer chains on the substrate, 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

SESSION T3: Poster Session: Surface Engineering:
Fundamentals and Applications
Chairs: Soumendra Basu and Joerg Patscheider
Tuesday Evening, November 30, 2004
8:00 PM
Exhibition Hall D (Hynes)

T3.1

Surface Nitridation of Amorphous Carbon by Nitrogen Ion Beam Irradiation. Chihiro Iwasaki, Masami Aono, Nobuaki Kitazawa and Yoshihisa Watanabe; MSE, National Defense Academy, Yokosuka, Japan.

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 difference in surface roughening between irradiation by 0.2 and 1.5 keV ions is hardly observed. XPS studies show that the nitrogen concentration near the surface increases after nitrogen ion irradiation and carbon-nitrogen bonding is confirmed in both C1s and N1s spectra. The depth profiles of nitrogen in the irradiated specimens display that the nitrogen concentration near the surface depends on the nitrogen ion energy. From the ball on disk testing, it is found that the friction coefficient of amorphous carbon after irradiation by 1.5 keV nitrogen ions approaches to that of graphite.

T3.2

C, Si and Sn Implantation of CVD Diamond as a Means of Enhancing Subsequent Etch Rate. P. W. Leech¹, T. S. Perova², R. A. Moore², G. K. Reeves³, A. S. Holland³ and M. C. Ridgway⁴,
¹CSIRO Manufacturing and Infrastructure Technology, Clayton, Victoria, Australia; ²Department of Electronic and Electrical Engineering, Trinity College, University of Dublin, Dublin, Ireland; ³School of Computer Systems and Electrical Engineering, RMIT University, Melbourne, Victoria, Australia; ⁴Department of Electronic Materials Engineering, ANU, Canberra, Australian Capital Territory, Australia.

The ability to selectively etch diamond on a fine scale has become an important requirement in producing new types of micro-mechanical and electronic devices. This work has examined for the first time the use of implantation-induced damage with C⁺, Si⁺ or Sn⁺ ions as a means of increasing the etch rate of diamond during subsequent reactive ion etching. C⁺, Si⁺ and Sn⁺ ions were selected in order to span a wide range of ion mass. Polycrystalline films of diamond were implanted with C⁺, Si⁺ or Sn⁺ ions at multiple energies in order to produce a near uniform concentration region of implantation-induced C vacancies or equivalent implantation-induced disorder. Analysis of the implanted surfaces by Raman spectroscopy has shown that the proportion of non-diamond or sp²-bonded carbon increased with ion dose in the range 5 x 10¹³ - 5 x 10¹⁵ ions/cm². Photoluminescence measurements of the Si⁺ implanted diamond have indicated a rising concentration of sp²-bonded carbon located within the grains with increase in the implant dose. For implantation with Si⁺ or Sn⁺ ions, a complete amorphization near to the surface was evident at a dose of 5 x 10¹⁵ 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).

T3.3

Development of Residual Stress Control in Thin Films by Substrate Vibration. Takamasa Suzuki, Yasutaka Matsubara and Akihito Matsumuro; Microsystem Engineering, Nagoya University, Nagoya City, Aichi, Japan.

The control of residual stress in thin film syntheses is very important processing in surfaces engineering. In this paper, we proposed a simple method for control of residual stress in thin films. This method can

control the residual stress by only vibrating the substrate using PZT with a voltage of up to 100V. Substrate vibration can change the residual stress in crystalline films irrespective of film thickness and substrate crystalline structure. The residual stresses are measured using Stoney's method. The results of our experiment show that for Ti, TiN films, compressive stresses are changed to tensile stresses. In order to clarify the origin of control for residual stress, the film microstructures were observed by TEM, SEM, AFM and XRD. The mechanical properties of the Ti and TiN films with the changed residual stress were then investigated. The results show that the grain size decreased while the gap between adjacent crystals at the point of coalescence increased with an increase of vibration amplitude. This is because the decrease in grain size stimulates the development of tensile stress caused by crystallite coalescence while an increasing gap in the columnar structure causes contraction in the film thus enhancing tensile stress. The mechanical properties investigated were hardness, young's modulus, friction coefficient, wear volume and adhesion strength. Hardness and Young's modulus were measured by nanoindentation. Friction coefficient, wear volume and adhesion strength were measured by ball-on-disk tribotester. Hardness and Young's modulus decrease when the residual stress changed from compressive stress to tensile stress. Friction coefficient did not change depending on residual stress. Wear volume increased when residual stress changed from compressive to tensile stress due to the effect of the decreasing hardness. Adhesion strength increased when residual stress decreases in both compressive and tensile stress. The above results show that substrate vibration can control residual stress. The mechanical properties change with the residual stress. Above all adhesion strength increases with decreasing residual stress. Therefore, substrate vibration is a simple method that can control the residual stress and mechanical properties.

T3.4

Limiting Catalytic Coke Formation by the Application of Adherent SiC Coatings via Pulsed Laser Deposition to the Inner Diameter of Tube Material Traditionally Used for Ethylene Pyrolysis Service. Alok Chauhan¹, Wilton Moran¹, Weidong Si² and Henry J. White¹; ¹Department of Materials Science & Engineering, Stony Brook University, Stony Brook, New York; ²Physics Department, Brookhaven National Laboratory, Upton, New York.

The demand for ethylene, one of the highest production chemical commodities in the world, will continue to grow as products derived from ethylene are displacing conventional materials in packaging, building, automotive and other applications. The production of ethylene involves steam cracking of feedstocks, ranging from ethane to gas oils, in the coils of a pyrolysis furnace. A range of hydrocarbons and coke are produced as byproducts. Coke formation is particularly damaging to the overall process because it accumulates on the inner walls of the tubing and eventually leads to localized increases in tube wall temperatures, poor heat transfer, increased pressure drop, reduction of inner tube diameter, tube plugging and tube failure. The production of ethylene is one of the most energy intensive processes in the chemical industry because furnace tubes must be decoked every 10 to 80 days to preserve tube life. The combination of in-service operation and decoking cycles has reduce tube life by 4- 6 years. High temperature pyrolysis of hydrocarbons has been practiced for over a half century and still ethylene producers worldwide currently consume \$400 million/ year of Fe-Ni-Cr alloy tubular products and are projected to consume \$600 million/ year by 2005. The market is typically 80% maintenance or re-tubing of existing furnaces and 20% new installations. Several researchers have attempted to limit coke formation in ethylene pyrolysis coils by adding small amounts of a variety of inhibitors to the feedstock and by changing or altering the materials of construction. Silicon based ceramics such as SiC have been identified as an attractive material for ethylene pyrolysis heater tubing due to their higher temperature capabilities relative to metals and alloys; high thermal conductivity; retention of mechanical properties at operating temperatures; and excellent thermal shock resistance. Although monolithic SiC tubing seems like a viable technology, the high temperatures and pressures experienced during operation has lead to catastrophic failures of metallic tubing and thus it will be very difficult to convince plant operators to consider "brittle ceramic tubing". As an alternative, we are proposing to limit catalytic coke formation by applying adherent SiC coatings via pulsed laser deposition to the inner diameter of tube material traditionally used for ethylene pyrolysis service. Protective coatings and coating-substrate systems are often multicomponent- multiphase systems. Complicated reactions will take place during their formation and use at high temperatures. Since diffusion underlies the self-healing mechanism of the coatings as well as the mechanism of coating degradation by interdiffusion with the substrate, knowledge of the diffusion characteristics of the system is of fundamental importance and will be described. We will also present our initial result on the transfer characteristics and stoichiometry of laser ablated SiC.

T3.5

Fabrication of Surface Nitridation Mask on GaAs Substrate for Nano-Lithography. Yo Yamamoto¹, Kohji Saito², Toshiyuki Kondo², Takahiro Maruyama^{1,2} and Shigeo Naritsuka^{1,2}; ¹Meijo 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 $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}=4:1:20$, GaAs (001) substrate was heated up to 580°C in a MBE chamber to remove the native oxide. Then, the surface of the substrate was nitrided by RF nitrogen source, changing the RF power between 200-400W, N_2 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 300 nm. On the other hand, when the substrate was nitrided 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 size of the particles was also enhanced, the formation mechanism 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 Matsumuro² and Toru Imura³; ¹Togo Seisakusyo Corporation, Aichi-gun, Aichi, Japan; ²Nagoya University, Nagoya-shi, Aichi, Japan; ³Aichi Institute of Technology, Toyota-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 which treated nanocrystalline surface layer 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 presented with the coil spring. 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 $\phi 0.25\text{mm}$ 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 $\phi 0.6\text{mm}$, projection speed is about 73m/s. Result of observation spring A, The dislocation cell structure of 100nm 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 2-3 μm , vickers hardness was about 10GPa (hardness of matrix was 5-6GPa). A metal flow layer is in the next of this nano crystalline layer. Thickness of the layer was about 5 μm . A matrix phase is in the next of this metal flow layer. A spring B is one-step shot peening, projection material is 0.6mm in diameter, and projection speed is 74m/s. The shot conditions of a spring B are the same as the 2nd step shot of a spring A. The microstructure of SPRING B consist of two phase. It is metal flow layer directly under the surface, and the next of a metal flow layer is matrix phase. Spring 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 1800 cycles/min until 107 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 $\tau_m \pm \tau_a = 600 \pm 535\text{MPa}$ at 107 cycles. And, springs B was $\tau_m \pm \tau_a = 600 \pm 490\text{MPa}$. Otherwise, this nanocrystalline surface layer improved fatigue strength 9%.

T3.8

Three-dimensional Characterization of the Morphology and Grain Orientation of a Chromium Coating. Valerie Sivel^{1,2}, S. Yu. Grachev³, G. C. A. M. Janssen³ and P. F. A. Alkemade²; ¹HREM, NIMR, Delft, Netherlands; ²HREM, Delft University of Technology, Delft, Netherlands; ³FCM, Delft University of Technology, Delft, Netherlands.

The combination of an electron beam (SEM) and a focused ion beam (FIB) was used to investigate the grain morphology in depth of a 9 micron thick chromium coating deposited on a silicon substrate in a PVD system. The top surface of the coating showed grains elongated in one direction. The FIB allowed cutting cross sections along this direction and the perpendicular one. Columnar grains were visible in SEM, wider in the direction of elongation. Next, lamella cross sections were cut with the FIB along the same directions. Electron backscattering diffraction (EBSD) was performed on each of them, in order to get information about the grains' crystallographic orientations. High quality diffraction patterns were collected on these thin specimens (100 nm). Diffracted patterns from a large set of points formed maps of the crystallographic orientations. A strong preferential orientation was thus evidenced. Besides, voids between the grains were also visible along the elongation direction, explaining the difference in stress, measured by wafer curvature, between the two perpendicular directions of the coating. The dual beam SEM/FIB combined with EBSD thus provided extensive morphological and crystallographic information about this chromium coating.

T3.9

Comparison of Hardness Enhancement and Wear Mechanisms in Low Temperature Nitrided Austenitic and Martensitic Stainless Steel. Stephan Maendl, Darina Manova, Horst Neumann and Bernd Rauschenbach; Leibniz-Institut Oberflaechenmodifizierung, Leipzig, Germany.

Nitriding of austenitic stainless steels with energetic ions between 1 and 50 keV at temperatures between 350 and 380 °C is a common process to obtain hard and wear resistant surface layers while retaining the corrosion resistance. In this temperature range, no CrN precipitates are formed, yet a fast nitrogen diffusion leads to a layer thickness of 1 - 10 μm within 1 hour. Furthermore, an anisotropic expansion of the austenitic lattice by 5 - 10% is observed. Nevertheless, the underlying physics of the formation of expanded austenite is still not fully understood. Recent experiments show that a similar effect is observed in martensitic stainless steel, where the same process conditions result in an expanded martensite structure. The relative hardness increase of a factor of 3 - 4 is similar for both materials, thus the martensitic steels with an initial higher hardness retain its advantage after the nitrogen implantation. However, the nitrogen insertion leads to the same absolute wear resistance, i.e. the wear rate is decreased by 3 - 5 orders of magnitude for austenites and 1 - 2 orders of magnitude for martensites. Investigations of the microstructure show that the initial microstructure is retained for both sorts of alloys, thus no additional precipitates are formed. At the same time, the formation of dislocations and stacking faults cannot account for the dramatic increase in hardness. Hence a metallurgical origin of the hardness increase in the modified surface layer can be ruled out for austenites as well as for martensites. It is argued that the build-up of compressive stress during the high-dose ion implantation may be responsible for the outstanding hardness properties of expanded austenite and expanded martensite, while the wear is independently determined by the nitrogen in solid solution.

T3.10

First-Principles Study of Mechanical Properties of Alumina-Copper Nano-Coating Interfaces. Shingo Tanaka¹, Rui Yang² and Masanori Kohyama¹; ¹MATSCI, UBIQEN, AIST, Ikeda, Osaka, Japan; ²Dept. of Comp. Sci., ANU, Canberra, Australian Capital Territory, Australia.

Mechanical properties of interfaces between different materials, such as ceramics/metal interfaces and semiconductor/metal interfaces, are of great importance. It is desirable to investigate the mechanical properties of such interfaces at the atomic and electronic scales. In this paper, we dealt with alumina-copper nano-coating interfaces, which were typical ceramics-metal systems frequently used in mechanical and electronic applications. Recently, we have performed the first-principles calculations of interfaces using a pseudopotential method and the first-principles molecular dynamics [1,2]. In order to clarify the stoichiometry effect, two types of the interfaces, an Al-terminated (stoichiometric) interface and an O-terminated (O-rich) interface, are treated. The stable atomic configuration of the O-rich interface is in good agreement with the recent HRTEM observation

[1,3,4]. The O-rich interface has a strong covalent and ionic bonding, whereas the stoichiometric interface has a weak metallic with partially covalent bonding. The adhesive energy of the O-rich interface is several times larger than that of the stoichiometric one [1,2]. A first-principles tensile test (FPTT) is a powerful method for investigations of the interfacial mechanical and electronic properties in micro level. In the rigid-type FPTT, we can select cleavage planes for the relaxed configuration, and the changes in the energy and electronic structure are examined for the rigid cleavage between selected planes. Using the FPTTs, we have estimated the Young modulus and the ideal tensile strength at the interface. The O-rich interface is stronger than the back Cu-Cu layer, and the stoichiometric interface is weaker than the back Cu-Cu layer. The fracture process of alumina-copper interface depends strongly on the interface stoichiometry. In the full-relaxed tensile test, the ideal tensile strength of the stoichiometric interface is rather weaker than the rigid FPTT case. The effective interatomic or interlayer potentials can be directly developed by the FPTT. Thermochemical properties of the alumina-copper interfaces strongly depend on the termination species and interfacial configurations. This work was performed as a part of Nanostructure Coating Project carried out by New Energy and Industrial Technology Development Organization. [1] S. Tanaka, R. Yang, M. Kohyama, T. Sasaki, K. Matsunaga and Y. Ikuhara, *Mater. Trans.* 45 (2004) in press. [2] R. Yang, S. Tanaka and M. Kohyama, *Phil. Mag. Lett.* 84 (2004) in press. [3] T. Sasaki, K. Matsunaga, H. Ohta, H. Hosono, T. Yamamoto and Y. Ikuhara, *J. Soc. Mat. Sci. Japan* 52 555 (2003). [4] T. Sasaki, K. Matsunaga, H. Ohta, H. Hosono, T. Yamamoto and Y. Ikuhara, *Sci. Tech. Adv. Mater.* 4 575 (2003).

T3.11

Double Interface Coatings on Silicon Carbide Fibers.

Jun Nable, Shaneela Nosheen, Steven L. Suib and Francis S. Galasso; Chemistry, University of Connecticut, Storrs, Connecticut.

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. A double interface coating had been applied onto 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 of choice were aluminum oxide and zirconium oxide 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.

Hyung-Jun Jang¹, Jae-Won Kim¹, Seong-Hwan Park¹, Seung-Soo Lee¹, Yeon-Gil Jung¹, Jung-Chel Chang² and Ungyu Paik³; ¹Ceramic Science and Engineering, Changwon National University, Changwon, Kyungnam, South Korea; ²Powder Generation Lab, Korea Electric Power Research Institute, Daejeon, South Korea; ³Ceramic Engineering, Hanyang University, Seoul, South Korea.

The effects of thermal fatigue conditions on mechanical and contact damage behaviors 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 fatigues are conducted at temperatures of 950 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 fabrication method are conducted on the TBCs surface by Hertzian contact tests. The TGO thickness is mainly depended 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 the TBCs to 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, thermal fatigue condition, 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.

Xinyu Wang^{1,2}, Sudheer Neralla^{1,2}, Cindy Water^{1,2}, Sergey Yarmolenko^{1,2}, Dhananjay Kumar^{1,2} and Jag Sankar^{1,2}; ¹Mechanical Engineering, North Carolina A&T State

University, Greensboro, North Carolina; ²Center 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 films are grown on Si (100) and Al₂O₃ 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 and adhesive properties of deposited Al₂O₃ thin films are investigated using nanoindenter 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.

T3.14

Tunable Superhydrophobic Surfaces. Jau-Ye Shiu, Chun-Wen Kuo and Peilin Chen; Research Center for Applied Sciences, Academia Sinica, Taipei, Taiwan.

Inspired by the water-repellent behavior of the micro- and nano-structured plant surfaces, superhydrophobic materials, with a water contact 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 such 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 ITO 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 Masataka 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 to 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 the wavelength. Being 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 V-UV 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 irradiating UV rays in oxygen atmosphere to change into inorganic glass. That is, the silicone oil was poured into the thin gap between the 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 siloxane 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 lamp irradiation. The results revealed that as the time of lamp irradiation increased, the absorption peak of the CH₃ group in the region of 2960 cm⁻¹ decreased but the transmittance of the light in the 190nm wavelength conversely became high. The UV transmittance of the silicone oil was 29.2% 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 of before-irradiation to 60 kgf/cm² of after-irradiation.

T3.16

Real Time Measurement of Functional Groups Substitution on Fluorocarbon Surface by ATR-FTIR. Yuki Sato and Masataka Murahara; Electrical Engineering, Tokai Univ., Hiratuka, Kanagawa, Japan.

The photochemical reaction process in substituting the functional groups on the surface of fluorocarbon [FEP] 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, the defluorination of the FEP and the hydrophilic group substitution. In surface modification, the sample surface is measured by infrared spectroscopy [FT-IR] or XPS before and after treatment for evaluation but the modification process is still a matter of conjecture. We, thus, developed a new method to measure 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 on 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 C-F 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, which has been modified into hydrophilic. 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 1190 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 3300cm⁻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 treated with water and 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. Naoki Kobayashi, Yuji Sato and Masataka Murahara; Department of Electrical and Electronic Engineering, Tokai Univ., Hiratuka, 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 for a biomaterial to have biocompatibility, chemical resistance and weather resistance. 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. Then, 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 rejections occur in the sample using 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 water to substitute the OH groups or in ammonia gas ambience 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 the ArF laser irradiation. In case of OH group substitution using the water as a reaction agent, the OH absorption

strength was observed in the region of 3300cm⁻¹; in case of NH₂ group substitution using the ammonia gas as reaction gas, the NH₂ absorption strength was appeared in the region of 3300 and 1650 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 it further improved to 38 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 FT-IR, using bovine serum albumin [ALB] and fibrin [FIB] solution as a protein index in biocompatibility test. From the results, it has been confirmed that the protein adsorption increased with the increase in the hydrophilic groups substitution density. The -OH substituted sample adsorbed the ALB and FIB more than the -NH₂ substituted sample; the amount of the albumin and fibrin sticking became 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. Yousuke Tezuka and Masataka Murahara; Electrical Engineering, Tokai Univ., Hiratuka, 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 boundary between cooling water and laser head when the lights reflect perfectly from the laser head, of which leakage causes 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 on the contact surfaces of cooling water and glass slab laser 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 coat becomes hard 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 is required. We, therefore, demonstrated photo-chemically 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 one after the other on the substrate surface. 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 250 degrees centigrade 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 antireflection coating. In conclusion, the SiO₂ film that is antireflective, inhibits evanescent wave leakage, 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. Tatsuya Mochizuki and Masataka Murahara; Electrical Engineering, Tokai Univ., Hiratuka, Japan.

The copper nuclei have been photo-chemically patterned on the fluorocarbon film surface in copper sulfate atmosphere via the reticle with just one shot of the ArF laser. In previously, we have reported 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 foil. Generally, a copper foil 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 made rough in pretreatment, which impairs its characteristics. Using the catalysts and epoxy adhesives also causes differences in a dielectric constant, generating a high frequency noise. Thus, we demonstrated the direct formation of copper nuclei on the fluorocarbon surface photo-chemically by using the Xe₂ excimer lamp and the ArF laser. Firstly, the sample surface was irradiated by the

Xe₂ excimer lamplight beforehand to modify into hydrophilic; which was then irradiated with the circuit patterned ArF laser light in the presence of copper-sulfate (CuSO₄) aqueous solution to substitute the Cu atom. The modified sample was immersed in the electroless plating solution at 60 degrees Celsius for 15 minutes, and the copper foil was locally formed on the area exposed to the light. As a result, the contact angle of the modified PTFE sample improved from 110 degrees that is of the non-treatment sample to 60 degrees, which enabled to form the Cu nuclei with only one shot of the ArF laser. It was confirmed from the result that the laser shot number depends on the contact angle of the sample surface. The highest Cu nuclei density was achieved when irradiating the Xe₂ excimer lamplight for 10 minutes and the ArF laser at the fluence of 18 mJ/cm² with the shot number of 4. Consequently, the PTFE print wiring board that possesses the properties of both metal and fluorocarbon has been developed by single shot only of the ArF laser.

T3.20
Photochemical Moisture Proof Coating on Nonlinear Optical Crystal by ArF Excimer Laser. Masaru Kojima and Masataka Murahara; Electrical Engineering, Tokai Univ., Hiratuka, Kanagawa, Japan.

Silicone oil was photo-chemically oxidized to change into SiO₂ on the crystal by using an ArF excimer laser; the protective moistureproof film has been developed for a nonlinear optical crystal that is deliquescent. The nonlinear optical crystals such as CsLiB₆O₁₀ (CLBO) and KH₂PO₄ (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 protect from moisture. We, therefore, demonstrated the growth of the SiO₂ film directly on the crystal so as to be moistureproof. 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 causes 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(CH₃)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 O atom on the substrate surface was photo-excited by the laser to generate a high active O atom; at the same time, the Si-CH₃ 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 -CH₃ adsorption 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/cm² 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 35%. 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.

T3.21
In-Plane Patterning of Functional Ceramic Thin Films via Electron-Beam Induced Selective Epitaxial Growth in Laser Molecular Beam Epitaxy. Norihiro Tateda, Atsushi Sasaki, Wakana Hara, Sei Otaka and Mamoru Yoshimoto; Materials and Structures lab., Tokyo Institute of Technology, Yokohama, Kanagawa, Japan.

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 (300K-400K) assisted by appropriate electron-beam irradiation during the pulsed laser deposition in UHV (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 as a buffer layer for AlN epitaxial growth at room temperature was deposited on the in-plane patterned sapphire substrate. Then, AlN was deposited on the selective epitaxially grown NiO buffer. As a result, the AlN thin film could be grown epitaxially on epitaxial NiO buffer region at room temperature, while amorphous AlN 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 formation of the in-plane microwalls on sapphire substrate surface. 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 Ultrasonically Joined Surfaces. Ibrahim Emre Gunduz¹, Emily D. Shattuck², Teiichi Ando¹, Peter Y. Wong² and Charalabos C. Doumanidis³; ¹Mechanical, Industrial and Manufacturing Engineering, Northeastern University, Boston, Massachusetts; ²Mechanical Engineering, Tufts University, Medford, Massachusetts; ³Mechanical 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 (4 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-β 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 0.07 at the joined surfaces of Al-Zn foils. These results support the experimental observations. It is speculated that similar 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 T_m) can assist phase transformations 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.

T3.23
Perpendicular and Parallel Diffusion of Polymers in Confined Geometries. Clive Li¹, Vladimir Zaitsev², Steven Schwarz², Miriam Rafailovich¹ and Jonathan Sokolov¹; ¹Materials Science, Stony Brook University, Stony Brook, New York; ²Physics, Queens College, Flushing, New York.

When a polymer film is thinner than twice its radius of gyration, its chain conformation will change relative to the bulk configuration, parallel to the surface. As a result, the mobility of the polymer chains in the in the direction parallel or perpendicular to the surface may be different from that in the bulk. A blend of deuterated and protonated polystyrene was allowed to migrate in thin protonated polystyrene matrixes confined by repulsive walls to study diffusion parallel to the confining walls and perpendicular to a single repulsive surface. Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) with lateral resolution approximately 0.5 μm was used to investigate the concentration profiles. We found that the motion of polymers close to the walls is enhanced in the parallel, but reduced in the perpendicular direction.

T3.24
Improving Fatigue Behavior of 316L Stainless Steel Using Glass-forming Coatings. Fengxiao Liu¹, C. L. Chiang², W. Yuan¹, J. P. Chu², P. K. Liaw¹ and R. A. Buchanan¹; ¹Materials Science and Engineering, The University of Tennessee, Knoxville, Tennessee; ²Institute of Materials Engineering, National Taiwan Ocean University, Keelung, Taiwan.

Coatings have been deposited extensively onto various substrates in order to improve the mechanical, thermal and chemical properties. Although the wear and corrosion characteristics of the coated materials can be improved, the fatigue properties are often compromised to some extent. Bulk-metallic glasses (BMGs) possess desirable properties, including extraordinary strengths, high hardnesses, excellent wear resistances, and exceptional corrosion resistances. Moreover, the BMG materials can exhibit good bending ductilities in the form of thin films. Thus, the fabrication of glass-forming coating materials to improve the fatigue behavior of structural materials becomes a challenging area for scientific studies.

The effect of the glass-forming coating on the fatigue behavior of the 316L stainless steel was investigated. The Zr-31Cu-13Al-9Ni (atomic percent) coating was deposited onto the stainless steel by 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 30 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 greatly influence the crack-initiation behavior during fatigue. 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 deposition. The fractography 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 and 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-9987548), and (3) the NSF Combined Research and Curriculum Development (CRCD) Program (DGE-0203415) with Dr. C. McHargue, Dr. W. Jennings, Dr. L. Goldberg, Dr. L. Clesceri and Ms. M. Poats as the contact monitors, respectively, and (4) the National Science Council of Republic of China in Taiwan (NSC92-2216-E-019-004).

T3.25

Study of Fundamental Interaction Mechanisms between Methane Plasmas and Nanostructured Catalysts in the IMPACT Facility. Martin de Jesus Nieto, Jean Paul Allain and Ahmed M. Hassanein; Energy Technology, Argonne National Laboratory, Argonne, Illinois.

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 advance 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. If combined with a plasma-assisted process, the synergy between the catalyst structure and the delivery of energy in the form of ionization and radical formation may make the process even more efficient 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 is well suited 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 and 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 operating 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. Phani Ratna Ayalamayajula¹ and James Krzanowski²; 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 metallization schemes, rectifying and ohmic 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 10mTorr background pressure of N₂. Si (111) and AISI 440C 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 200°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 400°C and shown preferential growth (111) at 600°C substrate temperature. The deposited films exhibited densely packed grain, with smooth and uniform structures. In both the cases single phase of TiN and CrN with 10% of O in the deposited films were observed. X-ray Photoelectron Spectroscopy (XPS) analysis of the films showed and 50% Ti and 40% of N in TiN films, 45% of Cr and 45% of N in CrN films deposited on Si (111), indicating near stoichiometric composition of the deposited nitride thin films. Fine grains of the TiN and CrN were observed by scanning electron microscopy. Hardness of the films changed from 22 GPa at 200°C to 30 GPa at 600°C in case of TiN, where as for CrN 26 GPa at 200 °C to 31 GPa at 600°C. Residual stress of the films have shown a change of compressive stress at 200 oC to tensile stress at 600°C in both the cases. Friction coefficient of the films were measured by Pin-on Disc technique for all films, up to the tested limit of 10,000 cycles at 1 N load and found to be very high 1.2 in both cases.

T3.27

The Use of Closely Spaced Vickers Indentation to Predict Erosion of Polycrystalline α -Al₂O₃. Adolfo Junior Franco and Steve George Roberts; Matematica e Fisica, Universidade Catolica de Goias, Goiania, Goiania, Brazil.

A wear map was constructed based on closely spaced quasi-static indentation loads arrays (square grids of 9 indents) produced by pyramidal diamond indenter (Vickers indentation) on each specimen (at room temperatura) performed on polycrystalline α -Al₂O₃, mean grain size G=1.2, 3.8 and 14.1 μ m. This was to simulate the observed erosion mechanism fo crack linkingh 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 (specimen G=14 μ m) due to 9 indentation were analysed. The wear maps based on closely spaced arrays of quasi-static indentation may thus be a guideline for predicting the wear resistance fo 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. Dellas 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 materials with high resistivity above 5000 $\mu\Omega$ cm. We found that the resistivity increases exponentially with 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 stationary substrate placed above silver and SiO₂ sputtering sources. This configuration allowed compositions 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

T3.31

Nanoscale-Surface Control and Patterning of Functional Thin Films by Using Thermal Flow of Silicate Glass Ultra-Thin Films. Shusaku Akiba, Akifumi Matsuda, Takashi Okada, Fumihiko Wakai, Takashi Akatsu and Mamoru Yoshimoto; Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Kanagawa, Japan.

Although glass materials surface-controlled at a nanoscale have possibility to develop new functionalities of nano-electronics, very few attempts have been made to investigate nano-scale behavior of glass at high temperatures. Softening behavior and viscous flow resulting from the supercooling state, which is characteristics to 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 glass 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 1000 °C (Appl. Phys. Lett. Vol. 67 (1995) 2615). The glass thin films (about 3 nm 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 process 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 roughening caused by 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 nanoimprint 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 Surface Coating for Silicon Carbide Whiskers. Heng Zhang, D. T. Xiao and David Reisner; Inframat Corporation, Farmington, Connecticut.

A mullite coating process has been conducted to form an electrical insulating layer on the surface of the silicon carbide whiskers for whisker enforcement application by a chemical deposition and hydrolysis. The phase, structure, morphology and electrical insulating property of the coated silicon carbide whiskers have been investigated by using x-ray diffraction, scanning electron microscopy and electrical measurement. The study indicates that a mullite coating layer can form after heat treating the precursor coating at high temperature. The formed mullite 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-C3058

T3.33

Adhesion Improvement of CVD Diamond Coatings on WC-Co Substrates for Machining Applications.

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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-cemented carbide inserts has been investigated. 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 migrations 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 °C for 6 hours. Rockwell indentation 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 Raman and X-ray diffraction methods.

T3.34

New Process Development for Low Temperature Deposition using Metal-Organic Plasma CVD. Seok-Jae Son^{1,2}, Jens

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TiCN layer as a under layer and DLC or Si-DLC layer as a top were deposited on a 100Cr6 and WC by using dimethylaminotitanium (diethylaminotitanium), 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 profile at the component surface-tappet is required to satisfy the uniform quality of specimens. And to satisfy this, appropriate gas inhalation and exhaustion system has to be adopted. But whole size scale experiment of the chamber is somewhat uneconomical and time-consuming. So numerical simulation approach for the phenomena in MO-PACVD system using FLUENT6.0 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 determining 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 was depends on the gas outlet system.

T3.35

Corrosion Resistance of Boronized Steel. Roumiana S. Petrova and Naruemon Suwattananont; 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 prepared by powder boronizing method at 850°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 catastrophe of metals and alloys in the severe environments.

T3.36

High-Speed Processing with Reactive Cluster Ion Beams.

Toshio Seki and Jiro Matsuo; 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 process. A cluster is an aggregate of a few to several thousands atoms. When many atoms constituting a cluster ion bombard 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 with using reactive cluster ion beams. Reactive cluster ion beams, such as SF₆, CF₄, CHF₃, 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 5-65 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 4600 atoms/ion at 65 keV. With this beam, 12 inches wafers can be etched 0.5 μm per minute at 1 mA of beam current. The TOF measurement showed that the size of SF₆ cluster was about 500 molecules and the number of fluorine atoms in a SF₆ cluster was about 3000. If the sputtered product was SiF, the yield has to be less than 3000 atoms/ion. 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 nano-devices. 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 Bottgger and Wim Sloof; Department of Materials Science and Technology, TU Delft, Delft, Netherlands.

Experimental values for segregation energies or surface energies are difficult to obtain. Surface (segregation) energies of metals can be related to peak shifts caused 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 life-time broadening of their photoelectron peaks. In this experimental study of single crystalline copper a new approach to XPS-profile fitting is applied, which allows to discern the contributions of surface and bulk to the spectra. It was demonstrated that the photoelectron response strongly depends on the type and quality of surface. Proper account for these factors in experimental setup and fitting routines allowed us to separate the surface contribution to the total XPS-intensity and to report the first successful extraction of surface core-level shifts for copper (100) and (111) surfaces. The experimental results are compared to the surface energy estimations obtained by the semi-empirical Miedema macroscopic atom model. The experimental results are found in a good agreement with the model estimates. The method can be applied for further studies on surface thermo-chemical properties for other metals of 3-d transition series.

T3.38

Pseudomorphic stabilization on crystal structure and mechanical properties of nanocomposite Ti-Al-N thin films.

Ayat Karimi, Themistoklis Vasco and Antonio Escudeiro Santana; Basic science, EPFL, Lausanne, Switzerland.

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 nanolayered thin films and recognized to 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 reduced below 10 nm. For this purpose, a series of Ti_{1-x}Al_xN 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 AlN, or nanocomposites of fcc-TiN, fcc-AlN, and wurtzite AlN appeared 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 AlN growing in their natural structures with misfit dislocation at the interface to relieve the strain. In contrast, further hardness enhancement was measured when nanocomposite with coherent interfaces were formed due to pseudomorphic stabilization of fcc-AlN on fcc-TiN crystallites. In this paper different hardening mechanisms operating in solid solution and nanocomposite films will be developed and discussed.

T3.39

Morphological and Compositional Analysis of the Formation of PtSi Films for subsequent mid-IR Characterisation. Shane M. O'Prey¹, **Paul Dawson**¹ and Harold S. Gamble²; ¹School of Maths & Physics, Queen's University of Belfast, Belfast, United Kingdom; ²School of Electronic & Electrical Engineering, Queen's University of Belfast, Belfast, United Kingdom.

Since platinum silicide (PtSi) forms a low Schottky barrier on p-Si(100), typically 225 meV, the PtSi/p-Si system has been used extensively in IR imaging sensors. Despite this application the infrared data on PtSi are not comprehensive, especially at low temperatures. Here PtSi is used as a test material for mid-infrared ($\lambda = 3.392 \mu\text{m}$), attenuated total reflection (ATR) characterisation in a novel prism coupler device. (This comprises of an in-vacuo prism/gap/sample arrangement where the gap dimension is remotely adjustable by means of piezo-actuators; the technique is similar to optical SPM technology except that a probe surface - rather than tip - is positioned relative to the sample with sub-100 nm precision. It is, in effect, an optical tunnelling arrangement.) However, the assumption of complete PtSi formation upon annealing a pre-deposited layer of Pt on Si must be critically assessed; the typical annealing conditions used here are a temperature of 600°C for 20 min. in a nitrogen atmosphere. Examination by atomic force microscopy (AFM) of both e-beam and sputtered Pt films reveals a very marked increase in the apparent grain size from 20-30 nm pre-anneal to 100-200 nm post-anneal. Investigation of the films was therefore extended to X-ray diffraction (XRD) and Auger electron spectroscopy (AES). The XRD data clearly show the presence of a significant Pt signal post-anneal, in addition to many of the PtSi crystal orientations typically observed, notably (110), (101), (220) and (130). The large granular structures in the AFM images of the post-anneal films are identified as Pt by the

introduction of an etch in aqua-regia. This etch removes residual Pt, confirmed by the disappearance of the Pt peak in XRD analysis; coincident with this is the disappearance of the large granular structures from AFM images and the recovery of a fine-grained (PtSi) structure, suitable for optical measurement and analysis. The failure of the Pt to react completely with the Si substrate, with some instead nucleating to eventually form the large Pt droplets is often attributed to the presence of oxygen and the consequent formation of an oxide barrier that inhibits the diffusion of the interacting Pt and Si atoms. The presence of an oxide component is confirmed in the AES data, though the origin of the oxygen introduction is not clear. Infrared results on the PtSi films will be presented. These constitute the detailed measurement of a set of ATR curves for different values of the coupling gap in the in-vacuo prism coupler at the HeNe laser wavelength of 3.392 μm . Fitting theoretical reflectance data to a set of such curves using the same dielectric function (and varying only the coupling gap dimension) imposes tight constraints on that dielectric function as a fitting parameter. The dielectric function for a 17 nm thick PtSi film is found to be $-100 + i 69$ at 300 K, but it is strongly dependent on film thickness.

T3.40

Tribological Aspects of Aluminum Nitride-Titanium Nitride Thin Composite Films.

Cindy Waters¹, Xinyu Wang¹, Sergey Yarmolenko¹, Dhananjay Kumar¹ and Jaq Sankar¹; 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 have good micromechanical and tribological properties. The adhesion, fracture 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 durability and functionality of thin films is subject to 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 this 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 those relative results compared to their fracture toughness 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.

T3.41

Pentacene Nucleation and Growth on Chemically Modified Si(001) Surfaces.

Kevin P. Weidkamp¹, Rudolf M. Tromp² and Robert J. Hamers¹; ¹Department of Chemistry, University of Wisconsin-Madison, Madison, Wisconsin; ²IBM Research Division, T.J. Watson Research Center, Yorktown Heights, New York.

Because of its high mobility and compatibility with plastic substrates, pentacene has been the subject of much study in the area of organic and molecular electronics. The growth of pentacene thin films 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. Cyclooctadiene, which on Si(001)2x1 forms an ordered array of exposed C=C double bonds, and cyclopentene, 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 time" that occurs when growing on clean Si(001)) and leads to very large pentacene grains (as large as 0.2 μm 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.

T3.42

Mechanical Relaxation Processes in Amorphous Diamond-like Carbon Oscillators.

David A. Czaplowski¹, John P. Sullivan¹, Thomas A. Friedmann¹, Dustin W. Carr², Bianca E. N. Keeler² and Joel R. Wendt²; ¹Nanostructure and Semiconductor Physics Department, Sandia National Laboratories, Albuquerque, New

Mexico; ²Sandia National Laboratories, Albuquerque, New Mexico.

Tetrahedral amorphous diamond-like carbon (ta-C) films are useful for the fabrication of wear-resistant micro-electromechanical systems (MEMS) and the creation of small, high frequency mechanical oscillators that are resistant to stiction and auto-adhesion. Mechanical oscillators have found widespread use in electronics (as clocks, filters, switches, etc.), sensors (for chemicals, biological agents, pressure, acceleration, etc.), and metrology (scanning probe microscopy). Miniaturization of the mechanical oscillators leads to higher operating frequencies and the potential for increased sensitivity. It has been commonly observed, however, that miniaturization leads to increased mechanical dissipation, and these mechanisms of dissipation are poorly understood, especially in structures at the micro- to nano-scale and in disordered or amorphous materials. In this work, we report the properties of micro-scale and nano-scale mechanical oscillators fabricated out of ta-C. This ultrahard material (about 80% sp³ bonding) has a large Young's modulus (about 700 GPa) and an abrupt surface termination – properties that favor high resonance frequencies and low surface losses. Three types of oscillator structures were produced, cantilevers with out-of-plane vibration modes, cantilevers with in-plane vibration modes, and free-beam oscillators. The resonant frequency for these oscillators ranged from about 1 KHz to over 5 MHz. Throughout this frequency range, a constant quality factor of about 3×10^3 was observed. The magnitude of the dissipation is similar to that which has been observed in a broad range of amorphous materials at low temperatures. We have compared the dissipation in these oscillators with the calculated dissipation due to thermoelastic dissipation, dissipation due to phonon-mechanical vibration interaction, mechanical clamping losses, and dissipation due to defects in the material. The observed dissipation is only consistent with dissipation due to a spectrum of defects. Over the frequency range that we have observed, the apparent activation energies for the defect-related mechanical relaxation range from about 0.3 eV to over 0.5 eV. These activation energies are lower than the interstitial or vacancy migration energies in crystalline diamond, suggesting that the defects giving rise to mechanical relaxation act locally, i.e. they do not involve long range diffusional processes. 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.

T3.43

Characterization of Electrochemically Activated Surface on Rolled Commercial AA8006 Aluminium. Yingda Yu¹, Oystein Sevik¹, Jan Halvor Nordlien² and Kemal Nisancioglu¹; ¹Department of Materials Technology, Norwegian University of Science and Technology, N-7491 Trondheim, Norway; ²Hydro Aluminium R&D Materials Technology, N-4256 Håvik, Norway.

Commercial alloy AA8006 (nominal composition in wt % 1.5Fe, 0.4Mn, 0.2Si) exhibits electrochemical activation in chloride media as a result of annealing at temperatures above 350 °C. Activation is manifested by a significant negative shift in the corrosion potential and a significant increase in the anodic current when polarized above the corrosion potential in aqueous chloride solution. This phenomenon was correlated with the enrichment of trace element Pb at the oxide-metal interface [1]. This work presents a more detailed electrochemical characterization of activation as a function of annealing temperature in the range 350 - 600 °C on as-received and etched surfaces, combined with SEM, TEM, and GD-OES characterizations. For fixed annealing time, maximum activation and Pb-enrichment are obtained at an annealing temperature of 450 °C independent of the original surface condition. Reduced activation with increasing temperature is attributed to evaporation of enriched Pb and its entrapment in a growing thermal oxide. The cause of activation is attributed to reduced passivity of the oxide caused by Pb segregation at the alloy surface as a result of heat treatment and selective oxidation of the aluminum component during corrosion. [1] J.W. Keong, J.H. Nordlien and K. Nisancioglu, J. Electrochem. Soc., 150, B547 (2001).

SESSION T4: Mechanical Properties of Surfaces,
Interfaces and Thin Films
Chairs: Vladislav Domnich and Michael Nastasi
Wednesday Morning, December 1, 2004
Room 203 (Hynes)

8:30 AM T4.1

Competition between Tensile and Compressive Stress Mechanisms during the Growth of Polycrystalline Films and Coatings. Abhinav Bhandari, Brian W. Sheldon, Eric Chason and Rod Beresford; Division of Engineering, Brown University, Providence, Rhode Island.

Both tensile and compressive intrinsic stresses are known to occur during the growth of polycrystalline films and coatings. A number of models 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 that increasing the growth rate leads to significant increases in 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, tensile stress creation 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 hard 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, variations in 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 T4.2

Stress Evolution in Chemically Vapor Deposited Nanocrystalline Diamond Film. 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 1% methane, 2-10% hydrogen and balance argon. The residual and intrinsic 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. Raman spectra revealed that 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/π-bonding at grain boundaries can be modified to produce significant variations in the residual stress in these films. The hydrogen plasma treatments were also used to modify stress 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 *T4.3

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 (σ_0), intrinsic fracture energy (G_0), and the total or the overall fracture energy (G_c) are parameters typically used to characterize the interfacial fracture process. The intrinsic strength and intrinsic fracture energy are related via the interface's atomic 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 G_0 and the plastic dissipative work (G_p). Since G_p depends upon 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 experiment which uses a laser-induced stress wave to separate the interface, while the intrinsic and total fracture energies are measured using a double cantilever beam experiment performed at ambient and cryogenic temperatures, respectively. In the first part of the talk, relationships between G_c and G_0 , and between σ_0 and G_0 , for interfaces between sputter-deposited polycrystalline Ta coatings and sapphire substrates will be presented. Relationships 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 (basal and prismatic), while Gp was varied by changing the test temperature (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 disclosed that improves the long term durability of the steel/E-glass joints by a factor of five. This information allows a robust design of such joints in newer types of lightweight ship structures. In the last part of the talk, a modified laser spallation technique is discussed which allows in-situ measurement of the solder joint strength in freestanding and board-mounted chip-scale packages. The technique is shown to be rather sensitive to the joint microstructure. This is shown by presenting the strength data on a matrix of samples made from eutectic and Pb-free solders, stressed by baking for specific temperatures and times. The substrate chemistry was also varied. The corresponding changes in the joint microstructures were obtained using SEM and FIB microscopy

9:30 AM T4.4

Structural Nanocomposite Bonding Reinforced by Graphite Nanofibers with Surface Treatments. Luoyu Roy Xu, Charles M.

Lukehart, Lang Li, Ping Wang and Sreeparna Sengupta; Civil and Environmental Engineering, Vanderbilt University, Nashville, Tennessee.

Graphitic carbon nanofibers (GCNFs) are attractive additives for fabricating carbon nanofiber/polymer composite materials of enhanced mechanical and physical properties due to their unusual atomic structures. Each GCNF atomic structure presents a unique, reactive surface and atomic spatial arrangement to an external polymer matrix, thus permitting a wide range of options for promoting GCNF/polymer binding. In this investigation, based on the herringbone GCNF with linker molecule bearing a pendant amino functional group, which was developed at Vanderbilt University, nanofiber/epoxy composites with selected weight fractions of nanofibers were fabricated as structural adhesives. Good wettability and uniform distribution of nanofibers in a polymer matrix are major efforts to obtain the resulted nanocomposites with excellent properties. Basic mechanical property characterizations including tension, shear and fracture tests of the nanocomposite bonding are conducted. Excellent wetting of the nanofiber inside epoxy resin was achieved in the nanocomposites. In order to obtain well-distributed nanofibers in epoxy resin, sonication was employed to mix the nanofiber and epoxy resin blends at different energy levels. Preliminary results from both mechanical measurement and thermomechanical analysis show that appropriate sonicating energy applied to the hybrids can uniformly distribute the fibers in epoxy resin, and thus, nanocomposites with improved mechanical properties could be obtained. Material structural analysis using electron microscopy is underway along with mechanics modeling for these nano-fiber composites.

9:45 AM T4.5

Elastic Properties of Silicon Nanoplates. Hyun Woo Shim¹, L.

G. Zhou¹, Hanchen Huang¹ and T. S. Cale²; ¹Department of Mechanical, Aerospace and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, New York; ²Department of Chemical Engineering, Rensselaer Polytechnic Institute, Troy, New York.

We report atomistic determinations of elastic properties of silicon nanoplates. Using the Stillinger-Weber and the Tersoff potentials, we have determined the Young's moduli of silicon nanoplates of various thicknesses with various surface orientations. Selected results are validated using ab initio calculations. Our results lead to two conclusions. First, the Young's moduli depend on the nanoplate thickness, and they may be larger or smaller than their bulk counterparts. Second, surface reconstruction affects the Young's moduli, and leads to substantial softening. The numerical results of the elastic properties of silicon nanoplates are discussed in connection with NEMS applications.

10:30 AM *T4.6

Tribological Applications of Microscopic Shape Memory and Superelastic Effects. Yang-Tse Cheng¹, Wangyang Ni^{1,2} and David

S. Grummon²; ¹Materials and Processes Lab, General Motors Research and Development Center, Warren, Michigan; ²Department of Chemical Engineering and Materials Science, Michigan State University, East Lansing, Michigan.

Although the macroscopic shape memory (SM) and superelastic (SE) effects are well known, very few studies have been conducted to investigate the SM and SE effects at the micro- and nano-meter length scales. Recently, we have investigated these effects in NiTi

alloys 1-3 and thin films by instrumented indentation experiments. The SM effect was quantified by the magnitude of the depth recovery of indents upon heating; the SE effect was determined by the ratio of reversible work to total work. We show that SM and SE effects exist under both spherical and pyramidal indenters for a wide range of indentation loads and depths. We have also performed scratch adhesion and wear studies in bulk and thin film shape memory 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 applications. In this paper, we provide several 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 materials. 1. W. Ni, Y.-T. Cheng, D. S. Grummon, "Recovery of microindents in a nickel-titanium alloy: a 'self-healing' effect," Appl. Phys. Lett. 80, 3310 (2002). 2. W. Ni, Y.-T. Cheng, D. S. Grummon, "Microscopic superelastic behavior of a nickel-titanium alloy under complex loading conditions," Appl. Phys. Lett. 82, 2811 (2003). 3. W. Ni, Y.-T. Cheng, D. S. Grummon, "Microscopic shape memory and superelastic effects under complex loading conditions," Surface and Coatings Technology 177-178, 512 (2004).

11:00 AM T4.7

Control of Strain Gradients in Tetrahedral Amorphous-Carbon Thin Films for MEMS Applications.†

Thomas A. Friedmann and J. P. Sullivan; Sandia National Laboratories, Albuquerque, New Mexico.

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 ta-C as the structural layer in the fabrication of many devices (e.g. electrostatic comb-drive actuators, nanomechanical resonators, and microtensile 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 m. 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. With 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 furnace annealed films. We will 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.

11:15 AM T4.8

Control of Stress in Surface Engineered Silicon. Yue Ma, Reinhard Job, Wolfgang Duengen, Yuelong Huang and Wolfgang R. Fahrner; Electrical Engineering and Information Technology, University of Hagen, Hagen, Germany.

Hydrogen plasma treatments applied on (100)-oriented standard Czochralski silicon (Cz Si) wafers cause a structuring of the surface regions on the sub-100 nm scale. The reconstruction of the nano-structured surface layers by high temperature annealing induces strong stress (about 3.0 GPa) at the surface and in the subsurface regions of the wafers, as can be verified by depth resolved micro-Raman spectroscopy. Although the H-plasma caused nano-structured surface layer is very thin (100-200 nm), the stressed subsurface regions of the annealed samples are quite extended, i.e. up to about 10 μ m depth. The impacts of several process parameters including 1) the doping type of the wafer substrate, 2) the frequency of the hydrogen plasma, 3) the duration of the hydrogen plasma exposure, 4) the temperature of the post-hydrogenation annealing, and 5) the duration of the post-hydrogenation annealing on the depth distribution of the stress are investigated. The elucidation of the observed stress is found with atomic force microscopy (AFM). AFM

analysis gives a strong hint that the reconstructed wafer surface is (111)-oriented, in contrast to the (100)-orientation of the underlying wafer substrate. Due to this discrepancy the appearance of stress is evident. The stressed region in the surface engineered silicon wafer can be controlled by the process parameters. The presented results might be important for various applications in semiconductor technology. For example, the H-plasma exposure could be done in local areas near electrically active regions on the forefront of the wafer. After appropriate annealing, stressed local regions for external getter purposes can be created. Such a method might especially be useful for the formation of getter regions on SOI substrates.

11:30 AM T4.9

Buckling Failure of Compressive Loaded Hard Layers in Flexible Devices. Piet Bouten¹ and Marcel van Gils²; ¹Philips Research Laboratories, Eindhoven, Netherlands; ²Philips Centre for Industrial Technology, Eindhoven, Netherlands.

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 outwards. The buckles have a characteristic width and height. These sizes might be used in the analysis of the compressive strain, present in the layer before failure, and the adhesion quality of the failed interface. In an experimental study, the compressive strain of a 100 nm ITO layer on top of an elastoplastic polymer substrate is estimated from three different techniques: curvature of the sample, hot stage microscopy and profile measurements. Using the measured curvature of the sample before failure an estimate of the stresses and strains can be derived using Stoney's formulas. With hot stage microscopy the failed sample is heated and the buckling profiles disappear at a specific temperature. From profile measurements on the buckle two length are compared: along the buckle and the base length. The three techniques give quite different estimates of the compressive strain. To resolve these inconsistencies, a finite element model is used to analyse 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 of the analysed system. The large elastic mismatch between polymer substrate and the applied inorganic layer together with the plastic deformation in the substrate seriously affects the dimension of the buckle. Due to the deformation of coating and substrate adjacent to the buckle, the buckle height 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 6H-SiC. Jennifer Huening¹, Mengning Liang¹, John A. Patten², Leah Bergman³, Xiang-Bai Chen³, Jae-il Jang⁴, George M. Pharr⁴ and Robert J. Nemanich¹; ¹North Carolina State University, Raleigh, North Carolina; ²Western Michigan University, Kalamazoo, Michigan; ³University of Idaho, Moscow, Idaho; ⁴The University of Tennessee and Oak Ridge National Laboratory, Knoxville, Tennessee.

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 6H-SiC and provides evidence of their bonding structures. In these materials, the short absorption depth of UV light allows for accurate probing of the surface 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 μ m depths. Wavelength

dependence analysis provides information on the depth of the amorphous zone. The study on 6H-SiC included measurements of machined basal plane surfaces and edges of (0001) wafers. For machined wafer edges, the structure is found to change when machined on the (01 $\bar{1}$ 0), (1 $\bar{1}$ 20), 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 indentations 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. *Research supported by the NSF FRG 0203552*

SESSION T5: Ion Beam, Laser and Plasma
Modification of Surfaces
Chairs: Soumendra Basu and James Harper
Wednesday Afternoon, December 1, 2004
Room 203 (Hynes)

1:30 PM *T5.1

Simultaneous Effects on Topography, Composition and Texture in Ion Assisted Deposition of Thin Films.

James M.E. Harper, Physics, University of New Hampshire, Durham, New Hampshire.

Ion bombardment during deposition may simultaneously affect thin film topography, composition and crystallographic texture. Ion etching can produce periodic ripples that depend on the angle of ion incidence and surface temperature. When applied during deposition, ion bombardment can produce in-plane crystallographic orientation in some materials for specific angles of incidence. In addition, ion bombardment changes the composition of multicomponent thin films according to the local angles of ion incidence and ion/atom ratios. Therefore, these three 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

Growth of Nanostructured GaN Thin Films by Matching Surface Diffusion Length with Ion-Induced Template.*

Bentao Cui^{1,2}, Phillip I. Cohen² and Amir M. Dabiran³; ¹Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota; ²Department of Electrical and Computer Engineering, University of Minnesota, Minneapolis, Minnesota; ³SVT Associates, Inc, Eden Prairie, Minnesota.

Periodic nano-patterns, such as ripple, dots, or dimples, can be produced by low-energy ion bombardment [1, 2] of a surface. We report a novel growth method using these nanostructured materials - epitaxial growth on ion-bombarded templates. The net growth rate is slightly reduced by the sputter rate. The production of periodic GaN nano ripples and dimples using this technique was first examined. Ga was provided by a thermal effusion cell from a gas MBE system; ammonia was used as the nitrogen source. A hot-filament Kaufman ion source and an RF source were used to supply sub-keV ions near glancing incidence. Desorption Mass Spectroscopy (DMS) was used to calibrate the growth temperature and the growth rate. During the growth, the surface morphology and film quality were monitored in situ by Reflection High Energy Electron Diffraction (RHEED). AFM was used to examine the surface morphology post growth ex situ. Dimple structures with diameters ranging from 90 nm to 800 nm, have been produced using both argon ions and nitrogen ions with energies ranging from 100 -1200 eV. The samples were rotated at 1.2 rpm to avoid ripple. Layer-by-layer removal of multilayer steps at the edges of GaN islands was observed at various sample temperatures. The terrace length of the debunched steps decreases with sample temperature and the terrace length increases with ion sputtering time. The slope of the dimple sides were less than the ion incidence angle. Small, adatom clusters were found at the edges of the debunched steps at room temperature. The separation between adatom clusters along the step edges decreases with ion energy. A novel growth mode can be achieved by combining ion induced step debunching and step flow growth on the terraces of the debunched steps. * Partially supported by the National Science Foundation and the Air Force Office of Scientific Research. 1. J. Erlebacher, M. J. Aziz, E. Chason, M. B. Sinclair, and J. A. Floro, Phys. Rev. Lett. 84, 5800 (2000). 2. S. Facsko, T. Dekorsy, C. Koerdert, C. Trappe, H. Kurz, A. Vogt et al., Science 285, 1551 (1999).

2:15 PM T5.3

Surface Engineering of Ti-6Al-4V and Co-Cr-Mo surfaces by pulsed intense ion beams for in-body applications*.

Timothy J. Renk¹, Paula P. Provencio¹, Somuri V. Prasad¹, Thomas

D. Petersen² and Donald W. Petersen³; 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 alloys 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 surface to multiple pulses from an intense ion beam. The 200ns ion pulse produces fast melt and cool cycles (10^9K/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 is a mixed 20at% Hf/80at% Ti layer, and with the 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 microstructure of treated samples was investigated by cross-sectional high resolution transmission electron microscopy (HRTEM), annular dark-field scanning TEM (STEM), and selected area electron diffraction (SAD). Compositional changes were measured by nanobeam energy dispersive spectroscopy (EDS) and energy filtered TEM imaging. Treated layers are subjected to tribological testing, to study the relation between the microstructures and friction and wear behavior. In the Hf/Ti case, improvements in friction and wear behavior are observed, compared to both untreated and uncoated/treated Ti alloy. In addition, a suspension of live Soas-2 cells was added to treated and sterilized Hf/Ti samples. Hexosaminidase enzyme activity was checked at 3 and 7 days, and shows significant increase over the control sample, indicating good biocompatibility of the treated surface. Corrosion testing showed the treated surfaces to have excellent corrosion resistance, similar to untreated controls. *Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Co., under US DOE Contract DE-AC04-94AL85000.

2:30 PM T5.4

On the Erosion of Material Surfaces caused by Electrical Plasma Discharging. Flavio Andres Soldera and Frank Muecklich; Materials Science - Functional Materials, Saarland University, Saarbruecken, Saarland, Germany.

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 methods 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 discharges made on electrodes, which are externally heated. It was shown, that in certain systems, e.g. intermetallic compounds, the surface can be additionally stabilized by controlling the protecting oxide coatings.

2:45 PM T5.5

Low Damage Smoothing of Magnetic Materials using Oblique Irradiation of Gas Cluster Ion Beam. Shigeru Kakuta^{1,2}, Shinji Sasaki^{1,2}, Kenji Furusawa^{1,2}, Toshio Seki^{2,3}, Takaaki Aoki^{2,3} and Jiro Matsuo³; ¹Storage 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 over the disk has 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) technology can provide ultra-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 components and structures. Before using the GCIB as 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 for a smoothing process using monomer 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 90°. In this paper, irradiation damages such as Ni/Fe 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 GCIB irradiated NiFe films were observed 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 decreasing thicknesses of Ni/Fe composition ratio changed layer and oxide layer. At normal GCIB irradiation with an acceleration voltage of 20 kV and a dose of 1×10^{15} ions/cm², the thicknesses of composition ratio changed layer and oxide layer increased, respectively, by 3 and 5 nm compared with 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.

3:30 PM *T5.6

Intrinsic Stress in Ion Synthesized Materials. Michael Nastasi, Los Alamos National Laboratory, Los Alamos, New Mexico.

The presence of intrinsic stresses in coatings and ion modified surfaces can be shown to be related to defects, microstructure, interfaces, and incorporated impurities. Typically, thin films formed by thermal evaporation have a high void fractions (i.e., low atomic density) and are in a state of residual tensile stress. Experience has shown that when thermally evaporated films are deposited with the aid of an ion beam, the microstructure begins to densify allowing even higher attractive interactions between adjacent atoms which can further increase the tensile stress to a maximum. Under high flux ion bombardment significant atomic compaction can occur, resulting in greatly increased densities which can drive the stress levels to a highly compressive state. In general most of these processes are assumed to occur athermally. However, past and recent experiments have shown that ion irradiation not only stimulates the evolution of stress, but that the evolving stress impacts the kinetics and thermodynamic driving forces which are responsible for steady state configuration of the material. In this lecture we will explore the atomic origins of stress and examine how ion bombardment can be used to engineer the stress in ion synthesized materials.

4:00 PM T5.7

Molecular Dynamics Study of Sputtering Process by Reactive Cluster Impacts. Takaaki Aoki and Jiro Matsuo; Quantum Science and Engineering Center, Kyoto University, Kyoto, Japan.

For the last decade, the surface modification processes utilizing the impact of large cluster ions have been proposed. Gas cluster ion beam (GCIB) can be generated not only from rare-gas materials such as Ar but also from reactive materials such like 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, when a cluster ion 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 a (F₂)₅₀₀ impacts on Si cluster with 6keV of total incident energy (=10eV/F atom), a crater-like structure with many F atoms absorbed is formed on the

target. As the number of F cluster impact increases, F atoms are accumulated on the surface and many Si-F precursors are formed in high-density. The Si etching yield also increases; after 40 impacts of F cluster impacts on $160\text{\AA} \times 160\text{\AA}$ ($=1.5 \times 10^{13}/\text{cm}^2$), about 150 Si atoms were desorbed from the surface with one cluster impact. The analysis about sputtered particles showed that most of Si atoms desorb as fluoridized molecule such like SiF_2 or SiF_3 . This result suggests that cluster impact enhances the chemical reaction. Through these results, the characteristics of sputtering process by reactive gas cluster impact will be discussed. This research is supported by New Energy and Industrial Technology Development Organization in Japan.

4:15 PM T5.8

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 individual layer period ranges from 3 nm up to 50 nm. It is shown that PVD-produced thin films down to a few nm-period show individual metallic layers without any intermetallic formation. The morphology of such thin multi-films is studied. The periodical formation of intermetallics by the interference pattern of two coherent Nd:YAG-ns-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 depth is relatively independent from the layer period to be around 100 nm for a ns-laser pulse.

4:30 PM T5.9

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

HfO_2 has generated attention in recent times as a new gate material for field effect transistors. However, many problems exist such as phase transformation after annealing and interface instability. Previously we showed that a N_2/He plasma as a reaction gas can inhibit O_2 diffusion and oxidation at the interface by the formation of a Si-O-N layer at the insulator/Si substrate interface.* In this work we explore a method of depositing a SiO_xN_y layer using a N_2/He plasma before HfO_x deposition. The Si substrate was nitrified and annealed at 650°C in the reaction chamber for 2 minutes before the hafnium precursor deposition. Films with a total thickness of about 40\AA were annealed at 800°C in an argon ambience for 2 minutes. The results show that a nitrated silicon layer thickness of 16\AA is appropriate to prevent diffusion and oxidation at the interface during the anneal. In these films the x-ray photoelectron spectra of the Si_{2p} peak at 102.5 eV binding energy, corresponding to a silicon oxynitride, have a smaller peak shift after anneal than the untreated substrate, and also the Si_{2p} peak of the underlying substrate at 99.7 eV has a smaller intensity change corresponding to a smaller thickness increase which is confirmed by ellipsometry. * Accepted for publication in Applied Physics Letters

SESSION T6/R10: Joint Session: Indentation and Phase Transformations

Chairs: William Gerberich and Neville Moody
Thursday Morning, December 2, 2004
Room 202 (Hynes)

8:30 AM T6.1/R10.1

Nanoindentation of SiGe thin films. Jodie E. Bradby¹, James S. Williams¹ and Michael V. Swain²; ¹Electronic Materials Engineering, The Australian National University, Canberra, Australian Capital Territory, Australia; ²Department of Oral Sciences, University of Otago, Dunedin, New Zealand.

The deformation behavior of 150 nm SiGe epitaxial films containing Ge compositions ranging from 9–67 atomic % have been studied as a function of Ge content using nanoindentation and atomic force microscopy (AFM). Initially, the mechanical properties of the films were measured using spherical indenters with a radius down to 1 μm .

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. Cross-section transmission electron microscopy images of residual indents reveal that the films undergo phase transformations during indentation similar to that previously observed in pure Si. Interestingly, however, some subtle differences in the mechanical responses 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.

8:45 AM T6.2/R10.2

Spherical Depth-Sensing Indentation on Silicon and Phase Transformation Pressure Dependence on Unloading Rate and Maximum Applied Load. Thomas Frank Juliano, Vladislav V. Dornich and Yury G. Gogotsi; Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania.

Many machining operations, including slicing, 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. Because 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 previously shown 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 spherical indenter 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 depth under the surface of the residual impression, where higher shear stresses are present. A stability range for Si-I, Si-II, Si-III, Si-XII 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.

9:00 AM T6.3/R10.3

In-situ Characterization of Phase Transformations During Nanoindentation of Deposited and Ion-Implanted Amorphous-Silicon. James S. Williams¹, Jodie E. Bradby¹, Bianca Haberl¹ and Mike V. Swain²; ¹Electronic Materials Engineering, The Australian National University, Canberra, Australian Capital Territory, Australia; ²Department of Oral Sciences, University of Otago, Dunedin, New Zealand.

Recently the deformation behavior of amorphous-silicon (a-Si) has been found to depend critically on both the method of preparation of the amorphous structure and the thermodynamic history of the sample. Whilst some forms of a-Si are significantly softer than crystalline-Si (c-Si) and appear to deform via material 'plastic' flow, annealed a-Si has mechanical properties that closely mirror those of c-Si including phase transformation as the main mode of deformation under indentation. In this study we investigate a range of continuous surface a-Si layers of varying thicknesses produced by both self-ion implantation and deposition techniques. A selection of these samples were annealed (450°C for 30 mins) to create both relaxed and unrelaxed a-Si. The response of the a-Si layers to spherical indentation was studied by in-situ electrical characterization to probe both the onset and depth of penetration of a metallic, high-pressure

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) a-Si samples but not in the other forms of a-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. Songqing Wen¹, James Bentley¹, Jae-il Jang^{1,2} and George M.

Pharr^{1,2}; ¹Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee; ²Metals & Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

It is well known that Si and Ge transform to a metallic state under pressure and that other crystalline and amorphous phases can form on the release of the pressure. Many of these same phenomena occur during indentation, making nanoindentation an important tool for exploring pressure-induced phase transformations. Studies have shown that the indentation-induced phase transformations depend on several important parameters including the maximum load, loading rate, and indenter geometry, e.g., whether the indenter is pyramidal or spherical. Here, a new parameter - the centerline-to-face angle of a triangular pyramidal indenter - is explored. Nanoindentations made in single crystals of Si and Ge with a series of pyramidal indenters with tip angles ranging from 35° to 75° were examined by cross-sectional and high resolution electron microscopy. The cross-sectional samples were fabricated to electron transparency using a dual beam focused ion beam mill. By comparing experimental observations with theoretical modeling, the influence of the indenter angle is examined. Results reveal how the phase transformations and deformation mechanisms facilitate the ductile machining of these normally brittle semiconductor materials. * This research was sponsored by the National Science Foundation under grant number DMR-0203552, and by the Division of Materials Sciences and Engineering (SHaRE User Center), U. S. Department of Energy, under Contract DE-AC05-00OR22725 with UT-Battelle, LLC.

9:30 AM T6.5/R10.5

In-Situ Infrared (IR) Detection of the High Pressure Phase Transformation of Silicon. John Patten¹, Lei Dong² and Jimmie A. Miller²; ¹Manufacturing Engineering, Western Michigan University, Kalamazoo, Michigan; ²Mechanical Engineering, University of North Carolina, Charlotte, Charlotte, North Carolina.

The phenomenon of high pressure phase transformations of semiconductor materials has been extensively investigated over the last 20 years. Previous efforts were mainly focused on studying different phases generated under various loading/unloading conditions using nanoindentation methods. Nanoscratching test however, which more closely resembles a real machining process, has only appeared in a limited number of papers. Additionally, only a very few papers, in addition to the current authors work, show in-situ or direct evidence to establish the existence of this phase change as it occurs. In this paper a new method of in-situ detection of the high pressure metallic phase transformation of semiconductor materials during dead-load scratching is described. This method is based on the simple fact that single crystal silicon is transparent to IR light while metallic materials are not. The sample material used here is silicon, but the same approach can be applied to germanium and other materials, such as ceramics, which have appropriate optical properties. It has been established that silicon goes through a Si-I to Si-II phase transformation under a pressure around 12GPa. This Si-II phase is metallic, which results in absorption of light at IR wavelengths. In this paper experiments are described in which an IR laser-detector system is used in conjunction with a pre-loaded (dead weight) scratching device to detect the metallic high pressure phase of Si. Loads used are 10, 20, 30 and 40 mN. The apparatus is designed so that IR light penetrates a diamond tip, which is a 60 degree conical tip with nominal radius 5µm, onto the scratching groove as the tip is translated on the silicon wafer. The IR diode laser used here is an 8mw Infrared laser with a wavelength of 1330 nm. An Infrared detector is placed below the silicon wafer to sense the transmitted IR light. Results show a decreasing trend of voltage (IR transmittance) after each scratch and an average of 10% decrease after 4 scratching cycles in the same groove. This indicates that a metallic phase has been generated during scratching and the metallic phase has preferentially blocked the IR laser light. Results also show that as the load increased the measured signal change increases, indicating

a greater amount of transformed metallic silicon AFM and SEM have been used to measure the groove shape and study the chips generated in the pile-up area. These images show that ductile deformation, for 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

High Pressure Surface Science and Engineering.

Vladislav Domnich, Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania.

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 (ceramic or semiconductor), 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 into 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 transformation that cannot occur under hydrostatic stresses, or would occur at much higher pressures. 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 testing, 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

Constant and Ramped Load Nano Scratch Test Behavior of Impregnated Hard Multilayer Coatings. Bala Kailasshankar, Devdas Pai, Sergey Yarmolenko and Jag Sankar; Center for Advanced Materials and Smart Structures, Dept of Mechanical Engg, North Carolina A&T State University, Greensboro, North Carolina.

Impregnated hard multilayer chromic oxide based coatings produced on 9.5 mm 1018 square steel bars were studied using 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 Jang^{1,2}, M.J.

Lance², Songqing Wen¹ and G. M. Pharr^{1,2}; ¹The 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 beta-tin phase (Ge-II) at about 10 - 11 GPa and re-transforms to Ge-III (st12 structure) or Ge-IV (bc8 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, in comparison to Si, the number of experimental studies that have examined indentation behavior of Ge is relatively small. This study was undertaken to answer to address several key unresolved questions. Nanoindentation experiments were performed (100) Ge single crystals using 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 any pronounced shape change, micro-Raman spectroscopy 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 indenter geometry significantly affects the transformation behavior. Micro-Raman mapping techniques were used to better understand the phenomena and evaluate the post-indentation stress distribution. Results are discussed in terms of prevailing descriptions of phase transformation in Ge and how the transformations progress and affect deformation during nanoindentation. * This research was sponsored by the National Science Foundation under grant number DMR-0203552, and by the Division of Materials Sciences and Engineering (SHaRE User Center), U. S. Department of Energy, under Contract DE-AC05-00OR22725 with UT-Battelle, LLC.

11:30 AM T6.10/R10.10

Nanomechanical Properties of Metal Surfaces Containing He Bubbles. James A. Knapp, David M. Follstaedt and Samuel M. Myers; Sandia National Laboratories, Albuquerque, New Mexico.

The mechanical properties of surfaces can be dramatically affected by a dispersion of fine precipitates such as is produced by ion implanting insoluble species. We previously formed nanometer-size precipitates of hard oxides (NiO, 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 He into Ni under several 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 arising from the combined influences 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 through the bubble, and, in fact, 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, where the layer can withstand 3 GPa shear stress 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-AC04-94A185000.

11:45 AM T6.11/R10.11

Dependence of Hardnesses on Band Gaps and Polarizabilities. John Joseph Gilman, MSE, UCLA, Los Angeles, California.

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 by the need for deformation on the higher order glide systems. The same is true for high-purity alkali halide crystals. 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 promotion 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 isoelectronic III-V crystals, this observed experimentally. The situation is somewhat more complex for the heteropolar III-V crystals because ionic charge centers play a role in them. Band gaps are related to polarizabilities, and to shear moduli so there are some additional links between hardnesses and electronic properties that are discussed.

SESSION T7: Synthesis and Characterization of
Engineered Surfaces and Coatings
Chairs: Yury Gotgotsi and James Krzanowski
Thursday Afternoon, December 2, 2004
Room 203 (Hynes)

1:30 PM T7.1

A Study of Surface Roughening in FCC Metals using Direct Numerical Simulation. Zisu Zhao¹, Raul Radovitzky¹ and Alberto Cuitino²; ¹Department of Aeronautics and Astronautics, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²Department of Mechanical and Aerospace Engineering, Rutgers University, Piscataway, New Jersey.

Grain-scale surface roughening due to plastic straining in polycrystalline aluminum is studied with the aid of a three-dimensional finite-element crystal-plasticity model. The aim is to improve our understanding of the origin of surface roughening profiles in plastically strained aluminum. Large-scale simulation enables the computation of full-field solutions and the explicit consideration of individual crystals' morphology as well as of their crystalline texture evolution and interaction with neighboring grains. Polycrystalline aluminum samples of flat sheet geometry consisting of 134 grains of idealized shape are stretched under uniaxial and biaxial boundary conditions. The simulation results show that the resulting surface profiles are controlled by several factors: applied boundary conditions, Taylor factor and shear tendency of the individual grains and the spatial distribution of grain neighborhood misorientations. The conditions leading to different ridging profiles, e.g., corrugated and ribbed surface profiles, are discussed. The simulation results also confirm the linear relationship between strain and roughness found in experiments and that the slope of the roughness curves can be controlled by manipulating the volume fraction of the predominant texture components in rolled aluminum sheets. In particular, they suggest that the overall roughness can be reduced by promoting certain texture components during material processing.

1:45 PM T7.2

Synthesis of Boron Nitride Coating on sintered SiC ceramics. Z. G. Cambaz¹, Gleb Yushin¹, Yury Gogotsi¹, A. Erdemir² and M. J. McNallan³; ¹Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania; ²Energy Technology Division, Argonne National Lab, Argonne, Illinois; ³Civil and Materials Engineering, University of Illinois, Chicago, Illinois.

Excellent tribological properties of boron nitride (BN) in combination with its high thermal stability promote a widespread research on BN. Various applications of BN include self-lubricating, wear-resistant and heat-dissipating coatings for dynamic seals and cutting tools, high temperature insulation, substrates for electronic devices. The conventional production methods of BN coatings, such as chemical vapor deposition, physical vapor deposition, or sputtering, suffer from a major drawback - poor adherence of the coating to a substrate, particularly for coating with thickness above 0.1 micron, needed for most of the applications. In this study, we introduce a method of BN synthesis on a carbide substrate, which offers excellent adhesion properties for both thin and thick coatings and is of low cost. The process cycle consists of three steps. The first step involves the production of a nanoporous carbide-derived carbon (CDC) coatings well adhered to the substrate (SiC discs) by the chlorination of SiC at 1000C for 5 hours. In the second step, boric acid was infiltrated into this porous carbon structure. In the last step, nitridation in ammonia at 1200C resulted in the formation of nano-crystalline BN coating. Microstructural characterization of the synthesized BN coatings was

performed by using Raman spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and x-ray diffraction (XRD). Pin-on-disk tribological tests were performed and the results were compared to tribological properties of CDC and untreated SiC.

2:00 PM T7.3

Synthesis and characterization of carbon nitride thin film with evidence of nanodomains. Shafiqul 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 nanodomains over a range of substrate temperature from 50 °C to 550 °C. An RF magnetron sputtering system was used for depositing carbon nitride films. The size of the nanodomains can be controlled by deposition temperature and increases from 40-80 nm at room temperature to 200-400 nm at high temperature (550 °C). 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 mΩ-cm was found for nanodomains of size 40-80 nm falling to 6 mΩ-cm for nanodomains 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 nanodomains increases. GAXRD results confirm that a crystalline graphitic 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. Arnoldo Bedolla-Jacuinte¹ and Mark W. Rainforth²; ¹Instituto de Investigaciones Metalúrgicas, Universidad Michoacana de San Nicolás de Hidalgo, Morelia, Michoacán, 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 M₇C₃ carbides in an austenitic matrix. The contact was shown to be plastic for the load range applied (42-238 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 strain induced 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

200mm Silicon Wafer-to-Wafer Bonding with Thin Ti Layer under BEOL-Compatible Process Conditions. Jian Yu, J. Jay McMahon, Jian-Qiang Lu and Ronald J. Gutmann; Rensselaer Polytechnic Institute, Troy, New York.

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, memory-intensive processors, smart imagers and mixed signal applications. The cornerstone for this 3D processing technology is the bonding in full wafer size, under back-end-of-the-line (BEOL) compatible process conditions. For the first time, we demonstrated nearly void free 200mm Si wafer-to-wafer bonding with blanket physical vapor deposition (PVD) sputtered Ti (12nm 20nm), annealed at BEOL-compatible temperatures ($\leq 400^\circ\text{C}$) with 10 kN down-force in vacuum. Bonding quality has been evaluated by both destructive means (such as razor blade inserting and sawing test) and non-destructive techniques (scanning acoustic microscope). Mechanical integrity test showed that bonded wafer pair survived after a stringent three-step thinning process (grinding/polishing/wet-etching) with complete removal of top Si wafer, while allowing optical inspection of bonding interface. Mechanisms contributing to the strong bonding at Ti/Si interface will be discussed, based on the sheet resistance change, glancing angle X-ray diffraction (XRD) analysis and atomic force microscopy (AFM) results.

3:15 PM T7.6

Growth Model and Observations of Soft Metal Whiskers. Elizabeth N. Hoffman, Michel W. Barsoum, Roger D. Doherty and Antonios Zavaliangos; Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania.

The room temperature spontaneous growth of low melting point metal whiskers, such as Sn, poses a serious reliability problem in the semiconducting industry; a problem that has become acute with the introduction of Pb-free technology. To date, this 50+ year old problem has resisted interpretation. In this paper we show that the driving force is essentially a reaction between oxygen and the sprouting metal. The volume expansion creates a local compressive stress that pushes the whisker up exposing fresh metal surfaces. The repetition of this process, a form of chemical ratcheting, results in long whiskers whose growth rates can be linear with time. The main evidence we present is that the growth rates of In and Sn whiskers, from the grain boundaries of Zr₂InC and Al, respectively, were much faster in air than in evacuated and sealed glass tubes. To accelerate whisker growth, some samples were in situ heated in a SEM chamber, and observed at a temperature below the melting temperature of In (157°C). The whiskers grew from their base at a rate that was constant with time and there was no correlation between whisker diameters and their growth rates. At the melting point the whiskers rapidly spheroidized, and many other spheres exuded spontaneously from the surface. The sphere population then rapidly coarsened in real time, unambiguously proving that in this case surface energy reduction was the driving force and that the In phase was interconnected. After coarsening, thin, collapsed In-oxide shells were observed on the surface indicating that some of the spheres had been covered by a thin oxide layer.

3:30 PM T7.7

Oxidative Degradation of Metal/Ceramic Interfaces in High Temperature Electrochemical Systems. Dirk Van Essendelft and Daniel R. Mumm; Department of Chemical Engineering and Materials Science, University of California, Irvine, California.

Fuel cell systems, utilizing direct electrochemical energy conversion mechanisms, have enormous potential for revolutionizing the way power is produced and used. However, fundamental challenges remain in developing the materials sets necessary to achieve required levels of performance and durability. This work addresses the development of metallic interconnects for intermediate temperature electrochemical systems, where substitution of metals for ceramic structures is expected to provide substantial cost and performance benefits. Initial work on metallic interconnect systems has identified a number of technical barriers. In particular, controlling the environmentally-induced surface degradation processes is key to utilizing metallic interconnects. The role of constituent chemistry, environmental conditions and current density on the oxidative degradation of interfaces in candidate interconnect/cathode systems was investigated - with the objective of better understanding the interplay between material exposure parameters (atmosphere, temperature, applied potential, presence of water vapor) and the development of protective, adherent, and electrically conductive oxide scales. The oxidation mechanisms are found to be sensitive to conditions relevant to SOFC operation - with consequences for system performance and durability. Understanding the oxide growth mechanism (in terms of cation, anion or mixed transport control) is critical in controlling stress evolution and growth rate for these high-resistance layers. In this work, candidate alloys (surface-modified in this effort), with Sm_{1-x}Sr_xCoO_{3-δ} (SSC) cathode overlayers, have been exposed to simulated electrolyzer and fuel cell operational environments. The resulting surface layers have been comprehensively characterized for oxide growth rates, ASR, chemical stability with adjoining layers and mechanical integrity. Implications of the observed oxidation processes for SOFC durability and performance are discussed.

3:45 PM T7.8

Structural factors determining the nanomechanical performance of transition metal nitride films. Kostas Sarakinos, Spyros Kassavetis, Panos Athanasios Patsalas and Stergios Logothetidis; Physics, Aristotle University, Thessaloniki, Greece.

Chromium Nitride (CrN) and Titanium Nitride (TiN) thin films were prepared employing reactive magnetron sputtering (MS) in unbalanced configuration in mixed Ar/N₂ atmosphere. The deposition was carried out at various values of substrate bias voltage (V_b). V_b affects the structure and morphology of the films in terms of preferred orientation, stoichiometry, cell size, internal stress and density. The microstructure, density and morphology of the films have been studied by X-Ray Diffraction in various geometries (Bragg-Brentano, sin²y method, grazing incidence asymmetric diffraction), X-Ray Reflectivity and Atomic Force Microscopy. The nanomechanical properties of the hard films were determined by nanoindentation using

continuous stiffness measurement technique in terms of hardness and elastic modulus, which varied between 15-25 GPa and 190-230 GPa, respectively. The nanomechanical 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 nanoindentation 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. Charitidis, 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 the interfacial width and adhesion strength will be also discussed. [1] Pireaux, J.; Kowalczyk, S.

P. in Metallization 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, Chunhua 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 this procedure created homogenous low-density nanocomposite films when the film thickness (L_0) was less than $2R_g$ where R_g is the polymer radius of gyration. On the other hand, in the case of the thicker film ($L_0 > 2R_g$), we found 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, C₆₀ 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, 125506. [2] Koga, T. et al., Macromolecules 2003, 36, 5236.