

SYMPOSIUM Y

Surface Interactions and Surface Engineering for Manufacturing Applications

November 28 - December 1, 2005

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Proceedings to be published in both book form and online
(see *ONLINE PUBLICATIONS* at www.mrs.org)
as volume 890
of the Materials Research Society
Symposium Proceedings Series.

* Invited paper

8:00 AM *Y1.1

Self-Lubrication of Machining Tools in Dry via In-situ Formed Tribofilms. Tatsuhiko Aizawa^{1,2}, Shigeo Yamamoto² and Taro Sumitomo²; ¹Materials Science and Engineering, University of Toronto, Toronto, Tokyo, Japan; ²Research Center for Advanced Science and Technology, University of Tokyo, Tokyo, Japan.

Green manufacturing technology has become a significant innovative keyword to reduce the environmental burden and CO₂ emission at the stage of manufacturing and production. Huge amount of lubricant oils and cleansing agents is wasted in daily operations by machining. Dry machining technology provides us a promising method to completely reduce these wastes. Among several candidate approaches toward dry machining, self-lubrication processing via in-situ formation of lubricious oxide films is developed to attain low friction and low wear state even at higher cutting speed range. Standing on the materials science over the low temperature oxidation of titanium to form a series of titanium oxides, the in-situ formed lubricious oxide films or TiO and Magneli phase oxide films are stated with consideration of accommodation mechanism of these intermediate oxides via the chlorine ion implantation. Precise evaluation of surface roughness and hardness via AFM and nano-indentation is made for evaluation on the wear behavior and elasto-plastic deformation of lubricious oxide films. Turning test is employed to evaluate dry machinability of various tools for wide range of cutting speeds. Self-lubrication in dry machining is described both for bare WC and TiCN-coated WC tools with and without chlorine implantation. Precise microstructure analyses are made by using the laser microscope, EDS and XPS. In-situ formation of lubricious oxides proves that self-lubrication process takes place even in dry machining to reduce the flank wear and friction coefficient.

8:30 AM Y1.2

Synthesis of CVD Diamond Coatings on Tungsten Carbide Substrates with Interlayer and Surface Pretreatments. Zhenqing Xu^{1,2}, Ashok Kumar^{1,2}, Leonid Lev³ and Michael Luckitsch³; ¹Department of Mechanical Engineering, University of South Florida, Tampa, Florida; ²Nanomanufacturing and Nanomaterials Research Center, University of South Florida, Tampa, Florida; ³General Motors Corporation, Warren, Michigan.

The obstacle that limits the commercialization of the diamond coated cutting tools is associated with the poor adhesion strength of diamond coating on the tool substrates like WC-Co due to high residual stress inherent in the film as a result of the CVD process. In our studies, we improved the adhesion strength of diamond coating by implanting a thin Cr/CrN interlayer and enhanced the nucleation density by surface pretreatment. Different size of diamond powders varying from 3 μm to 150 μm was selected to sandblast the sample surface. SiC and c-BN powders have also been utilized for the treatment. Polycrystalline diamond films were synthesized from hydrogen (99% vol) and methane (1% vol) gas mixture in a low temperature of 700 °C by the chemical vapor deposition (CVD) process. Coating morphology has been characterized by scanning electron microscopy (SEM). Mechanical properties such as hardness and Young's modulus were obtained by nanoindentation measurements. Dependence of the treat conditions on the adhesion has been studied. Residual stress as a function of the coating thickness has been obtained by Raman spectroscopy and the curvature method using Stoney's equation. Adhesion strength and fracture toughness of the coating will be predicted by finite element modeling. The predicted results will be compared with the experimental data.

8:45 AM Y1.3

Residual stress, hydrogen, and friction in nanocrystalline diamond films. Hao Li^{3,1}, Wangyang Ni^{1,2}, Brian W. Sheldon¹ and Yang T. Cheng²; ¹Engineering Division, Brown University, Providence, Rhode Island; ²Materials and Processes Laboratory, General Motors Research and Development Center, Warren, Michigan; ³Department of Mechanical & Aerospace Engineering, University of Missouri-Columbia, Columbia, Missouri.

The properties of nanocrystalline diamond films make them excellent candidates for wear resistant coatings. In these applications, large residual stresses in the film can be a serious problem. In many coating materials, these residual stresses are controlled primarily by the thermal mismatch between the substrate and the films, however, growth stresses that arise during the chemical vapor deposition of diamond films are large enough to compete with thermal stresses (1 GPa or larger). These growth stresses were investigated with precise wafer curvature measurements. The results show that changes in the growth chemistry can be used to produce significant variations in the film stress. In particular, the hydrogen content of the plasma has a

substantial effect on the growth stress. Post-deposition annealing was also used to alter the film stress. TEM and Raman spectroscopy were used to characterize the relationship between the process changes and the film structure and chemistry. The properties of the films were also investigated with nanoindentation and with pin-on-disk friction tests. The results of these experiments provide important insight into the use of CVD growth conditions and specific annealing treatments to engineer better wear resistant coatings. The key properties that were studied, residual stress, hardness, modulus, and friction, are also critical in small scale devices (i.e., MEMS). The experimental results will be discussed in this context as well.

9:00 AM Y1.4

Diamond/carbide nano-composite gradient films: A route to solve the adhesion issues of diamond films. Thorsten Staedler, Srikanth Vadali and Xin Jiang; Institute of Materials Engineering, University of Siegen, Siegen, Germany.

Due to their outstanding mechanical properties diamond films are ideal candidates for many cutting and machining applications. However, industrial applications of these films are limited due poor adhesion. Two main reasons causing this poor adhesion, which are based on the extrinsic physical and chemical properties of diamond, can be identified: High mechanical stresses induced by a difference of the thermal expansion coefficient between the diamond film and the substrate as well as a catalytic effect in case of metallic substrates containing iron-, cobalt- and nickel that, in combination with a methane atmosphere during deposition, leads to soot formation. One option to overcome these difficulties is to provide an interfacial layer that acts as adhesion layer as well as barrier layer to prevent the catalytic effect of the substrate elements. Even though some successful examples exist, this approach usually requires a time consuming and expensive multi-step process. In this paper, the synthesis of nanocrystalline diamond/carbide composite films with a compositional gradient will be reported. Focusing on the example of diamond/ β -SiC the possibility to create a gradient layer ranging from β -SiC to diamond in a controlled manner will be shown. The films are prepared by a microwave assisted plasma chemical vapour deposition process (MWCVD) using H₂, CH₄ and tetramethyl silane (TMS) as reactive gases. The structure, grain sizes, and volume fractions of the components of these composite films, which consist of a mixture of diamond and carbide phase, can be controlled by adjusting the concentrations of the reactive gases in the gas mixture. This strategy, which handles all depositions in one process step, should allow for an improved diamond film adhesion on tools. The preparation and characterization of the composite films with special emphasize on their mechanical and tribological properties will be discussed and a short outlook on other diamond/carbide systems will be given.

9:15 AM Y1.5

Development of Multilayer TiAlN + γ -Al₂O₃ Coatings for Difficult Machining Operations. Kirsten Bobzin, Erich Lugscheider, Otto Knotek, Michel Maes and Carmen Pinero; Chair of Surface Engineering IOT, RWTH Aachen University, Aachen, Germany.

The continuous advances in the aircraft and nuclear industry demand the development of new materials that among other properties offer a good resistance at elevated temperatures. For this reason, Ni super alloys were developed from a simple Ni-Cr matrix to multi-element, multi-phase systems. These new super alloys are specially favored for their exceptional thermal resistance and ability to retain mechanical properties at elevated temperatures. They are classified as difficult-to-machine materials due to their high shear strength, work hardening tendency, content of abrasive carbide particles within the microstructure, strong tendency to weld and to form built-up edges. Their low thermal conductivity leads to elevated temperatures during machining. Consequently, their tendency to maintain a high strength at elevated temperatures leads to elevated cutting forces. On this account, the development of an adequate coating for machining Ni alloys is today an important challenge. Nowadays, TiAlN is well known because of its excellent overall cutting performance. However, Al₂O₃ possesses better chemical and thermal properties than TiAlN, especially regarding hot hardness, oxidation resistance, diffusion resistance. Motivated by the advantages offered by PVD-Technology, γ -Al₂O₃ was synthesized by reactive bipolar pulsed magnetron sputtering in previous works. PVD-Processes allow the deposition of insulating coatings such as alumina at reduced temperatures, which implies a lower substrate thermal load. At the same time using PVD-Technology it is possible to produce high compressive stresses in the coatings (high alternating thermal stress resistance), keep sharp cutting edges, synthesize pure structures and deposit various coating combinations such as multilayer multilayer TiAlN + γ -Al₂O₃. Therefore, a PVD-multilayer coating TiAlN + γ -Al₂O₃ is very promising for machining of Ni alloys such as Inconel 718. However, due to the very different characteristics of the nitrides and oxides, particularly the good coating cohesion of this coating concept

constitutes a challenge. In this work different multilayer combinations were deposited on cemented carbide cutting inserts. In order to improve the adhesion between the nitride and oxide layers and consequently the coating cohesion, a special gradation was developed. The reactive gas flows (N_2 and O_2) was gradually changed during the coating deposition. The result was a soft gradation consisting of different nitrides and oxides species synthesized in very thin layers. Tribological tests demonstrated that the developed soft gradation offers an important improvement of the coating cohesion and fatigue resistance. For the evaluation of the coating adhesion and cohesion calorimetric, Rockwell- and scratch-tests were carried out. Mechanical properties were investigated by impact and pin-on-disc tests at room and high temperatures in order to investigate the potential of the deposited multilayer coatings in cutting operations.

9:30 AM Y1.6

Effect of Gas-Phase Composition on the Microstructure and Growth Rate of CVD Mullite Environmental Barrier Coatings. Tushar Kulkarni, Vinod Sarin and Soumendra Nath Basu; Manufacturing Engineering, Boston University, Brookline, Massachusetts.

The operating temperature in advanced gas turbines has been increasing steadily for improved fuel efficiency and reduced emissions. To accommodate this increase, Si-based ceramic components have been introduced into the hot section of gas turbines. Although these ceramics have excellent high-temperature oxidation resistance, they are susceptible to hot corrosion and recession in corrosive atmospheres containing Na, S, and high-pressure steam. In order to overcome these limitations, environmental barrier coatings (EBCs) are being developed. Due to its excellent corrosion resistance, creep resistance, close coefficient of thermal expansion (CTE) match with the Si-based ceramics as well as good high temperature strength and toughness, mullite ($3Al_2O_3 \cdot 2SiO_2$) is an excellent candidate material for environmental barrier coatings on Si-based ceramics used in high temperature corrosive atmospheres. Dense, crystalline mullite coatings of uniform thickness have been deposited by chemical vapor deposition (CVD) on SiC substrates, using the $AlCl_3$ - $SiCl_4$ - CO_2 - H_2 system. These mullite coatings have exhibited excellent high temperature oxidation and hot corrosion resistance and have proven to be very effective in protecting the SiC substrates from corrosive atmospheres. The effect of the gas phase composition on the coating microstructure and growth kinetics will be discussed. This study enables the growth of functionally graded CVD mullite EBCs with the Al/Si ratio being stoichiometric at the coating/substrate interface for CTE match, and increasing monotonically towards the outer coating surface for superior hot-corrosion and recession resistance.

9:45 AM Y1.7

Investigation of New Protective Coatings for Ultra-High Density Hard Disk Drives. Yanfeng Chen and Yip-Wah Chung; Materials Science and Engineering, Northwestern University, Evanston, Illinois.

The hard disk industry is working towards achieving an areal storage density of 1 Tbit/in². One of the requirements to reach this goal is to reduce the protective coating thickness for hard disk drives to about 1 nm. Experimental results show that the current material CNx does not work well below 2 nm thickness. New protective coatings are needed. In our work, we investigated the possibility of using boron carbide (B₄C) and boron carbonitride (BCN) thin films. They were synthesized by pulsed DC magnetron sputtering. Effects of target power, target pulse frequency, substrate bias and pulse frequency on surface roughness were studied. Nitrogen incorporation into B₄C films, which gives BCN thin films, has a beneficial effect. When deposited under similar conditions, the root-mean-square surface roughness of BCN films decreases substantially to 0.19 nm, compared with 0.28 nm for B₄C. These B₄C films have a hardness of 30 GPa and BCN films have a hardness of 20 GPa. Auger electron spectroscopy was used to characterize the film composition. High-resolution cross-sectioned TEM images and diffraction show that both films are amorphous. Corrosion studies indicate that BCN is a better protective coating for hard disk substrates than B₄C and CNx, probably due to its smoother and denser morphology.

10:30 AM *Y1.8

Surface Engineering in a Tooling Perspective. Torbjorn I. Selinder¹, C. Bjormander¹ and M. Lundblad²; ¹Coating Technology, Sandvik Tooling, Stockholm, Sweden; ²Metal Cutting Research, AB Sandvik Coromant, Sandviken, Sweden.

Since the advent of the first surface engineered cemented carbide (WC/Co) indexable insert, a TiC-coated WC/Co grade, more than three decades ago, there has been a massive development of ceramic coatings. Today very few WC/Co inserts are uncoated, and the dominant process is CVD for reasons of high wear resistance, and superior adhesion. When physical vapor deposition (PVD) of, e.g. TiN,

was developed it offered lower deposition temperatures and also processes apt for coating of cermets and steels. For many years PVD remained an exotic alternative for the coating of carbides, due to limited maximum thickness and insufficient adhesion. Over the last 10 years there has, however, been a rapid development of new coating materials. There has been a concurrent development of treatment techniques serving to engineer the tool surface, i.e. adapt the tool to the particular cutting situation. Not only surface engineering of the cutting insert is a necessary component of the design of today's modern tool grades, but also tool substrate, geometry and cutting data: The driving force for tool development is machining components at lowest cost and highest productivity. We realize that the cutting data need to be optimized to achieve both these goals. The rate of tool wear is not only affected by the work piece material and type of coating on the insert but also by the temperature and contact pressure at the interface between insert cutting edge and the chip of the work piece. These are factors strongly dependent on cutting parameters, like, speed and feed. In this paper we will describe numerical possibilities to accurately predict the thermal and mechanical load on surface on the cutting insert, which may provide a better insight into the nature of wear mechanisms of the coated insert. Thermal and mechanical loads are also used to predict strain and stresses in both the substrate and coating of the insert. These calculations will be discussed in view of the fundamental aspects of PVD vs CVD techniques and coating properties: PVD yields tough coatings, essential for inserts with weak positive cutting edges and ground sharp edges. On the other hand CVD produces high temperature stable coatings thanks to the possibility to grow high quality alumina. Trends in our development of new coating materials will be discussed, including both metastable alloys, superfine layered coatings, and crystalline alumina by PVD, as well as multilayered CVD coatings with exotic properties.

11:00 AM *Y1.9

Using Thin Film Coatings on Rolling Element Bearings. Gary Doll, Materials Technology, Timken Research, Canton, Ohio.

This presentation summarizes the successful development and implementation of thin film coatings for rolling element bearings. In particular, metal carbide reinforced amorphous hydrocarbon (MC/aC:H) coatings have proven to be particularly beneficial in enhancing the fatigue life of bearings operating under boundary layer lubrication conditions, as well as providing abrasive and adhesive wear resistance.

11:30 AM *Y1.10

Large Area Coatings for Architectural Glass. Jose M. Gallego, European Technical Centre, Pilkington Plc, Lancashire, United Kingdom.

Large area high throughput coated glass for automotive and architectural applications started in 1975 and 1977 respectively following the invention of the planar magnetron in 1971. The industry has since evolved and expanded considerably and sputtering has become the prevailing technology for large area coated products. This has been primarily the result of the ability to manufacture high quality products at low cost. After more than a quarter of a century the industry is facing considerable challenges with greater competition and reduced profit margins. These have been to a certain extent the result of the fact that large area coated products have become a commodity due to the high demand resulting from the availability of products and also more importantly because of changing in building and transport legislation requiring ever greater performance to satisfy the increased social and political awareness of environmental issues. However these challenges present the industry with an opportunity to reshape itself by looking at the way coated products are changing in response of consumer needs and legislative changes and also by taking advantage of opportunities derived from the fast development in the electronic and telecommunication industrial sectors. This presentation will briefly outline the history of this important technology, concentrating primarily on the various events and milestones that have shaped its success. It will also discuss the reasons and consequences of the changes in the transport and architectural fields and the challenges and opportunities that these changes present.

SESSION Y2: Mechanical and Functional Properties of Thin Films
Chair: Steve Bull

Monday Afternoon, November 28, 2005
Back Bay A (Sheraton)

1:30 PM *Y2.1

Superhard Nanocomposites: Their Development, Properties, Present and Future Industrial Applications. Stan Veprek,

Chemistry Department, Technical University Munich, Garching, Bavaria, Germany.

Nano-Sized and Nano-Structured materials represent nowadays the leading edge of the research and technological development in many different areas including inorganic, organic and biological materials. This paper will focus on the preparation and properties of superhard nanocomposites with a high thermal stability and an unusual combination of mechanical properties, which were developed on the basis of our generic design concept that was published in 1995. These superhard nanocomposites were successfully introduced into a large-scale industrial production. After a brief historical overview of the development, I shall discuss the deposition conditions needed for reproducible preparation of these nanocomposites with high hardness of ≥ 50 GPa and high thermal stability. The spinodal phase segregation leads to the formation of a nanostructure with sharp, strong interfaces and a high thermal stability. Several possible reasons for the lack of success of some workers to reproduce these results will be identified. The unusual combination of the mechanical properties, such as a very high hardness of 50 to ≥ 100 GPa, large resistance against brittle failure and high tensile strength approaching the ideal strength of flaw-free materials can be understood on the basis of conventional fracture physics scaled down to a nanometer size. The last part of the lecture will summarize the presently available, large-scale industrial applications of these coatings and the possible, future development. The major present applications are found in the field of dry, fast machining where the temperature exceeds 800 °C. The high oxidation resistance of these coatings is the main reason for their success as compared with the state-of-the art (Ti_{1-x}Al_x)N coatings. Finally, I shall briefly summarize new applications, such as dry machining of nickel-based superalloys, carbon reinforced aluminum alloys, as well as a variety of forming, stamping and extrusion operations which are being developed by several industrial companies.

2:00 PM Y2.2

A New Method Based on Work-Displacement Curve to Assess the Toughness of Coated System. Jinju Chen and Steve J. Bull; Univ. of Newcastle Upon Tyne, Newcastle, United Kingdom.

Traditional indentation models relating the toughness to applied load and the length of well-developed radial cracks were initially developed for monolithic bulk brittle materials. Their application can also be extended to coated systems if sufficiently thick, however, the use of such models for thin coatings will be influenced by other factors such as substrate deformation and it is difficult to use traditional approaches to assess sub-threshold cracking. The method of extrapolating the indentation load-displacement curve has been widely used to assess the toughness of a coating when a step in the load-displacement curve is observed which is clearly associated with chipping. This approach completely ignores the change of other mechanical behaviour associated with the fracture event (e.g. the change of elastic-plastic deformation behaviour of the cracked system) and it cannot be applied to displacement control experiments. The irreversible work vs. load relationship for a range of applied loads can be used in this case but is time consuming. Also this method does not work well for sub-threshold cracking. Therefore, it is necessary to find a method to solve such problems if the fracture properties of very thin coatings (<1µm in thickness) are to be assessed. In this paper, a method which is based on extrapolating the total work vs. displacement curve (Wt vs.dp method) at a load where cracking occurs is presented to estimate the fracture toughness of the coated system. This approach can de-couple other deformation mechanisms from the fracture event. It can be equivalently applied to load control and displacement control experiments, and it is useful for sub-threshold cracking as well as well-developed cracking (including radial cracking, chipping). Comparisons between the toughness results for various ceramic coatings on soda-lime glass and fullerene-like CN_x coatings deposited on different hard substrates (e.g. SiC) determined by various methods are discussed in this paper and it is shown that the Wt vs.dp method provides reasonable results.

2:15 PM Y2.3

Residual Stress Estimation from the Elastic Recovery of Nanoindentation. Xiaodong Li and Zhi-Hui Xu; Department of Mechanical Engineering, University of South Carolina, Columbia, South Carolina.

Residual stresses widely exist in the devices and components for various engineering applications and often play a vital role in their performance and failure. Hence, determination of residual stress in materials has long been a topic of both scientific and technological interests. Nanoindentation is a very powerful technique for the measurement of mechanical properties and the determination of residual stresses at micro/nanoscale. In this study, we presented an empirical model based on finite element simulations for residual stress determination from the elastic recovery of nanoindentation. Finite

element simulations show that the ratio of elastic recovery of nanoindentation to the maximum penetration depth, h_e/h_{max} , has a linear relationship to the ratio of residual stress to yield stress, and increases for compressive residual stress while decreases for tensile stress. Nanoindentation tests performed on a bonded fused quartz beam in this study and on DLC and Au coatings in literature also confirm the existence of residual stress effects on the elastic recovery of nanoindentation. The empirical model has been applied to derive the plastic properties and to estimate the residual stress of the mechanically polished fused quartz beam.

3:30 PM *Y2.4

Nanostructural Design of Wear Resistant Coatings; Contemporary Applications of Electron Microscopy. Lars Hultman, Department of Physics, IFM, Linköping University, Linköping, Sweden.

Case studies are presented for the design of nanostructured functional materials in advanced surface engineering: 1) cutting tools with wear-resistant coatings that undergo age hardening during operation; 2) protective coatings for components based on resilient fullerene-like carbon nitride; 3) contacts of electrical and mechanical quality that are coated with new nanolaminated MAX-phase ductile ceramics; and 4) superhardening of nano-multilayer and nano-composite coatings. The application of state-of-the-art electron microscopy techniques for such problem-oriented research is also presented, including XTEM, HREM, HAADF, EELS, EDX, and in situ nanoindentation. CASE 1: The concept of age hardening of ceramic coatings is introduced first with the example of metastable TiAlN. Spinodal decomposition with coherent cubic-phase nm-size domains of TiN and AlN that hinder dislocation glide is thus demonstrated in films annealed to temperatures corresponding to cutting operations. CASE 2: Fullerene-like CN_x ($x \leq 0.3$) compounds present a material with large-scale application (e.g., as top coats for hard discs or mechanical components) only a few years after discovery. The material is resilient, i.e., both hard and extremely elastic. It consists of sp²-coordinated graphene planes that are buckled from the incorporation of pentagons, but also cross-linked due to the substitutional bonding of N. CN_x can store deformation energy by bending of such fullerene-like units. Topics for electron microscopy include the imaging of a non-crystalline solid material, nature of N bonding, and mechanical deformation. CASE 3: The class of so-called MAX phase ceramics with metallic attributes such as ductility and conductivity has attracted a growing interest with the introduction of thin film processing. These have a nanolaminated hexagonal structure with M_{n+1}AX_n stoichiometry ($n=1,2,3$; M=transition metal; A-group element; X=C/N). For archetypical Ti₃SiC₂, reversible plasticity was proposed to operate. Our studies reveal kink formation and cohesive delamination on the basal planes during deformation. CASE 4: For nanoscale multilayer coatings, XTEM combined with nanotribological analysis reveals for TiN/NbN superlattices that dislocation glide within the layers is the dominant deformation mechanism. That confirms the present models for superhardening that presumes plasticity and postulates dislocation hindering at interfaces between layers of different shear modulus. In consequence, these coatings also exhibit crystal rotation during deformation. Finally, recent electron microscopy findings give useful insights to constitution of nc-TiN/a-Si₃N₄ nanocomposites and their potential superhardness. Evidence is presented for the existence of a cubic SiN_x phase as well as deformation preferentially located to the softer silicon nitride phase.

4:00 PM Y2.5

Coherent growth and mechanical properties of nanostructured Ti-Al-N thin films. Giulio Allidi, Farida Medjani and Ayat Karimi; IPMC-Faculty of Basic Science, Swiss Federal Institute of Technology, Lausanne, Switzerland.

As the dimensions of materials are reduced to the nanometer scale range, the stabilization of pseudomorphic crystal structures that differ from their bulk equilibrium phases can occur. The pseudomorphic growth is a well known phenomenon in multilayer thin films allowing the formation of coherent interfaces and superlattice structures with a substantially larger bulk modulus and greater hardness than the average of the constituent materials. In this paper emphasis will be made in nanocomposites developing coherent nanodomains. A convenient model-material for such investigations is the Ti-Al-N system since it allows the formation of nanolayers as well as nanocomposites. Two series of nanostructured films were prepared: a) AlN/TiN multilayer films with bilayer period between 50 nm and 1 nm, b) nanograined Ti_{1-x}Al_xN films with $x = 0.4 - 0.7$. The samples were characterised in terms of structure-property relations using RBS, HRTEM, XRD, and nanoindentation. Conditions to obtain coherent structures and different strengthening mechanisms operating in these nanostructured thin films will be discussed and compared.

4:15 PM Y2.6

Structural, Mechanical, Tribological Properties of MOS₂ / C

Multilayers Deposited by Pulsed Laser Deposition Technique.

Phani Ratna Ayalasaayaajula¹ and James E. Kraznowski^{1,2};

¹Physics, CASTI-INFM Regional Laboratory, L'Aquila, Abruzzo, Italy; ²Mechanical Engineering, University of New Hampshire, Durham, New Hampshire.

Multilayers of MoS₂/C have been deposited on polished AISI 440C steel and silicon substrates by Pulsed Laser Deposition (PLD). MoS₂ and C targets were ablated in a background gas of 10 mTorr Ar at room temperature. Several sets of experiments with increasing MoS₂ content and lowering Carbon content and vice versa have been deposited. Structural, microstructural, and mechanical properties of the multilayers have been measured by X-ray diffraction, scanning electron microscopy, transmission electron microscopy and nano-indentation techniques, respectively. Tribological evaluations were also conducted using a pin-on-disc friction and wear test. The MoS₂/C films were found to have a crystalline structure, although the degree of crystallinity was low. The presence of composition modulations in MoS₂/C multilayered films has been confirmed by both wavelength dispersive spectroscopy (WDS) and X-ray photoelectron spectroscopy (XPS). Nano-indentation tests of the MoS₂/C multilayers showed close to rule-of-mixtures hardness levels (12-16 GPa). MoS₂/C multilayers showed increasing hardness with decreasing MoS₂ content, but reached maximum hardness 16 GPa, possibly due to substrate effects. The pin-on-disc tests gave friction values ranging from 0.08 to 0.2 for different sets of films. These results are correlated with the degree of crystallinity and grain structure of the films.

4:30 PM Y2.7

Bio-mimetic Scaling of Mechanical Behavior of Thin Films, Coatings, and Surfaces by Laser Interference Metallurgy.

Claus Daniel¹, T. John Balk², Thomas Wuebben³ and Frank Muecklich⁴; ¹Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; ²Dept. of Chemical and Materials Engineering, University of Kentucky, Lexington, Kentucky; ³Max-Planck-Institute for Metals Research, Stuttgart, Germany; ⁴Materials Science Department, Saarland University, Saarbruecken, Germany.

Biological solutions to enhance strength and stability often use lateral and hierarchical composite structures from nano- to micro-scale. Bones and shells incorporate these composite effects to scale their mechanical behavior and structural stability in the manner smaller is stiffer. The effect is not based on large chemical variations, but instead is realized by structural composites, namely phase changes and orientations with long-range order. Laser Interference Metallurgy is a newly developed technique that utilizes this biological approach to optimize the mechanical properties of surfaces and thin films. In the past, the local influence of micro-structure on local mechanical properties of different metallic and ceramic systems has been studied extensively. The current study analyzes the possibility of scaling the mechanical properties of thin films, coatings, and surfaces in a controlled manner. The bio-mimetic possibility of scaling mechanical properties by this technique is quantitatively analyzed and compared with the biological approach.

4:45 PM Y2.8

Study on the Influence of Surface Roughness and Substrate Properties on Partially Rapidly Solidified as Plasma Sprayed Alumina-3 wt % Titania Nanocrystalline Coatings.

Venkataraman Ramanathan Iyer¹, B. Pramanick¹, Arvind Sinha¹, Pathak Lokesh¹, Das Goutham¹, S. R. Singh¹, D. K. Das² and B. Venkataraman²; ¹Materials Science and Technology Division, National Metallurgical Lab, Jamshedpur, Jharkand, India; ²Surface Engng Group, Defence Metallurgical Lab, Hyderabad, India.

plasma sprayed coupons of Alumina-13 wt % titania tends to show enhanced fracture toughness and interfacial toughness with increased amount of partially rapidly solidified α phase. In this paper an attempt has been made to impose different degrees of rapid solidification by spraying on diverse substrates of varying thermal properties. Substrates such as copper, Aluminum, Stainless steel, Low alloy steel material were used to alter the imposed cooling rate and thereby the amount of residual α phase. In addition to understand the role of solute titania a start powder of 3 wt % titania instead of 13 wt % titania powder was used for spraying the coating to a thickness of 250 μ m on the specified substrates. In all cases the rapidly solidified phases show nanocrystalline sizes with the most rapidly solidified metastable γ phase showing finer crystalline size of less than 25 nm. The surface roughness of the coating and the substrate were measured by AFM. From the X-ray analysis of as sprayed coating the amount of residual α phase, which was found in conjunction with the metastable γ phase was dependent on the thermal property and the surface roughness of the substrate. The roughest stainless steel material and similarly low thermal conductivity low alloy steel material showed similar behavior with a resulting residual α phase larger than 50 %.

Whereas, high thermal conductivity material such as Aluminum and copper had offered the lowest of thermal contact resistance to rapid solidification resulting in larger proportion of rapidly solidified metastable γ phase. Despite this and in contrary to the results of alumina-13 wt % titania coatings for all cases Alumina-3 wt % titania had shown poor indentation fracture toughness with increased amount of residual α phase. Coupons particularly of the stainless steel and low alloy steel which had shown larger preferential stabilization of α phase showed poor fracture toughness when tested with micro indentation techniques at loads of 3 to 5 N. In contrast with these results the interfacial toughness when measured by rockwell indentation technique at loads of 150 N was found to be dependent on the elastic modulus of the substrate more than the coating hardness.

SESSION Y3: Micro-/Nano- Manufacturing

Chair: Costas Prigoropoulos

Tuesday Morning, November 29, 2005

Back Bay A (Sheraton)

8:00 AM *Y3.1

Adhesive and frictional contact between nano-rough surfaces in MEMS.

Maarten P. de Boer¹, Frank W. DelRio^{1,2}, Martin L. Dunn² and Alex D. Corwin¹; ¹MEMS Device Technologies, Sandia National Labs, Albuquerque, New Mexico; ²Mechanical Engineering, University of Colorado, Boulder, Colorado.

Understanding the detailed interactions between contacting nano-rough surfaces will help technologies such as microelectromechanical systems (MEMS) to become more widely implemented. Nanometer-scale surface topography plays a critical role in the performance of these interfaces. In this presentation we will discuss adhesive and frictional characteristics of polycrystalline silicon (polysilicon) MEMS. Nano-roughness inherently results from the deposition and annealing sequence of this material. With respect to adhesion, most models of contacting surfaces attribute adhesion to areas of contact. Using microcantilever beams as test samples, our experiments and analysis demonstrate that dispersion forces between non-contacting portions of the surface dominate the adhesion of hydrophobic nano-rough surfaces. Hydrophilic surfaces are susceptible to water condensation and hence capillary forces can dominate their adhesion. A strong interaction between relative humidity and adhesion is expected because the Kelvin radius is on the order of the surface roughness. Using a thermodynamic control volume analysis, we show that heat supplied by the system walls reduces capillary adhesion by a factor of two or more. Experimentally, we find that nano-particulates play a crucial role in the dependence of adhesion on relative humidity. Regarding sliding interfaces, our measurements show that static and dynamic coefficients are insufficient to characterize friction in MEMS. For short sliding distances (less than 200 nm), stable pre-sliding tangential deflections can dominate the behavior. This result can be understood by considering friction as dependent on local position. This joint experimental and modeling work improves our fundamental understanding of adhesion and friction in MEMS devices and will ultimately lead to improved model-based designs, higher performance and greater reliability. 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.

8:30 AM Y3.2

Selective Laser Melting of High Aspect Ratio 3D Metal Structures on Silicon Substrates for MEMS Applications.

Paul Raymond Chalker, Sean Davies, Christopher J. Sutcliffe and Sozos Tsopanous; Engineering, University of Liverpool, Liverpool, United Kingdom.

The advent of silicon-based micro-electro-mechanical systems (MEMS) has been largely born out of processes developed for manufacturing essentially two-dimensional (2D) integrated circuits. In order to extend MEM technologies to 3D applications such as microfluidic valves, inkjet nozzles, and projector micro-mirrors for example, high aspect ratio patterning techniques were developed such as 'LIGA' or X-ray photoresist processing [1]. More recently a range of direct-write methodologies, such as ink-jet printing or selective laser melting [2,3] have been developed to manufacture MEM component structures. In the selective laser melting process a succession of individual part cross sections are created from powdered materials by melting them with a 100 W Ytterbium Fibre Laser of wavelength 1068-1095nm. A layer of the build powder is pre-deposited and spread uniformly by a wiper blade. The laser 'writes' the layer pattern in the powder bed melting the material and joining it to the previously formed build structure. By this technique, between 25 and 200 microns thickness of material can be built in each layer. To build the 3D metal structures on silicon substrates a metallization layer is

required to promote adhesion and to act as an electrical contact if necessary. In this paper we describe the application of selective laser melting to build high aspect ratio metallic MEMS structures onto silicon substrates. The influence of the laser process parameters on the substrate - build interface will be discussed. [1] M.J. Madou, Chapter 6 in 'Fundamentals of Microfabrication', CRC Press, Boca Raton, FL., 1997 [2] See for example the selective laser sintering process described by Xiaochun Li, Hongseok, Choi, Yong Yang, 'Micro rapid prototyping system for micro components' Thin Solid Films 420-421 (2002) 515-523. [3] R. Morgan, C. J. Sutcliffe, W. O'Neill, 'Density analysis of direct metal laser re-melted 316L stainless steel cubic primitives', Journal of Materials Science 39(4) (2004) 1195-1205.

8:45 AM **Y3.3**

Metal Micromolding with Surface Engineered Inserts.

Dongmei Cao and Wenjin Meng; Louisiana State University, Baton Rouge, Louisiana.

The LIGA (Lithographie, Galvanoformung, Abformung) technique, combining deep lithography, electrodeposition, and molding replication, is a leading micromanufacturing process for making high-aspect-ratio microscale structures (HARMS) out of polymer-based and metal-based materials. Molding replication is the key to economical fabrication of metal-based HARMS. Using a hybrid technique, we have fabricated microscale metallic mold inserts with improved high temperature mechanical properties. Surface engineering of mold inserts by electrochemical polishing and conformal coating deposition has enabled the successful high-temperature micromolding of Al and Cu. A suitably chosen coating alters the chemical/mechanical interactions between the insert and the molded metal, and is critical to successful micromolding of reactive metals. In this talk, the molding performance of carbon-based coating and silicon nitride-based coatings will be compared. Issues of maximum molding force, demolding force, and coating durability will be addressed.

9:00 AM **Y3.4**

Interfacial Stresses in Tetrahedral Amorphous-Carbon Thin Films. Thomas Aquinas Friedmann and J. P. Sullivan; Sandia National Laboratories, Albuquerque, New Mexico.

Tetrahedral Amorphous-Carbon thin films are typically deposited by a process that produces energetic carbon species (20–1000 eV) such as cathodic-arc or pulsed laser deposition. The impinging carbon ion energy affects the structure of the growing film and in general leads to high values of residual compressive stress (2–8 GPa). The average in-plane stress can be totally relieved by annealing; but these low average stress samples can have stress gradients in the growth direction. In situ stress measurements (wafer curvature) made during etch-back of the annealed films reveal that these gradients typically consist of three components. They are a linear stress gradient in the bulk of the film that disappears in properly annealed samples, a compressive stress at the substrate interface (~7 nm in thickness), and a tensile stress at the film surface (2 nm in thickness). The interfacial stresses in the annealed films are high with values that are in the GPa range. Evidence of these interfacial stresses is also seen in the stress profile of unannealed films indicating the interfacial structure is different than that of the bulk of the film and does not share the same stress relief properties. These features of the through-thickness stress profile in ta-C films are roughly consistent with those calculated in molecular dynamics simulation of film growth¹ and will be compared to the calculations. Finally, ta-C films are being explored as a material for the manufacture of microelectromechanical machines (MEMS). Control of these stress gradients is necessary for production of flat released devices, and strategies for accomplishing this control will be discussed.¹A. Yu. Below, Comput. Mater. Sci. **27**, 30 (2003). 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.

9:15 AM **Y3.5**

Bending of Bridge Structures Due to Residual Stresses at an Interface. Peter J. Ryan^{1,2}, George G. Adams¹, Nicol E. McGruer² and Sinan Muftu¹; ¹Mechanical and Industrial Engineering, 334 SN, Northeastern University, Boston, Massachusetts; ²Electrical and Computer Engineering, Northeastern University, Boston, Massachusetts.

Residual stresses frequently occur at a solid-solid interface due to the deposition process of the thin-film material. During release of a cantilever structure, the uniform portion of the axial normal stress acting on a cross-section in the bonded region is partially relieved resulting in a "take-off angle" whereas the corresponding stress in the suspended portion is completely relieved resulting in an inconsequential axial contraction/expansion. When the stress-gradient through the thickness is relieved, the take-off angle is affected and a residual curl of the cantilever is produced. Only the latter effect is

well described with conventional beam theory. Our recent SEM observations of released nano-bridge structures show noticeable and consistent bending deflections. However, the release of a bridge structure with residual stress would at first appear not to produce any deflection provided that any compressive stress is insufficient to cause buckling. Certainly if classical beam theory is used, the uniform component and the stress-gradient portion of the normal stress acting on a cross-section are unaffected by the release process. The purpose of this investigation is to achieve an understanding of this observed phenomenon of bending of bridge structures at an interface due to residual stress, even if the pre-stress is insufficient to cause buckling. For bridge structures we have found that the bending deflections can be predicted based on the release of residual stress by using a beam theory that accounts for both shear and axial deformations. The analysis shows that a tensile residual stress causes the bridge to bend upward whereas a compressive residual stress produces downward bending. Similarly a stress-gradient which is more tensile/compressive at the free surface than at the interface affects bridge deflections in a manner similar to tensile/compressive uniform stresses, but to a lesser degree. Also for cantilever structures the take-off angle has been predicted by Fang and Wickert [1] using a two-dimensional finite element elasticity analysis. We show that similar results can be obtained for a cantilever using beam theory which includes shear and axial deformations. These theoretical predictions are accompanied by measurements of residual deflections in cantilever and bridge structures of different lengths. The deflections of bridge structures are less sensitive to residual stresses than are the cantilevers. Reference [1] W. Fang and J.A. Wickert, 1996, "Determining Mean and Gradient Residual Stresses in Thin Films Using Micromachined Cantilevers," Journal of Micromechanics and Microengineering, Vol. 6, pp. 301-309.

9:30 AM ***Y3.6**

Ultrafast Laser-Surface Interaction and Its Applications to Micro-Machining and Nanomaterial Synthesis. Samuel Mao, Lawrence Berkeley National Lab, Berkeley, California.

This talk will provide an overview of recent progress in the understanding of high power ultrafast laser surface interactions. Both experimental and theoretical evidence of the formation of a non-thermal laser plasma will be presented. This plasma is significantly different from conventional laser-induced thermal plasmas bearing a hemispherical feature. For the application of ultrafast laser-surface interaction, the topics will include (1) laser micro-machining with clean side wall structures and (2) laser-assisted synthesis of alloy particles and crystalline nanowire materials.

10:30 AM ***Y3.7**

Surface Engineering and Micromachining of Ultrananocrystalline Diamond. John A. Carlisle, Materials Science Division, Argonne National Lab, Argonne, Illinois.

Despite a vast amount of work there are few examples of really successful MEMS-based devices and NONE to date that involve repetitive sliding contacts. This is due to the simple fact that performance and reliability of MEMS are critically dependent on surface properties. Most popular MEMS structural materials (poly-Si, SiGe, etc.) do not have stable surface chemistries that cannot be satisfactory overcome via surface engineering (i.e. self-assembled monolayers). In recent years carbon-based thin films, in particular ta-C and nanocrystalline diamond, have attracted interest as MEMS structural materials in this context. Carbon thin films with high sp³ content are naturally hydrophobic and chemically inert, due to hydrogen surface termination, and when smooth exhibit very low friction and stiction. Conducting diamond films exhibit unparalleled electrochemical properties, including high overpotentials for H₂ and O₂ evolution and low background currents, making diamond attractive for electrochemical sensing of chemical and biological analytes. In this talk we will present our recent work to understand and modify the surface properties of ultrananocrystalline diamond (UNCD) thin films, as well as the development of surface micromachining and materials integration strategies to enable UNCD-based RF- and Bio-MEMS devices. UNCD thin films are grown using microwave plasma chemical vapor deposition with unique argon-rich (hydrogen-poor) plasma chemistries, and consist of diamond grains 3-5 nm in size. UNCD thin films exhibit a number of interesting materials properties, including high hardness, modulus and fraction strength, low as-deposited roughness and stress, and tunable electrical and thermal transport properties. Particular emphasis will be placed on recent work to covalently modify the surface chemistry of UNCD films to control hydrophobicity and immobilize biological molecules for biosensors, and the development of low-temperature growth chemistries to enable the direct integration of high acoustic velocity UNCD thin films with CMOS-containing microchips. *This work was supported in part by the US Department of Energy, BES-Materials Sciences, under Contract W-13-109-ENG-38

11:00 AM Y3.8

Growth and Characterization of Plasma Nano-Coatings for Surface Modification of Complex Shaped Nano-structured Materials. Pratik P. Joshi¹, Steve Higgins² and Sharmila M. Mukhopadhyay³; ¹Mechanical and Materials Engineering, Wright State University, Dayton, Ohio; ²Chemistry Department, Wright State University, Dayton, Ohio; ³Mechanical and Materials Engineering, Wright State University, Dayton, Ohio.

Effective surface modification of complex shaped nano-structured materials is important for their incorporation into advanced engineering applications. Surface modification of such materials can successfully be achieved by film deposition, provided the film is substantially smaller than the bulk material and yet durable and effective at nano-scale. The goal here is to develop a fundamental understanding of the initial growth stages and coverage of plasma-assisted nano-films on model flat substrates, and then test their applicability on uneven shaped nano-structured materials. Two types of plasma assisted films are studied: viz. oxide films for surface reactivity (or hydrophilicity) and fluorocarbon films for surface inertness (or hydrophobicity). Ex-situ XPS was used for detailed study of chemical composition of the substrate and coating atoms at various stages of deposition and Ex-situ AFM was used to study the morphology of these films on nano-scale. Combined XPS and AFM results in both cases indicate complete coverage of substrate on nano-meter scale (subsequent film thickness ~3-5nm), and also indicate that these films are effective on nano-scale. These studies show that plasma-assisted chemical deposition can be a very viable approach for effective surface modification of nano-structured solids. The effectiveness of these coatings on carbon nano-fibers and micro-cellular foam structures, for enhanced surface properties will be discussed.

11:15 AM Y3.9

Temperature-Dependent Behavior of Tetrahedral Amorphous Carbon MEMS Resonators. J. P. Sullivan¹, D. A. Czaplowski¹, T. A. Friedmann¹, X. Chen², P. G. Kotula¹ and J. R. Wendt¹; ¹Sandia National Laboratories, Albuquerque, New Mexico; ²Cedarville University, Cedarville, Ohio.

Many applications of MEMS resonators require thermal stability of the oscillator resonant frequency and the maintenance of low mechanical dissipation even at elevated temperatures. For silicon resonators, high temperature annealing has been found to reduce mechanical dissipation, at least temporarily, due to a reduction in surface-related losses. Tetrahedral amorphous carbon resonators exhibit high resonance frequencies and mechanical losses that are controlled by bulk defects, not surface-related processes. In this work, we have characterized the temperature-dependent behavior of tetrahedral amorphous carbon flexural-mode and shear-mode MEMS resonators. Resonance measurements were performed in vacuum throughout the temperature range from 300 K to over 1000 K. The temperature-dependent Young's and shear moduli were measured, and, from these, the temperature-dependent Poisson's ratio was calculated. Measured at elevated temperature, the Young's and shear moduli decreased by approximately 3% from the initial values of 658 GPa and 271 GPa, respectively, over the temperature range from 300 K to 900 K. As measured at elevated temperature over this same temperature range, the quality factor decreases by about 80%, from a room temperature value of approximately 4×10^3 . These changes are reversible; the moduli and quality factor recover upon cooling back to 300 K. The large increase in mechanical dissipation at elevated temperature is due to the thermal activation of a broad spectrum of bulk dissipative defects in this material. A plot of defect concentration versus defect activation energy for these defects shows a large increase over the activation energy range from 0.4 eV to over 1.9 eV. The existence of a broad spectrum of dissipative defects that is observed in this material is similar to what has been observed in other bulk amorphous solids. At higher temperatures, typically greater than 1200 K, irreversible structural changes have been observed. These changes are accompanied by a permanent change in modulus (up to 1 to 2%) and a change in medium range order, as indicated by fluctuation microscopy. Transmission EELS does not show a significant change in sp^3/sp^2 content of the films, indicating that the structural changes are likely associated with ordering or clustering, as opposed to thermal decomposition. 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.

11:30 AM Y3.10

Fabrication of nanostructures over a large area in ultra thin polymer films. Wei Lu and Dongchoul Kim; Mechanical Engineering, University of Michigan, Ann Arbor, Michigan.

This paper reports the theoretical and experimental work using an electric field to induce ordered morphological patterns in an ultra thin

polymer film over a large area. The film was spin-coated onto a glass wafer, and subsequently heated to above its glass transition temperature to allow viscous flow. An electric field was applied by two parallel electrodes spacing 10 mm apart. The initially flat polymer/air interface evolves into islands. The self-assembled islands exhibited a narrow size distribution and demonstrated spatial ordering. We attribute the pattern formation to the minimization of combined interface energy and electrostatic energy. Experiments have shown that a thin polymer film subjected to an electrostatic field may lose stability at the polymer-air interface, leading to uniform self-organized pillars emerging out of the film surface. We present a three dimensional dynamic model that accounts for the behavior. Attention is focused on the interplay of the thermodynamic forces and the kinetic processes. The coupled diffusion, viscous flow, and dielectric effect are incorporated into a phase field framework. The semi-implicit Fourier spectral method and the preconditioned conjugate-gradient method are applied in the simulations for high efficiency and numerical stability. Numerical simulations reveal rich dynamics of the pattern formation process. The kinetic constraint of the substrate plays a critical role in structural uniformity. The pillar size is insensitive to the film thickness, but the distance between pillars and the growth rate are significantly affected. The study suggests an approach to control structural formation in thin films with a designed electric field.

11:45 AM Y3.11

Gold Substrates of Sub-nm Surface Roughness with Molecular Adhesion Monolayer Technique Well-Suited for Molecular Engineering. Ajit K. Mahapatro and David B. Janes; School of Electrical and Computer Engineering, Purdue University, West Lafayette, Indiana.

Realizing a gold (Au)-surface with roughness at the atomic scale using techniques compatible with integrated device fabrication is of great interest to future molecular engineering. In this work a technique has been developed to realize Au films with surface roughness comparable to the best available techniques and suitable for formation of patterned device structures. The technique utilizes room temperature e-beam evaporated Au films over a chemically grown self assembled monolayer of (3-Mercaptopropyl) trimethoxysilane (MPTMS) on oxidized silicon substrates. The oxane-siloxane-silsesquioxane bond at the SiO₂ side and the sulphur-gold bond at the top evaporated Au side makes MPTMS a good adhesive layer between SiO₂ and Au. Surface morphology is studied using atomic force microscopy (AFM), which shows a rms surface roughness of $\sim 2\text{Å}$ over a $1\mu^2$ area (and $\sim 6\text{Å}$ over a $10\mu^2$ area), for Au surface with MPTMS as the adhesive monolayer, for "as-deposited" Au evaporated at room temperature using Ti as the adhesive layer on the SiO₂ substrate. In order to verify the suitability of this surface for formation of well-ordered organic monolayers, a self-assembled monolayer (SAM) of an alkanethiol molecule is formed on the surface and characterized. The physical stability of the Au thin film towards commonly used chemicals and processes during photo-lithography and self-assembly is also studied. Various lateral and vertical devices were successfully fabricated using electromigration and stamping techniques respectively. Here the top Au is successfully transferred to the SAM prepared Au-substrate. Electrical measurements are studied for dithiol molecules considering the metal-molecule-metal vertical device configurations. This study indicates that the atomic flat Au films prepared in this technique will be useful as an efficient substrate for studying molecular monolayer characterizations and for fabricating metal-molecule-metal vertical devices with larger active area for electrical measurements, which is still challenging for today's technology.

SESSION Y4: Photo/Laser/Plasma Based
Manufacturing
Chair: Maarten De Boer
Tuesday Afternoon, November 29, 2005
Back Bay A (Sheraton)

1:30 PM *Y4.1

Micro-Manufacturing Using Laser Direct-Write. Alberto Pique, Materials Science & Technology Division, Naval Research Laboratory, Washington, District of Columbia.

The use of direct-write techniques might revolutionize the way microelectronic components such as interconnects, passives, ICs, antennas, sensors and power sources are designed and fabricated. The Naval Research Laboratory has developed a laser-based microfabrication process for direct-writing the materials required for the above components. This laser direct-write (LDW) technique is capable of operating in subtractive, additive, and transfer mode. In subtractive mode, the system operates as a laser micromachining workstation capable of achieving precise depth and surface roughness control by adjusting the distance between overlapping laser pulses. In

additive mode, the system utilizes a laser-forward transfer process for the deposition of metals, oxides, polymers and composites under ambient conditions onto virtually any type of surface. Finally, in transfer mode, the system is capable of transferring a single device, such as semiconductor bare die, inside a trench or recess in a substrate, thus performing the same function of the pick-and-place machines used in circuit board manufacture. The use of this technique is ideally suited for the rapid prototyping of microelectronic components and systems while allowing the overall circuit design and layout to be easily modified or adapted to any specific application or form factor. This presentation will discuss several examples of the types of mesoscopic electronic devices fabricated using LDW techniques. This work was supported by the Office of Naval Research.

2:00 PM Y4.2

Design and Calculation of Advanced Microstructural Patterns by Laser Interference Metallurgy. Andres Fabian Lasagni, Holzapfel Christian and Frank Muecklich; Materials Science, Saarland University, Saarbruecken, Germany.

Laser Interference Metallurgy is a recently developed method for the laser material surface modification by which various interference patterns can be transformed directly, permanently, and efficiently to the surfaces of different kinds of materials. By using of this technique, different metallurgical effects such as melting, recrystallization, quenching, recovery, defect or phase formation can be exploited. In this work, advanced microstructural patterns are previously designed and by means of the Fast Fourier Transformation, the geometrical configuration for the laser interference experiments is calculated. After that, metallic samples are irradiated in order to demonstrate the viability of the presented method. The resulted structures were studied by means of FIB (Focus Ion Beam), TEM (Transmission Electron Microscopy) and WLI (White Light Interferometry).

2:15 PM Y4.3

A Fracture Mechanics Model for the Repair of Microcantilevers by Laser Induced Stress Waves. Zayd Chad Leseman, Sai Koppaka and Thomas Mackin; Mechanical Engineering, University of Illinois Urbana-Champaign, Urbana, Illinois.

A fracture mechanics model has been developed that describes stress wave repair of stiction-failed microcantilevers. This model allows one to predict accurately the number of laser pulses, at a specific fluence and wavelength, required to fully repair stiction-failed microcantilevers. A full range of experiments have been performed to validate the model. The proposed fracture mechanics model includes the strain energy stored in a stiction-failed microcantilever and the strain energy supplied by a laser induced stress-wave propagating in a material. The "unstuck" portion of the microcantilever is modeled as a crack such that crack growth reduces the stiction-failed length of the microcantilever. Stress waves are initiated on the back-side of the device, opposite the microcantilevers, by laser illumination. A laser pulse hitting the substrates surface imparts a radiation pressure on that surface that launches stress-waves into the device. The magnitude of the radiation pressure is found using a matrix method derived from Maxwell's Equations. This method includes the laser's fluence and wavelength as well the optical properties of the substrate. On the first pass, the stress wave travels through the substrate as a compressive wave that does not repair the stiction-failed microcantilevers. Upon reflection from the far-side free surface the stress wave becomes tensile, stretching the interface bonds to failure. The energy balance equations include a length scale term that is obtained experimentally. This length scale is shown to be identical to the surface roughness of the substrate and cantilever. Experiments using two different wavelengths and a range of fluences were carried out to validate the proposed model. Experiments were performed using microcantilevers fabricated by the Summit IV process. Stiction lengths were determined using an interferometric microscope, while stress-waves were launched using a Nd:YAG laser illuminating the back-sides of the test samples. In all experiments all beams were fully repaired. These experiments are compared with theory and show that one can predict, to one pulse, the number of pulses required to fully repair stiction-failed microcantilevers.

3:30 PM *Y4.4

Laser-Assisted Nanoprocessing. Costas P. Grigoropoulos, David Hwang and Anant Chimmalg; Laser Thermal Laboratory, Department of Mechanical Engineering, University of California, Berkeley, Berkeley, California.

Recent research results on laser-assisted nanomachining, nanolithography and nanodeposition will be presented. Ultra-fast and nanosecond pulsed lasers have been coupled to near-field-scanning optical microscopes (NSOMs) through apertured bent cantilever fiber probes as well as with atomic force microscope (AFM) tips in apertureless configurations. Experiments have been conducted on the

surface modification of metals, polymers and semiconductor materials in both ambient air and controlled environments. By combining nanoscale ablative material removal with subsequent chemical etching steps, ablation nanolithography and patterning of fused silica and crystalline silicon wafers has been demonstrated. Confinement of laser-induced crystallization to nanometric scales has also been shown. Nucleation and growth of semiconductor materials has been achieved by Laser Chemical Vapor Deposition (LCVD) at the nanoscale level. Related work on nanoengineering applications will be discussed.

4:00 PM Y4.5

Scaled Up Pulsed Deposition Technology: Carburization Resistant Ablation Coatings for Ethylene Pyrolysis Coils. Alok Chuahhan¹, Henry White¹, Weidong Si² and Jianming Bai³; ¹Materials Science, Stony Brook University, Stony Brook, New York; ²Physics, Brookhaven National Laboratory, Upton, New York; ³High Temperature Materials Laboratory, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Products derived from ethylene have and will continue to replace metallic materials traditionally used for transportation, building materials, and products we use in our everyday lives. As the demand continues to increase, a more suitable material for the outlet coils of ethylene pyrolysis heaters will have to be identified. In this study, we discuss utilization of scaled up pulsed deposition technology to deposit carburization resistant coatings on the inner diameter of ethylene pyrolysis tubing with the intent of extending tube life. Ablation target material selection was based primarily on elevated temperature properties and the ability of the coating to prevent transformation of the inherent protective chromium oxide surface film to metal carbides while in service. The logistics [i.e. issue regarding the external sources (lasers, electron guns, etc); ablation target (surface finish, inlays, geometry, etc.); deposition atmosphere (vacuum, inert/ active gases composition and pressures, etc.); fluence (energy, frequency, spot size, etc.); nature of plume (atoms, ions, particles, clusters etc.); and specimen/ tube considerations (i.e. translation speed, length, diameter, roughness, wall temperature, etc.) related to depositing silicon carbide and aluminum oxide on austenitic heat resistant tubing traditionally used for ethylene pyrolysis service will be discussed. We are able to deposit uniform thin films up to 0.5 um on ≥ 50 mm inner diameter x 75 mm length tubing. Preliminary fitness for service tests indicate limited carbon diffusion and satisfactory adhesion as determine by the results of our pack carburization and x-ray stress measurements.

4:15 PM Y4.6

Towards laser-based nanomanufacturing of ordered metal nanoclusters. Christopher Favazza^{1,2}, Justin Trice^{1,2} and Ramki Kalyanaraman^{1,2}; ¹Physics, Washington University in St. Louis, St. Louis, Missouri; ²Center for Materials Innovation, Washington University in St. Louis, St. Louis, Missouri.

Metals in the form of spatially ordered nanoclusters have numerous applications, including as chemical sensors, plasmon waveguides and in non-linear optical applications. Laser-processing is well suited for a manufacturing environment. However, laser-based assembly of nanometer scale features with ordering in length scales below the diffraction limit is a significant challenge. Here, we present investigations of ordering of ultrathin metal films into one and two dimensional ordered patterns containing clusters in the size range of 20 to 200 nm on various surfaces. By a combination of fringe-shifting interferometry using UV (266 nm) laser light and self-assembly driven by surface effects, evidence for ordering at length scales below the diffraction limit has been observed for Co metal. Using finite element modeling in conjunction with experiments, the mechanism of nanoassembly and the ultimate limits to ordering using laser-interference irradiation will be discussed for Co metal films. This nanomanufacturing technique promises to be a simple and inexpensive approach to make large-area ordered thin film nanostructures.

4:30 PM Y4.7

Modification of Nanocomposite PMMA-POSS Surfaces by Oxygen Plasma Exposure. Chris Hughes¹, Brian H. Augustine², Jessica Maidment³ and Rebekah Esmaili¹; ¹Physics, James Madison University, Harrisonburg, Virginia; ²Chemistry, James Madison University, Harrisonburg, Virginia; ³Physics, Randolph-Macon Womens College, Lynchburg, Virginia.

Thin films of the nanocomposite copolymer polymethylmethacrylate-polyhedral oligomeric silsesquioxane (PMMA-POSS) have been deposited via-spin casting from a THF solution onto glass and polymeric substrates and modified in a remote oxygen plasma environment. A change from hydrophobic to hydrophilic was observed after exposure to an oxygen plasma for time periods on the order of tens of seconds. This change was quantified by measuring water contact angles on the surface which varied from greater than 90° before plasma exposure to less than 10° afterwards.

A model for this behavior in which the isobutyl groups around the POSS cage are selectively removed by the oxygen plasma leaving a SiOx-rich surface is proposed. Time-of-flight secondary ion mass spectroscopy (ToF-SIMS) data were performed to test this model and show that the number of isobutyl groups on the surface does decrease with exposure time. On-going experiments involving UV-ozone exposure show similar results and will be discussed. Modified surfaces have been incorporated into polymeric microfluidic separation devices and the electro-osmotic flow characteristics of these devices in comparison to conventional glass or PMMA devices will be discussed.

4:45 PM Y4.8

Microstructure of Nitrided Aluminum Alloys Formed by Electron Beam Excited Plasma Technique. Li Liu¹, Atsushi Yamamoto¹, Takanori Hishida², Hiroaki Shoyama², Tamio Hara² and Harushige Tsubakino¹; ¹University of Hyogo, Himeji, Hyogo, Japan; ²Faculty of Engineering, Toyota Technological Institute, Nagoya, Japan.

The nitriding of the AA5052, Al-1%Si, Al-7%Si and Al-12% Si aluminum alloys were carried out using an electron beam excited plasma (EBEP) technique. The specimens were characterized with respect to the following properties: wear resistance (ball-on-disk method), crystallographic structure (X-ray diffraction), the surface and cross sectional microstructures of the nitrided layer (AlN layer) observed by means of scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The friction coefficient of AA5052 is about 0.2 and that of Al-7%Si is about 0.1. The AlN layer was uniformly formed on the AA5052 and other aluminum alloys. A compressive residual stress acted on these aluminum alloys surface. In the AlN layer, pillar-shaped grains were formed perpendicular to the surface with different orientations. On the surface of the AlN layer in AA5052, the nitrogen concentration was high, and in the middle of the AlN layer, it had a constant concentration as similar as aluminum, and the concentration decreased as it approached the interface. The magnesium concentrates at the Al/AlN interface due to the formation of MgAl₂O₄ in AA5052.

SESSION Y5/NN7: Joint Session: Surface Engineering -
Scanning Probe Microscopy Session
Chair: Scott Sills
Wednesday Morning, November 30, 2005
Back Bay C (Sheraton)

8:00 AM *Y5.1/NN7.1

Scanned Probe Microscopy-based Nanomechanics and Microtribology of Solid Lubricants. Kathryn J. Wahl, Richard R. Chromik and Gunyoung T. Lee; Tribology Section, U.S. Naval Research Laboratory, Washington, District of Columbia.

Friction, wear and endurance of solid lubricant films are controlled by interfacial processes involving "third body" transfer films. These third body films are thin (nanometers to microns), inhomogeneous on the micron scale, and differ from the originating solid lubricant film both chemically and mechanically. *In situ* tribological studies have shown that these films also exhibit dynamic rheological properties that depend strongly on sliding conditions. In this talk, we will illustrate how spatially resolved, surface sensitive nanomechanics and microtribology experiments can be used to study solid lubrication processes. SPM-based instrumented nanoindentation is used to correlate nanomechanical properties of the interfacial films with macroscopic tribological response. Also, by rastering the indenter tip laterally, instrumented indentation apparatus can be used to examine microscale sliding processes and address scaling effects in solid lubrication. In both cases, knowledge of indenter/counterface geometry, penetration depth, load, and position are key, enabling evaluation of the lubrication mechanisms as well as comparison with contact mechanics models. Ultimately, these micro- and nanoscale approaches can provide new insight into tribological phenomena at all scales.

8:30 AM Y5.2/NN7.2

Measurements of Creep on an OTS Monolayer Coated Microactuator. Alex D. Corwin¹, Robert W. Carpick², Erin E. Flater², Robert W. Ashurst³ and Maarten P. de Boer¹; ¹MEMS Technology, Sandia National Labs, Albuquerque, New Mexico; ²Engineering Physics, University of Wisconsin - Madison, Madison, Wisconsin; ³Chemical Engineering, Auburn University, Auburn, Alabama.

Organic monolayer coatings are used in contacting micromachined devices to reduce friction, wear, and adhesion. We have developed a "nanotractor" actuator, which is a friction-based microelectromechanical (MEMS) device that can be used to make sensitive measurements of both adhesion and static and dynamic

coefficients of friction. We have used the nanotractor to look at a variety of self-assembled monolayer (SAM) coatings, including octadecyltrichlorosilane (OTS), (tridecafluoro-1,1,2,2-tetrahydrodecyl)tris(dimethylamino)silane (FOTAS), as well as uncoated devices dried in a critical point drier (CPD) using carbon dioxide as the supercritical fluid. These are precisely the treatments used in actual MEMS devices, and the coatings are extremely effective in reducing adhesion. Measurements of friction show that at the micro-scale, friction is proportional to the sum of the adhesive and applied loads. Both coatings reduce static and dynamic friction compared with the uncoated devices, with the OTS coating being significantly more effective. However, our recent measurements with OTS show complex effects beyond simple reductions in the friction coefficient. In particular, OTS-coated devices show significant time-dependent creep even under an applied normal load large enough to prevent slip based on the measured coefficient of static friction. While FOTAS and CPD-treated films do not exhibit perceptible creep within our measurement resolution of 10 nm, we have measured motions up to three microns occurring over a period of four minutes for the OTS coating. We hypothesize that OTS, consisting of an 18 carbon chain and significantly longer than FOTAS molecules, enables the entanglement and slow disentanglement of the chains, leading to the observed creep. We will discuss these results in comparison with single-asperity measurements of the same materials conducted with atomic force microscopy. We further examine the temperature dependence of the creep in the MEMS device using a thermal stage with 0.1 C temperature stability. 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.

8:45 AM Y5.3/NN7.3

A few asperities determine the work of adhesion in nanometer contacts. Erik Thoreson¹, J. Martin² and N. A. Burnham¹; ¹Department of Physics, WPI, Worcester, Massachusetts; ²Analog Devices, Inc., Cambridge, Massachusetts.

The surface roughness of a few asperities and their influence on the work of adhesion is of scientific interest. Engineering and nanoscopic scale adhesion data have seemingly given contradictory results. Despite the importance of bridging the gap between the two regimes, little experimental work has been done, presumably due to the difficulty of the experiment, to determine how small amounts of surface roughness might influence adhesion data in between the two scales. To investigate the role of few-asperity contacts in adhesion, the work of adhesion was measured between different sized AFM tips (with different roughnesses) and sample surfaces that had well-controlled material properties. There were seventeen tips of four different types, with radii from 200 nm to 60 μ m. The samples were unpatterned amorphous silicon dioxide die with two types of surface conditions (untreated and treated with a few angstroms of vapor deposited diphenylsiloxane). We observed that the work of adhesion decreased as the radius of the AFM tip increased, which was contrary to all continuum-mechanics model predictions. To explain this behavior, we assumed that the interactions between the AFM tip and sample were additive, material properties were constant, and that the AFM tip, asperities, and sample surfaces were of uniform density. Based on these assumptions, we calculated a simple correction due to the surface roughness of the AFM tips. The simple correction for the surface roughness resulted in the expected independence of the work of adhesion from radius, but the magnitudes were higher than expected. Normal and heat-treated AFM tips have minimal surface roughness and result in magnitudes that are more reliable. The relative uncertainty for the work of adhesion was 15%. In this presentation, we derive how the cantilever and tip parameters contribute to the measured work of adhesion and show how the corrected results compare with theory. Although much work is still needed, the work presented here should progress the understanding of adhesion between the engineering and nanoscopic scale.

9:00 AM Y5.4/NN7.4

Mechanical load assisted dissolution: Influence of contact loads and residual stresses. Andrew Mitchell and Pranav Shrotriya; Mechanical Engineering, Iowa State University, Ames, Iowa.

Mechanical load assisted dissolution is identified as one of the key mechanism governing material removal in phenomena such as fretting corrosion or chemical mechanical planarization (CMP). Repeated contact of biomedical implants in a corrosive physiological environment leads to fretting corrosion resulting in formation of soluble and particulate debris that may induce a cascade of inflammatory events or failure of the implant. Similarly, CMP involves removal of material through small particles abrading the surface in a reactive environment. While it is well known that stress affects the dissolution rate of material the exact mechanisms governing stress-assisted dissolution are still not well understood. In order to

identify the governing mechanism, dissolution of a stressed metallic surface subjected to single asperity contact is investigated. For this study, specimens are mounted in four point bending configurations such that a range of stress levels are applied to the specimen surface. The testing configurations are designed for easy accessibility to facilitate in-situ mechanical stimulation and imaging by Atomic Force Microscope (AFM). To develop a thorough understanding of stress effects on dissolution two material systems were investigated; CoCrMo (ASTM F75) commonly used in total hip and knee replacements, and a Cu alloy commonly used in the investigation of CMP process. Using the tip of an atomic force microscope (AFM) as a well characterized //asperity, controlled contact forces are applied to mechanically stimulate the loaded specimen surface in ambient and oxidizing environments. This would be analogous to a wear particle (the AFM probe) coming into contact with the stressed surface of an implant or work piece. Volume of the material removed is measured to determine the dissolution rate as a function of applied surface stress and contact loads. In addition, a kinetic model of stress-assisted material dissolution is developed to analyze the experimental observations and identify critical stress and loading levels required to initiate accelerated material dissolution.

9:15 AM Y5.5/NN7.5

In - Situ Raman Tribometry Studies on Adaptive Nanocomposite Coatings. Richard Chromik^{1,2}, Colin Baker^{2,3}, Andrey Voevodin³ and Kathryn Wahl¹; ¹Code 6176, Naval Research Laboratory, Washington, District of Columbia; ²Department of Physics, North Carolina State University, Raleigh, North Carolina; ³Materials and Manufacturing Directorate, Air Force Research Laboratory, Dayton, Ohio.

For tribological applications where temperature and humidity vary over a wide range, the design of a suitable coating system becomes especially challenging. Solid lubricant materials typically perform best within a narrow range of environmental conditions. One solution is to develop nanocomposite coatings with multiple phases, each with advantageous tribological properties for a given environment. Previous research on nanocomposite coatings containing yttria stabilized zirconia (YSZ), diamond like carbon (DLC), Au and MoS₂ has demonstrated frictional adaptation to that of the component exhibiting the lowest friction coefficient for humid, dry or elevated temperature conditions. *Exsitu* characterization tied this behavior to changes in the chemistry of the transfer film. Using a custom-built reciprocating tribometer, we have studied the transfer film formation, chemistry and dynamics of YSZ/DLC/Au/MoS₂ coatings as a function of humidity and sliding cycles. Steady state friction coefficients were 0.07-0.08 in ambient conditions (45-55%RH) and 0.04-0.05 in a dry nitrogen environment (4-6%RH). A transparent sapphire counterbody allowed for *insitu* video imaging of the sliding contact and chemical analysis of the transfer film using micro-Raman spectroscopy. Both of these analysis techniques, as well as *exsitu* Raman and optical profilometry, indicated that the transfer film is thicker for dry environments than for wet. Additionally, the velocity accommodation modes in dry and humid environments were different – dry conditions resulted in primarily interfacial sliding while wet conditions allowed for some transfer film shearing. However, for both environments, debris exchange between the counterface and the track was very dynamic and, in the case of dry conditions, led to frictional spiking. During humidity changes, images of the contact revealed that the transfer film breaks down and re-grows, but at a slower rate than the friction adaptation.

9:30 AM Y5.6/NN7.6

Characterization of Tribo-chemistry in Hard Nanostructured Carbon Materials using PEEM-NEXAFS Spectromicroscopy. Anirudha V. Sumant¹, David Grierson¹, Jason Bares¹, Mike Abrecht², Brad Frazer², Gelsomina De Stasio², Orlando Auciello³, John Carlisle³, Thomas Scharf⁴, Mike Dugger⁴, Thomas Friedmann⁴, John Sullivan⁴ and Robert Carpick¹; ¹Engineering Physics, University of Wisconsin at Madison, Madison, Wisconsin; ²Department of Physics, University of Wisconsin at Madison, Stoughton, Wisconsin; ³Materials Science Division, Argonne National Laboratory, Argonne, Illinois; ⁴Sandia National Laboratories, Albuquerque, New Mexico.

Tribo-chemistry of sliding surfaces in contact plays an important role in determining the wear and friction properties of interfaces from macro to nano-scale applications. Ultrananocrystalline diamond (UNCD) and tetrahedral amorphous carbon (ta-C) films are particularly promising materials for a range of demanding applications to macro, micro, and nanodevices, because of their exceptional mechanical and tribological properties. However, the mechanisms controlling friction and wear of UNCD and ta-C are not well understood because of lack of understanding of tribo-chemical processes at play. Furthermore, as-deposited ta-C films have high residual stresses, and full stress relief is possible by post-annealing at elevated temperatures (~650 oC). However, no systematic experimental studies were previously reported to understand the

surface chemistry and bonding configuration of these films after annealing, which most likely will affect their tribological properties. We present studies aimed at elucidating the fundamental tribo-chemical mechanisms of wear and friction in UNCD and ta-C films. We have performed fretting and sliding wear measurements using a ball-on-disc apparatus for UNCD and ta-C films in contact with both self-mated and Si₃N₄ balls in ambient and controlled atmosphere conditions. The micron-scale wear tracks produced on these films have been analyzed by atomic force microscopy (AFM) and PEEM-NEXAFS (PhotoElectron Emission Microscopy combined with Near-Edge X-ray Absorption Fine Structure) spectromicroscopy to obtain quantitative information on structural modifications and chemical changes inside the wear track. The ability of the PEEM-NEXAFS technique to spatially resolve (10 nm in ideal case) and chemically characterize regions of interest is unparalleled and therefore ideally suited for this work. The results show for the first time that it is possible to detect chemical changes with great details occurring within the micro-scale wear track of these materials. Furthermore, we are able to establish correlations between spectroscopically-identified chemical changes within the wear track and corresponding changes in the friction coefficient recorded during tests. In the case of a UNCD film in contact with a Si₃N₄ ball, we see formation of SiO_x complexes within the wear track, and corresponding increases in friction coefficient. In the case of a ta-C film in contact with Si₃N₄ ball, we observed a decrease in friction coefficient after annealing, and complex changes in the carbon bonding configuration on the surface. We will discuss the chemical changes within the wear tracks, the possible mechanisms behind them, and the resulting effect on friction and wear behavior in these films.

9:45 AM Y5.7/NN7.7

The Effect of Surface Atomic Structure on the Nanotribology of Ultrananocrystalline Diamond and Tetrahedral Amorphous Carbon Thin Films. D. S. Grierson¹, A. V. Sumant¹, J. E. Gerbi², J. Birrell³, O. Auciello^{5,4}, J. A. Carlisle^{5,4}, T. A. Friedmann⁶, J. P. Sullivan⁶ and R. W. Carpick¹; ¹Engineering Physics, UW-Madison, Madison, Wisconsin; ²University of Illinois at Urbana-Champaign, Champaign, Illinois; ³Advanced Diamond Technologies, Inc., Champaign, Illinois; ⁴Materials Science Division, Argonne National Laboratory, Argonne, Illinois; ⁵Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois; ⁶Sandia National Laboratory, Albuquerque, New Mexico.

High performance carbon-based thin films are attracting interest as candidate materials to enhance the tribological characteristics of mechanical components from the macro- to the nanoscale. These materials have been studied at the macroscale, and the resulting tribo-mechanical properties have been shown to be excellent. However, at the micro- and nanoscale, little is known about the tribological properties and how they are affected by the surface atomic structure. We have gained new fundamental insights into how differences in bonding structure, film microstructure, surface chemistry, and chemical environment produce different nanotribological behavior. We have investigated two distinct carbon-based thin film materials: ultrananocrystalline diamond (UNCD) and tetrahedral amorphous carbon (ta-C). To understand the surface chemistry of these materials, we use near edge x-ray absorption fine structure (NEXAFS) spectroscopy to determine the chemical composition and the nature of the bonds in the near-surface region. To study the corresponding nanotribological properties, we use the atomic force microscope (AFM) to measure the work of adhesion and frictional forces between diamond AFM tips and the materials of interest. We find that the nanotribological properties depend sensitively on the surface chemistry and bonding. In the case of UNCD, we can lower the work of adhesion between a diamond tip and the UNCD surface by terminating the surface with hydrogen. We find that the adhesion can reach the van der Waals' limit (<30 mJ/m²) by this process, and we find that adhesion and friction are significantly lower than for silicon self-mated interfaces. Studies of ta-C demonstrate how bonding structure and nanotribological properties are affected by thermal annealing, which is a critical step in the film synthesis required for relieving internal stresses. Specifically, we find that annealing ta-C above 600° C increases the amount of sp²-bonded carbon near the surface (graphitization), but the work of adhesion between the diamond tip and the ta-C is not affected. Preliminary results indicate that friction forces are modestly reduced by this process. We will discuss possible mechanisms that account for this surprising behavior. We will also discuss how our results can be used to tailor the surfaces of carbon-based materials to optimize their tribological response. 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 and the Air Force Office of Scientific Research under Contract FA9550-05-1-0204.

10:30 AM Y6.1

Aggregation Structure of Polyurethane Ultrathin Films.

Ken Kojio, Yusuke Uchiba, Yoshitaka Mitsui and Mutsuhisa Furukawa; Materials Science and Engineering, Nagasaki University, Nagasaki, Japan.

Polyurethane (PU) is one of the most important polar polymers. This strong polarity might affect on the aggregation structure for the PU ultrathin films because the effect of surface and interface of the ultrathin films is quite effective with decreasing film thickness. In this study, we investigated the relationship between aggregation structure and film thickness using atomic force microscope (AFM) and Fourier transform infrared (FT-IR) spectroscopy. The PU was synthesized with poly(oxytetramethylene)glycol (PTMG), 4,4'-diphenylmethane diisocyanate (MDI) and 1,4-butanediol (BD) by a prepolymer method. The hard segment contents were 34 wt%. The PU ultrathin films were prepared onto a silicon wafer from the PU tetrahydrofuran solution by a spin coating method. Microphase-separated structure was clearly observed for all PU films, which the hard segment domains were surrounded by the soft segment matrix. For the thick film (>200 nm), the size of the hard segment domains was ca. 20 nm. This is almost same as bulk one. On the other hand, the domain size for the ultrathin film with 8 nm thickness was ca. 10 nm. This seems to be simply related to a decreasing space.

10:45 AM Y6.2

Electrophoresis of Proteins Using Flat Surfaces.

Perumal Radha Ramasamy¹, Miriam Rafailovich¹, Jonathan Sokolov¹, Lisa Miller² and Peter Brink³; ¹Materials Science and Engineering, SUNY - Stony Brook, Stony Brook, New York; ²NLSL, BNL, Brook Haven, New York; ³Biophysics and Physiology, SUNY - Stony Brook, Stony Brook, New York.

Proteomics is a relatively new field of Biology that deals with protein structure and protein - protein interactions. Separation of proteins is conventionally done using gels. The separation of the proteins is depends on the charge, size of the proteins and also the pore size of the gel. Protein separation becomes difficult when the size of the proteins is very small or large when compared to the pores size of the gel. The mobility of proteins influenced by its interaction with a surface and the ions in the buffer can be used to identify different proteins based on their migration velocities on the surface. We have studied the electric field distribution on different cell geometries using E-Stat field calculations. We have studied the Electro osmotic flow (EOF) of the buffer using fluorescently tagged Poly styrene beads of size 1 Micron. We use salt solution to anchor proteins on surfaces and we have studied the secondary structure of the proteins on the drop and in solution using FTIR spectroscopy. The drops are placed under a confocal microscope and the migration of the aggregates is studied for different TBE buffer concentrations. It is found that the migration of the FITC tagged proteins largely depends upon the EOF of the liquid and not on the Isoelectric point of the protein. The migration of proteins on Conducting surfaces and semiconducting surfaces are presently being studied.

11:00 AM Y6.3

The Effect of Surface Interactions on the Viscosity of Polymer Thin Films. Chunhua Li¹, Clive Li¹, Jun Jiang¹, Tadanori Koga¹, Hyunjung Kim², Laurence Lurio³, Suresh Narayanan⁴, Sunil Sinha⁵, Miriam Rafailovich¹ and Jonathan Sokolov¹; ¹Department of Material Science, State University of New York at Stony Brook, Stony Brook, New York; ²Department of Physics and Interdisciplinary program of Integrated Biotechnology, Sogang University, Seoul, South Korea; ³Department of Physics, Northern Illinois University, DeKalb, Illinois; ⁴Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois; ⁵Departments of Physics, University of California San Diego, La Jolla, California.

Previously, we reported that the viscosity of ultra thin polymer films can be measured by three independent techniques: Bilayer dewetting measurements where the viscosity is derived from dewetting velocity; X-ray Photon Correlation Spectroscopy (XPCS) where the viscosity is determined from the relaxation rate of thermally induced surface roughness and Dynamic Secondary Ion Mass Spectroscopy (DSIMS) where the viscosity is derived from the measurements of the tracer diffusion coefficient. In this work, we apply these techniques to study the effect of film thickness on viscosity. All three different techniques show a consistent thickness dependence: the viscosity of polymer thin film was observed to increase about two orders of magnitude near the

solid substrate. DSIMS and Neutron Reflectivity (NR) measurements indicated that a layer of PS, approximately 2Rg thick, remained permanently adsorbed at the Si substrate. Measurements performed on split layer substrates indicated that this layer was responsible for trapping subsequent layers, and propagating the effect of the surface interactions to chains without direct contacts to the surface. If this layer was applied prior to the rest of the film, it in fact screened the surface interactions and even caused auto-dewetting of the other layers in the film. These results will be discussed in terms of the two fluid hypothesis first postulated by Bruinsma et al [1]. [1] R. Bruinsma, *Macromolecules*, 23, 276 (1990) Supported in part by the NSF-MRSEC

11:15 AM Y6.4

A technique to measure the cohesive energy density via evaporating drops. Xiaohua Fang, Bingquan Li, Jonathan Sokolov and Miriam Rafailovich; Material Science and Engineering, Stony Brook University, Stony Brook, New York.

In this paper, we gave proof that drop-drying behavior at a specific temperature was actually controlled by the physical properties of the liquid itself, such as the molecular weight, the density, the diffusion coefficient of the drop vapor molecules in air, and the heat of vaporization of the drop liquid. Assuming no adsorption, the surface function is to define the drops initial states, from where the evaporation starts. A model was developed to predict the relationship between contact angle and contact base diameter values of the drops at any time during the drying. From the study results, we developed a new simple technique to measure the cohesive energy density between the molecules of the testing liquid. (This work is supported by the NSF-MRSEC program, the Department of Energy-DMS, and the NIH.)

11:30 AM Y6.5

Ultra sensitive Bio-Chemical sensors Based on Optical Resonance. Shalini Prasad, ECE, Portland State University, Portland, Oregon.

We have developed bio-chemical sensor technology by adapting the principle of optical resonance. Micro-cavity based sensor arrays were fabricated using standard wet lithography techniques. A number of geometries namely, disc, cylinder and ring were explored and characterized. The ideal geometry for developing a cost effective off clean room based portable device was identified and optimized. Surface chemistry based modifications was employed to render specific micro cavities sensitive to specific bio-chemical agents. The detection of the chemical agents was achieved in an electro-optical manner. Agent identification was achieved due to contact based sensing. The micro cavities were irradiated with light of specific wavelength and intensity from a substrate coupled diode laser. The binding of the chemical agent to the sensing sites in the micro cavity resulted in a change in the light intensity associated with individual cavities. This was identified by optically amplifying the change using evanescent coupling. The optical signal was analyzed and translated into the electrical domain to yield unique markers corresponding to specific chemical agents. The micro cavity based sensor array was used to detect a broad range of analytes in gaseous media up to parts per trillion sensitivity. The response time at the ultra low detection thresholds was identified to be in the order of milliseconds.

11:45 AM Y6.6

Probing the Molecular Transformation from Diblock to Triblock Copolymer by Progressive Endblock Growth.

Michelle Bowman¹, Richard Spontak¹, Steve Smith², Mark Hamersky², Kim Rasmussen³ and Arif O. Gozen¹; ¹Materials Science & Engineering, North Carolina State University, Cary, North Carolina; ²Procter & Gamble Co., Cincinnati, Ohio; ³Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico.

Fundamental phase and property studies of AB diblock and molecularly symmetric ABA triblock copolymers conducted over the past 25 years have provided a firm understanding of the conditions under which these technologically important macromolecules spontaneously self-organize. While the results of such studies have been enlightening and necessary, these two copolymer classes have often been treated separately due to pronounced differences in mechanical properties, normally attributed to midblock bridging in ABA copolymers. In this work, we seek to follow the phase, morphology and property changes that accompany two microphase-ordered diblock copolymers differing in composition and molecular weight as they transform into A1BA2 triblock copolymers by progressive endblock growth. Two poly(styrene-*b*-isoprene) diblock copolymers, as well as several molecularly asymmetric triblock copolymers grown from each diblock copolymer by subsequent living anionic polymerization, have been synthesized via living anionic polymerization. Dynamic shear measurements have been conducted to discern the order-disorder transition (ODT) of each copolymer from

precipitous reductions in the dynamic elastic and viscous moduli during isochronal temperature sweeps. Experimental transition temperatures, exhibiting an initial reduction due to mixing of the B midblock and the short A2 endblock, compare favorably with predictions from the mean-field theory proposed by Mayes and Olvera de la Cruz for molecularly asymmetric triblock copolymers. Complementary morphological characteristics of the copolymers have been determined from transmission electron microscopy and small-angle x-ray scattering. These results are compared with self-consistent field (SCF) predictions to ascertain the location of the short A2 endblock, the endblock length at which molecular bridging first commences and the nature of the bidisperse brush formed by A1 and A2 blocks differing in size.

SESSION Y7: Modeling and Simulation
Chair: Steve Bull
Wednesday Afternoon, November 30, 2005
Back Bay A (Sheraton)

1:30 PM Y7.1

Persistent Step-flow Growth of Strained Films on Vicinal Substrates. Wei Hong¹, Ho Nyung Lee², Mina Yoon², Hans M.

Christen², Douglas H. Lowndes², Zhigang Suo² and Zhenyu Zhang^{2,3,1}; ¹DEAS, Harvard University, Cambridge, Massachusetts; ²Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; ³Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee.

Many applications demand high-quality thin films of complex materials, yet proper choice of their growth conditions still largely relies on trial-and-error rather than a thorough understanding of the underlying mechanisms. We propose and experimentally verify a model of persistent step flow, emphasizing dominant kinetic processes and strain effects. Within this model, we construct a morphological phase diagram, delineating a regime of step flow from regimes of step bunching and island formation. In particular, we predict the existence of concurrent step bunching and island formation, a new growth mode that competes with step flow for phase space, and show that the deposition flux and temperature must be chosen within a window in order to achieve persistent step flow. The model rationalizes the diverse growth modes observed in pulsed laser deposition of SrRuO₃ on SrTiO₃.

1:45 PM Y7.2

Surface Dislocation Injection and Motion on Au {001} Surface: A Combined HREM and Molecular Dynamics Simulation Study. Chun-Wei Pao^{1,2}, Henny W. Zandbergen³ and David J. Srolovitz^{1,2}; ¹Mechanical & Aerospace Engineering, Princeton University, Princeton, New Jersey; ²Princeton Institute for the Science and Technology of Materials, Princeton University, Princeton, New Jersey; ³National Centre of HREM, Kavli Centre of Nanoscience, Delft University of Technology, Delft, Netherlands.

Recent real-time high resolution TEM images of Au surfaces show adatoms on {001} terraces being injected into a terrace, forming what can be described as a straight surface dislocation or a 1-d string of interstitials. The surface dislocation is mobile and easily glides along the terrace and is often trapped near the terrace edges. We report a series of static and dynamic atomistic simulations of the formation and motion of such dislocations on the Au {001} surface. We find that forming a surface dislocation is energetically favorable compared with adatoms on a surface. The simulations also show that the dislocation tends to trap near the terrace edge. A detailed analysis of the atomic structure of the dislocation is also performed. All of these results are consistent with experimental observations. The simulations also provide information on the surface dislocation formation and migration energies. The relative ease with which these surface dislocations form from adatoms, their high rate of migration and mechanisms for escape through steps (with the dislocation either parallel or perpendicular to the steps) suggest that such dislocations may provide an effective means of transporting adatoms from the top of one terrace to the next that effectively circumvents the Ehrlich-Schwoebel barrier for surface adatom diffusion.

2:00 PM Y7.3

Oscillatory Temperature-driven Morphological Relaxation of Surface Ripple Using Weak Pulsed Laser. Mikhail Khenner, Mathematics, SUNY at Buffalo, Buffalo, New York.

A continuum (Mullins-type) model is proposed for the non-isothermal, isotropic evolution of a crystal surface on which mass transport occurs by surface diffusion. The departure from constant temperature is assumed induced by incident pulsed laser beam. It has been shown experimentally and theoretically (M.M. Yakunin, *High Temperatures* 26(4), 585 (1988); B.S. Yilbas, M. Kalyon, *J. Phys. D: Appl. Physics*

34, 222 (2001) that such heating mode gives rise to the quasistationary regime, in which the surface temperature of a thick solid film oscillates about the mean value with the pulse repetition frequency. The implications of high-frequency oscillatory driving on relaxation of surface ripple are examined; in particular, the traveling wave solutions are detected numerically for some values of the parameter that governs the horizontal shift of the (time-oscillatory) temperature perturbation with respect to the ripple. Pulsed heating also results in faster smoothing of the ripple, compared to the case when the surface is at constant temperature which is same as the mean temperature in the pulsed heating mode. Impact on ripple shape is minor for ripple amplitudes considered. Model can be extended to include the anisotropic (and temperature-dependent) surface energy, deposition (probably pulsed) of material on the surface and stress. The model may prove useful in the theory and practice of thin film growth (pulsed laser deposition and laser-assisted chemical vapor deposition), laser etching and pattern formation on surfaces (self and induced assembly of surface structures). Regular paper is accepted for publication in the Physical Review E.

2:15 PM Y7.4

Asperity Evolution during Repeated Contacts: molecular dynamics simulation. Jun Song and David Srolovitz; Princeton Institute for the Science and Technology of Materials, Princeton University, Princeton, New Jersey.

Many MEMS devices employ mechanical contacts as high frequency electrical switches. These contacts occur on the nano- and micro-scales. Elastic/plastic deformation, adhesion and morphology evolution all play important roles in the operation of these devices. We perform molecular dynamics simulations of single asperity (EAM) contacts under cyclic loading and unloading. We monitor the full force-displacement curve, the evolution of the atomic structure/asperity morphology, dislocation nucleation and motion. The evolution of the system, including material transfer and morphology evolution, is related to both adhesion and plastic deformation. We separate these effects by performing simulations of both gold contacts and gold contacts with modified adhesion.

3:30 PM *Y7.5

Monitoring at the Sub-NM Level the Structure, Chemistry and Bonding of Deposited Thin Films and Associated Interfaces with EELS Spectrum-Imaging Techniques. Christian Colliex, Laboratoire de Physique des Solides, Université Paris Sud, Orsay, France.

(Scanning) Transmission Electron Microscopy ((S)TEM) on cross-sections offers quite unique insights to analyze at the ultimate level the local properties of layers deposited on substrates, with the direction of the incident electrons parallel to the involved interfaces. Furthermore, the acquired information is quite diversified, in particular when spectroscopic Electron Energy Loss (EELS) data and structural-sensitive high angle annular dark field (HAADF) images are simultaneously recorded for each probe position, in a spectrum-image (or spectro-microscopic) approach. EELS signals are quite efficient for monitoring elemental composition variations, while fine structures on specific edges are very sensitive to local environment and bonding states. The present state of instrumental performance will be described, with recent progress in electron optics (introduction of aberration correctors) bringing the smallest available electron probes below the angstrom level. On the other hand, the huge data sets acquired when scanning the probe over increased area sizes which can encompass the substrate, the grown film and the relevant interface, require updated processing tools to investigate the likely occurrence of inhomogeneities as well as the specific structures at boundaries. Moreover, the sensitivity of the technique to detect weak spectrum variations recorded with increased energy resolution (typically down to 0.2 eV), constitutes a strong incentive to the development of *ab initio* modeling tools for spectral interpretation. These complementary aspects (instrumentation, data processing and spectrum simulation) will be emphasized through the description of different specific issues involved in coatings growth and stability problems as well as in nanocomposite particle-matrix interactions.

4:00 PM Y7.6

Quantum Tuning of the Electronic and Catalytic Properties of Ag-Au(111) Films. Li Huang^{1,2}, Xingao Gong¹ and Zhenyu Zhang^{2,3,4}; ¹Department of Physics, Fudan University, Shanghai, China; ²Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; ³Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee; ⁴Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts.

The evolution of the Ag(111) electronic structure with film thickness is examined by first-principles calculations. The minimum overlayer thickness for quantum well states (QWS) formation on Au substrate

is quantitatively established to be 10 monolayers. QWS spanning across the whole (Ag+Au) system are established when an ultrathin Ag (Au) film is grown on an Au (Ag) (111) slab of comparable thickness. The existence of such synergetic QWS is attributed to nearly perfect lattice match and same crystal symmetry of Ag and Au. The quantum size effect induced modification of the chemisorption properties are illustrated by the O and CO adsorption energetics on Au films supported Ag(111) substrate.

4:15 PM **Y7.7**

Wettability of inorganic surfaces tuned from hydrophobic to superhydrophilic via submonolayer interface modification.

Sheng Meng^{1,2,3}, Zhenyu Zhang² and Efthimios Kaxiras³; ¹Physics, University of Texas at Austin, Austin, Texas; ²Oak Ridge National Lab, Knoxville, Tennessee; ³Physics, Harvard University, Cambridge, Massachusetts.

Microscopic understanding of the wettability of various surfaces is fundamentally intriguing, and is also vital to many biomedical and industrial applications. The two extreme limits of wettability are superhydrophilicity (SHPL) and superhydrophobicity (SHPB). SHPL is highly desirable in a wide range of biomedical applications, protecting biomolecules from damage in their interaction with the biomaterials (commonly known as the "non-fouling" effect. Both SHPL and SHPB can be immensely useful in industrial applications such as anti-fogging and self-cleaning. Whereas substantial progress has been made in designing SHPB materials since the discovery of the "lotus effect", relatively little effort has been devoted to the development of SHPL materials, particularly biocompatible ones}. Here we show, using first-principles calculations, that the water affinity of an initially highly hydrophobic hydrogen-passivated diamond (111) surface can be substantially improved with the addition of only a fraction of a monolayer of alkali metals. In particular, substitution of one third monolayer of H by Li produces a surface with SHPL behavior, rendering it a perfect candidate for biomedical applications. The superhydrophilicity is mainly attributed to the significant charge transfer from Li to C and the concomitant strong dipolar coupling between the modified surface and the water molecules.

4:30 PM **Y7.8**

Numerical study on multifunctional films deposition for scale-up of Metal-Organic Plasma CVD. Seok-Jae Son^{1,2}, Jens Mahrholz², K.-T. Rie² and Kyoung-Woo Yi¹; ¹School of Materials Science and Engineering, Seoul National University, Seoul, South Korea; ²Technische Universität, Carolo-Wilhelmina zu Braunschweig, Institut für Oberflächentechnik(IOT), Braunschweig, Germany.

The phenomena in TiN bottom layer and DLC or Si-DLC top layer deposition process by using TDMAT:Tetrakis(diMethylamido)Titan or TDEAT:Tetrakis(diEthylamido)Titan, hydrogen and nitrogen with the Plasma MO-CVD process was numerically investigated for up-scaling reason. The phenomena of, the flow patterns, pathlines and chemical reaction which are mostly effective factor of uniform coating of specimens in laboratory-size chamber were calculated by using numerical simulation and compared with experimental results. In this study, a simulation model of a Plasma MO-CVD coating process for low temperature deposition of TiN layer was developed. The behavior of the decomposition of precursor in gas phase and the deposition of TiN layer on the substrate would be discussed based on the results of the model. Deposition rates can be increased by increasing flow rate. However, increase of deposition rates deteriorate uniformity of the depth of the deposition film.

SESSION Y8: Poster Session
Chairs: Steve Bull, Paul Chalker, Shaochen Chen, Roya Maboudian and Wen Meng
Wednesday Evening, November 30, 2005
8:00 PM
Exhibition Hall D (Hynes)

Y8.1

The measurement of surface heat transfer coefficient of SUS 304L using a parameter estimation method. Youngman Kim, Seunghwan Ma and Sang Ryu; Materials Science and Engineering, Chonnam National University, Gwangju, South Korea.

A method for measuring the surface heat transfer coefficient h is presented, which combines a parameter estimation technique with the fast-response capabilities of thin film thermocouples. The developed method was applied to the SUS 304L specimens while quenching from 300 and 400 C to RT deionized water bath. The surface of specimens were abraded with #200, #800 abrasive papers and polished with 0.3 micrometer alumina powders. The measured h values showed the range of $10^4 \sim 10^5$ W/m² C depending on the surface roughness, which were related to the boiling of water. Acknowledgment : This study

was sponsored by the KOSEF CAPST and the authors are grateful for the support.

Y8.2

Modification on Hydrophilic property for Harsh Environment. Hsin-Chang Tsai, Yu-Ru Chang and Tai-Kang Shing; MEMS Research Center, Delta Electronic Inc., Kuei San, Taoyuan Hsien, Taiwan.

Hydrophilic property is a useful material property used in many applications, such as mono-layer self-assembly or fluid transport by combining with the capillary force. In the case of fluid transport application, the higher hydrophilic property will make higher transport efficiency. Besides, using the fluid circulation to remove heat from chip is an emergent technology in electronics cooling. In this kind of application, the Cu and Al are usually used as the structure materials due to its higher thermal conductivity and acceptable hydrophilic property. Unfortunately, the harsh operating environment would oxidize the surface of structure material and then reduce the fluid transport efficiency. So, how to protect the material surface from oxidation and maintain or even increase its hydrophilic property will become a vital issue in future. In this research, a NiCo film coated by electroplating technique as protection film in high temperature environment was studied. The electroplating technique used in this research is a technique usually used in surface treatment application. The improvements of hydrophilic property and high-temperature stability by coating NiCo film upon pure Cu plate have been characterized through experiments. In thermal stability characterization, the specimens were put into a temperature-controlled oven and applied a thermal load at 300 Celsius degree. The hydrophilic property was represented by the contact angle between the DI water and material surface. All the contact angle during experiments were measured by contact angle instrument. In application of this protection film, a 1~2 um thick electroplated NiCo film was used for case studied. It is shown that the contact angle was improved from 68.57°, for a pure Cu plate, to 42.87° by coating the NiCo film. The thermal stability of NiCo film was characterized by determining the contact angle variations under thermal load with different duration. The experimental results showed that the contact angle variation slightly decreased as thermal load duration increased. In addition, the contact angle could be less than 30° as the applied thermal load duration exceeded 6 hours. It could be further improved to about 20° with 8 hours thermal load. It means that the oxidation of NiCo film does not decrease its hydrophilic property. Oppositely, it seems to be able to slightly improve hydrophilic property after applying appropriate thermal loads. So, the NiCo film has a good thermal stability regarding the hydrophilic property. In conclusion, the NiCo film coated upon Cu plate can improve the hydrophilic property of Cu plate. In addition, the NiCo film can also be used as protection film to protect devices against the harsh environment. The electroplated NiCo film has advantages of good hydrophilic property, high temperature stability and easy fabrication. Therefore, the NiCo film could help the development of thermal related products.

Y8.3

Effect of micro-patterned substrates on deformation of molten Alumina droplet. Makoto Kambara, Yamada Atsushi, Kojima Yoichi, Shinoda Kentaro and Yoshida Toyonobu; The University of Tokyo, Tokyo, Japan.

Deformation of a droplet upon impinging on substrate is a critical elemental step in thermal plasma spraying, as it influences quality and adhesion of the coating. On a rough substrate, in particular, the spread dynamics of a droplet may be hampered by the roughened structure itself, and also the heat extraction is potentially altered by the way that the droplet covers substrate during spreading. These could result in an air entrapment, splashing and/or fingering during spreading and also in modified microstructure during solidification, both of which occur at the same time mutually affecting each other. Although the effect of substrate roughness on splashing and fingering has been analyzed with the arithmetic average roughness, Ra, the effect of specific shape and layout of textured surface on flattening is not yet fully understood. In the present work, therefore, the deformation of alumina droplet during plasma powder spraying was investigated on the line-and-space (L/S) and convexo-concave array (C/C) patterned substrate with various alignments fabricated by photolithography and wet etching techniques. The characteristic dimensions of micro-patterned substrates, such as line and groove width of L/S and the diameter of dimple and pole of C/C, were designed identically with a depth / height of -1 micron. These substrates were exposed once to the plasma flame on a rotating holder, allowing consistent spraying of a single droplet to all the substrates. The temperature of all the substrates were maintained at around 500C, at which disk shape alumina splats were confirmed on a smooth substrate from droplets with averaged diameter of 35~60 micron, estimated from the flattening degree. In the case of L/S with 5 micron width, a droplet was deformed similarly to that observed on a smooth substrate, whereas its deformation was extended in a

direction perpendicular to the lines. Such unique elongation was, however, not observed when the groove width was decreased to 2.5 micron, despite the constant Ra. This significantly contrasts to the formation of only disk shape splats both on the C/C arrays with 2.5 and 5 micron square grid alignment. In the case of the same dimensional dimple and pole arrays with triangular layout, however, fingering was exhibited for both patterns and the degree of fingering was found similarly to vary not with dimple/pole size but with the characteristic groove size relative to the droplet diameter. These suggest that the simple Ra is not sufficient to describe the effect of roughness and both the array layout and its characteristic dimension with respect to the droplet size should be considered.

Y8.4

Analysis and comparison of semiconductor materials processed at IR vs. UV laser wavelengths for DRAM yield enhancement applications. Andy Hooper¹, Allen Kawasaki¹, Paul Kirby¹, Robert Hainsey¹, Jeongho Bang², Kyeongseon Shin² and Kungu Lee²; ¹Electro Scientific Industries, Portland, Oregon; ²Samsung Electronics, Kiheung, South Korea.

Laser processing has a wide range of applications in the semiconductor industry. One specialized area of laser processing involves the high-speed modification of electronic circuitry for repair and yield enhancement. For example, laser energy can be used to program components at the final stages of assembly by hardwiring the circuit through cutting or activating a series of metal conductors (called laser fuses). As electronic components have continued to shrink, laser processing must keep pace. The smallest practical laser spot size that can be achieved using current laser technology (IR wavelengths at $\sim 1\mu\text{m}$) in industry is about 1.6 μm . A smaller spot size is required to process increasingly smaller components, and this can be achieved by moving to ultraviolet wavelengths. For this presentation, we show results for ultraviolet processing of laser fuses at 355 nm, which allows a theoretical spot size of less than 0.6 μm . Data will be provided that compares how UV and IR lasers interact with the sample passivation layer, metal layer, dielectric layers, and the underlying Si, which could validate the feasibility of UV lasers replacing IR lasers for DRAM processing.

Y8.5

Effect of O₂ plasma on Cr cladding for Cu electrode. Eugene Zakar¹, Brian Mary² and Unchul Lee¹; ¹ARL, U.S. Army, Adelphi, Maryland; ²ARDEC, U.S. Army, Adelphi, Maryland.

The surface roughness, electrical sheet resistance, and chemical composition of a thin 20 nm film Cr (chrome) cladding changes when exposed to O₂ (oxygen) plasma during a photo resist mask pattern removal process. Mask removal becomes challenging after a 50 minute long time ion beam etching of a relatively thick 2.5 μm layer Cu electrode on non heat conducting glass substrate. The Cr film can wear away completely leaving the Cu electrode exposed and unprotected to the environment. Cr films prepared by e-beam evaporation method erode away completely whereas for sputter deposition method remains intact. Sputter prepared Cr films exposed to O₂ plasma at 350 W for 10, 15, 20 minutes had a measured surface roughness Ra (nm) of 8.1350, 6.9987, 8.3493 and an electrical sheet resistance (m Ω /sq) of 6.165, 6.595, 6.346 respectively. The lowest electrical resistance is achieved after 10 minutes, and the smoothest surface after 15 minutes of plasma exposure. X-ray photoluminescence spectroscopy (XPS) analysis reveals the final Cr film partially transforms to Cr₂O₃. The percent of O, C, Cr, and Cu (copper) changes with time and any traces of C (carbon) on the surface are eliminated after a short Ar⁺ ion beam cleaning treatment. Cr film prepared by sputter method remains reliably intact to the Cu conductor.

Y8.6

Plasma Surface Modification of Polymeric Materials. Ali Razavi, Engineering, Wilkes University, Wilkes-Barre, Pennsylvania.

This study was undertaken to improve the bonding of fluorinated and non-fluorinated polymers to acrylic and silicone based adhesives. The polymeric materials were exposed to plasma which is comprised of methane and a second gas selected from air, oxygen and nitrogen or a mixture thereof. By application of surface analysis (XPS), the optimized functionality can be incorporated in the surface of desired polymers to enhance the bondability of prepared films for pressure sensitive tape applications. Four mil thick Polytrafluoroethylene PTFE were exposed to this plasma for 30 seconds, and the following contact angle measurements and surface analysis by XPS method were conducted. The table below shows the contact angles and XPS analysis before and after treatment. The treated samples were coated with adhesives and the adhesion to steel, holding power and other properties associated with tapes performances were shown to be superior to commercially available tapes.

Y8.7

Active Stressing Technique for Delaying Fracture during Laser Cutting of Alumina. Ravindra Kumar Akarapu and Albert Segall; Penn State Univ, State College, Pennsylvania.

During a variety of high-speed laser cutting operations, full work-piece support is not always practical or possible. As a result, costly premature fractures and associated damage such as chips, burrs, and cracks (ranging from the micro- all the way to the macro-scale) can result. In most instances, the resulting stresses are primarily mechanical in nature and arise from the bending and/or twisting moments from the still attached scrap. Even if the scrap weight remains relatively constant (as is usually the case), mixed-mode fracture is all but inevitable since the remaining (supporting) section is continuously diminishing as the cut progresses. Given the predominantly mechanical, and therefore predictable nature of the resulting stresses, it is conceivable that intentionally induced compressive stresses due to an off-focus laser might be used to control (or at least, delay) such fractures. In this paper, the possibility of using a tailored laser-heating scenario ahead of a progressing cut to actively induce compressive thermal-stresses to control fracture, during cutting of cantilevered plate, was investigated. A numerical simulation of this active stressing approach was achieved by using a customized finite-element formulation that was previously employed to model dual-beam laser machining. During the complex 3-D simulations, probabilistic fracture mechanics was used to quantify the influence of the induced compressive stresses on the time and nature of the fracture. The parameters such as laser beam diameter, incident power density, positioning of the laser with respect to cut, as well as timing effect the extent to which fracture is delayed. Model is used to obtain right combination of the above parameters. Experiments are run using those parameters and the feasibility of the active stressing is tested. The results of the experiments are used to modify the probabilistic fracture criterion used in the Finite Element Model, to develop a realistic fracture criterion for the case of laser cutting of ceramics.

Y8.8

Waterproof coating on nonlinear optical crystal surfaces by photo-oxidation of silicone oil. Nobuhiro Sato¹, Yuji Sato¹, Yoshiaki Okamoto² and Masataka Murahara¹; ¹Electrical Engineering, Tokai Univ., Hiratuka, Japan; ²Okamoto Optics Co., Yokohama, Japan.

Organic silicone oil was photo-chemically oxidized to change into SiO₂ by using an ultraviolet (UV) excimer lamp, which developed an over-coating for a nonlinear optical crystal. In general, nonlinear optical crystals are used as a wavelength conversion element for laser. The crystals are, however, deliquescent and absorb moisture in the air, which causes clouding. They need heating in the oven to prevent it. It is desired to develop a protective film on the nonlinear optical crystals so as to be waterproof and transmit UV rays. We have, then, developed the waterproof and protective film on a KH₂PO₄ (KDP) surface, which was photo-chemically oxidized by using a silicone oil and Xe₂ excimer lamp. The silicone oil was spin-coated on the KDP crystal surface, and then the Xe₂ excimer lamp was vertically irradiated to the crystal surface. The O atoms in the air were photo-excited with the UV photon to generate high active O atoms. At the same time, the C-H and the Si-C bonds of the silicone oil were photo-dissociated because the photon energy of the UV photon is higher than the bonding energies of the C-H and Si-C. The siloxane of the silicone oil was consequently linked with the O₂ that had been absorbed on the crystal surface to form SiO_n. As a result, the SiO₂ film was formed on the KDP crystal surface by the photo-oxidation of silicone oil. The infrared spectroscopy analysis (ATR-FTIR) was carried out to investigate the modified film. The results showed that as the time of lamp irradiation extended, the absorption peak of the -CH₃ groups at 2900 cm⁻¹ decreased, but the absorption peak of the -SiO groups at 1050cm⁻¹ increased. At the lamp irradiation time of 90 minutes, the UV transmittance of the treated silicone oil improved to 88.9 % at the 260 nm, which is the wavelength of the fourth harmonic generation, while that of the untreated silicone oil was 56 %. The treated and untreated KDP crystals were tested for their waterproofing. The untreated crystal was completely dissolved thirty minutes after soaking in the water, and on the contrary, the KDP crystal with the film coating has neither been dissolved nor gotten cloudy for three months when soaking in water.

Y8.9

Real time measurement of photochemical surface reactions by using a total reflection prism. Yuki Sato, Yuji Sato and Masataka Murahara; Electrical Engineering, Tokai Univ., Hiratuka, Japan.

The photochemical reaction mechanisms, i.e. photo-dissociation of the reaction solution and hydrophilic groups substitution, were investigated by the infrared spectroscopy analysis [FT-IR] in actual

time, when placing a reaction solution between the attenuated total reflectance [ATR] prism made of germanium and the fluorocarbon [FEP] placed on it, and irradiating a Xe₂ excimer lamp to substitute hydrophilic groups on the FEP surface. To modify the fluorocarbon surface, a chemical treatment as a wet-process and an ion-beam irradiation, plasma irradiation, or X-ray irradiation method as a dry-process are generally employed. In these methods, the wettability is improved by roughening the material surface. When the surface is modified by these methods, the comparative analysis of the before and after can be done by X-ray photoelectron spectroscopy [XPS], atomic force microscopy [AFM] and FT-IR but not the sequential analysis in reaction process. The reaction mechanism is still a matter of conjecture. Thus, a real-time analysis method of surface modification process is desired. We, thus, developed a new method to measure the photochemical reaction on the sample surface in real time when irradiating the reaction solution and the FEP placed on the ATR prism with UV rays. Water or ammonia water was used as a chemical solution in order to modify the FEP surface into hydrophilic. First, the solution was dropped on the ATR prism made of germanium and then covered with the FEP. Second, the Xe₂ excimer lamp was irradiated to the FEP as well as the solution. In case of ammonia water, the solution was photo-dissociated with the irradiation to produce H atom and NH₂ radical. The C-F bond of the FEP was at the same time photo-chemically decomposed into C and F atoms; the F atom was pulled by the H atom, and the C's dangling bond was linked with the NH₂ radical. That is, the hydrophilic group was substituted on the surface, which has been modified into hydrophilic. The infrared spectroscopy was carried out in real time to investigate the process of the photochemical reaction. In case of ammonia water, before lamp irradiation, the absorption peaks of O-H and N-H in ammonia water were observed at 3300cm⁻¹ and 1650cm⁻¹, and the peaks of C-F radicals in FEP, observed at 1210cm⁻¹ and 1150cm⁻¹. With the increase in irradiation time, the absorption peaks of 3300cm⁻¹ and 1650cm⁻¹ gradually decreased, and the new absorption of -CH₂-NH₂ gradually came at 1410cm⁻¹, which presented the strongest after the UV photon irradiation for 30 minutes. As the absorption coefficient of -CH₂-NH₂ increased, the contact angle with water became smaller from 110° for the untreated sample to 30°.

Y8.10

Anti-scatter coating on slab laser head for preventing evanescent wave by photo-oxidation of silicone oil.

Takayuki Funatsu¹, Nobuhiro Sato¹, Takayuki Okamoto² and Masataka Murahara¹; ¹Department of Electrical Engineering, Tokai University, Hiratsuka, Japan; ²Okamoto Optic Co., yokohama, Japan.

A low refractive index, hard SiO₂ film was photochemically coated on the slab laser head surface at room temperature using silicone oil and a Xe₂ excimer lamp. LD (laser diode) pumped Nd⁺:glass slab laser is a promising candidate for the reaction driver of Inertial Fusion Energy (IFE). This laser produces high power laser because the light is amplified with a repeated total reflection in the laser medium. However, the evanescent wave arises on the total reflection interface, which causes a loss of the light energy. A low refractive index film of 2μm thickness is, therefore, needed to prevent this problem. In addition, the slab laser head is cooled in high-speed running water, and so the film must be hard. The vacuum vapor deposition method as a dry process and the spin-coating method as a wet process are generally used for making optical thin films. The former method can laminate a hard thin film, but requires the temperature of 500°C and above, and the thermal denaturation of the optical substrate cannot be avoided. On the other hand, the latter method can form a low refractive index thin film, but the produced thin film has a poor adhesiveness and a low hardness. Besides, all these films are inferior in water resistance. We, therefore, demonstrated a water resistance, hard, and low refractive index protective coating directly on the laser glass surface at room temperature with photochemical reaction by the Xe₂ excimer lamp. Firstly, silicone oil [-O-Si(CH₃)₂-O-]_n was spin-coated on the substrate for making a silicone oil thin layer. Then, the Xe₂ excimer lamp was irradiated on the sample vertically. The methyl group (-CH₃) of the silicone oil was photo-dissociated because the photon energy of Xe₂ excimer lamp (165 kcal/mol) is higher than the bond energies of C-H (81kcal/mol) and Si-C (105kcal/mol). At the same time, the oxygen in the atmosphere was photo-excited by the UV photon to produce active oxygen O (¹D), which reacted with the dangling bond of Si. As a result, the silicone oil was modified into SiO₂. The FT-IR spectrum analysis of the silicone oil was conducted before and after the Xe₂ lamp irradiation. The two absorption peaks of the CH₃ and SiO stretch bands were confirmed from the results in the region of 2960 cm⁻¹ and 1030 cm⁻¹, respectively, before the lamp irradiation. After the irradiation for 120 minutes, the CH₃ peak decreased while the SiO peak increased. Furthermore, the refractive index and hardness of the film modified with 120-minute lamp irradiation were measured by the ellipsometer and Mohs' scale. The results clarified that the refractive index was 1.43, and the hardness was 5, which is equivalent to that of apatite. Being measured by the 3-dimension roughness

meter (ZYGO), the film thickness of the SiO₂ film was 2μm.

Y8.11

Electrowetting-induced photochemical surface modification onto fluorocarbon. Hiroyuki Anai, Yuji Sato and Masataka Murahara; Electrical Engineering, Tokai Univ., Hiratsuka, Kanagawa, Japan.

The PTFE was modified into hydrophilic with 1/100 of the shots number required to obtain the same contact angle with water by the laser irradiation alone, when irradiating an ArF excimer laser on the sample surface at the moment of applying a 6 kV to the water placed on the PTFE surface to decrease the contact angle with water. A plasma treatment method is widely used for plastic surface modification, but the hydrophilic property generated by this method fades away soon. On the other hand, we have previously reported that the ArF excimer laser light was applied on a sample surface in the presence of water to substitute hydrophilic groups, which was modified to have a long-lasting hydrophilic property. This method, however, needed 3000 to 10000 shots of the laser irradiation, and it is less economical compared with the plasma processing that requires only one-minute irradiation. There is an electro-wetting method, in which the contact angle with water decreases temporarily when a high voltage is applied between the water and the sample, but the contact angle is restored to its original position when stopping the voltage application. Thus, we demonstrated the surface modification of PTFE maintaining the hydrophilic property for a long period with only 100 shots, by irradiating the ArF excimer laser on the sample at the moment when the wettability became high by the electro-wetting method. Water was placed in the gap between the silica glass and the PTFE to create a thin liquid layer with capillary phenomenon. A high voltage (6 kV) of direct current (DC) or alternating current (AC) was applied on the gap, and the ArF excimer laser was vertically irradiated on the sample surface. The water was photo-dissociated to produce H and OH. At the same time, the C-F bond of the PTFE was also photo-dissociated, and the F atom bonded to the H atom to produce HF. The OH group united with the dangling bond of C, which resulted in modifying the PTFE surface to be hydrophilic. To evaluate the wettability of the modified sample, the contact angle with water was measured. Improving the contact angle with water from 110 degrees for the untreated sample to 50 degrees for the treated sample had needed 10000 shots at the laser fluence of 5 mJ/cm². By combined high voltage application and ArF excimer laser irradiation treatments, however, the 50-degree contact angle was yielded with 500 shots, 1/20 of 10000, when applying the DC of 6 kV, and with 100 shots only, 1/100 of 10000, when applying the AC of 6 kV. Moreover, the modified sample was observed for a change in contact angle with passage of time. The contact angle was 60 degrees after applying the high voltage, and 110 degrees when stopped. On the other hand, the sample modified by combined the high voltage application and ArF excimer laser irradiation maintained the 50-degree contact angle for one month after stopping the voltage application.

Y8.12

Hydrogen Radical Etching Effect on Carbon Nanotube Growth. Hiroaki Sato¹, Hiroshi Nagayoshi¹, Suzuka Nishimura² and Kazutaka Terashima²; ¹Electronic Engineering, Tokyo National College of Technology, Tokyo, Japan; ²Material Engineering, Shonan Institute of Technology, Kanagawa, Japan.

Process temperature of CNTs generally needs more than 700 C, however low temperature process of below 400°C is required for the applications such as field emission displays using glass substrates and so on. Plasma CVD has been used as low temperature CNTs growth technique. In this method, hydrogen dilution is the key technique to reduce the process temperature. Some groups have reported the possibility that an etching reaction by hydrogen radicals on a catalyst surface reduced the process temperature. Hydrogen radicals generated in RF plasma selectively etch graphite layer on the catalyst and enhance the CNTs growth. However, it is difficult to confirm the hydrogen radical etching effect independently in the conventional RF plasma CVD method. We introduced microwave remote plasma CVD method to confirm the hydrogen radical etching effect and low temperature CNTs growth. A quartz tube, 30 mm in diameter, was used as a microwave discharge cavity. Hydrogen gas was decomposed at the cavity and hydrogen radicals are introduced into the reaction chamber. C₂H₂ is introduced into the chamber directly and react with hydrogen radicals. Nickel plate or carbon plate with thin nickel film was used as substrates. Hydrocarbon radicals generated in the chamber react with sample surface and CNTs are grown on the substrate. In addition, hydrogen radicals could reach the sample surface directly at appropriate conditions. This means that this method can control hydrogen radical etching on the sample surface and confirm hydrogen radical etching effect. We confirmed CNTs effectively grown under appropriate condition at 370C. Hydrogen radical etching effect distributes on the substrate position. CNTs did not grow on the area just below the quartz tube when hydrogen

radical etching was strong. On the other hand, on the area distant from the center, only graphite layer was observed in the same condition. The areas between excess etching and graphite deposition, CNTs growth area was observed. This result clearly means that appropriate etching reaction enhances the CNT growth at low temperature.

Y8.13

Reactive ion etching of TiN, TiAlN, CrN and TiCN Films in CF₄/O₂ and CHF₃/O₂ Plasmas. Patrick William Leech¹, Geoff K. Reeves² and Anthony S. Holland²; ¹CMIT, CSIRO, Clayton, Victoria, Australia; ²School of Computer Systems and Electrical Engineering, RMIT University, Melbourne, Victoria, Australia.

In processes of replication such as hot embossing, a critical requirement has become the fabrication of a micro-pattern on the surface of the die or molding tool. We report on the reactive ion etching of a range of coatings (TiN, TiAlN, CrN and TiCN) of high hardness (1,750-3,000 HV) which were suitable for application on the die. Novel aspects of this study have included the reactive ion etching (RIE) of the TiAlN, CrN and TiCN and TiN layers. Each of the films was deposited by physical vapor deposition onto the flat surface of polished discs of M2 tool steel. The surfaces of the substrate films were then lithographically patterned in a grating structure (~1 micron pitch). Reactive ion etching of the patterned surfaces was performed as a function of rf power (200-400 W) in CF₄/O₂ and CHF₃/O₂ plasmas. The TiN and TiAlN layers have shown higher etch rates (100-250 nm/min) in CF₄/O₂ plasmas than the CrN and TiCN (~5 nm/min) coatings. These high and low etch rate regimes were identified as ion-enhanced chemical etching and physical sputtering, respectively. The CF₄/O₂ plasmas produced significantly higher etch rates than the CHF₃/O₂ gases. In addition, a comparison has been made with etch rates obtained by the alternative technique of ion beam etching (IBE) of the films in the presence of Ar/CF₄ gases. The potential applications of these techniques in the micro-patterning of hard coatings will be discussed in the paper.

Y8.14

Conformal deposition of a silicon-oxide and a fluorocarbon on a nano-shaped material in a supercritical carbon dioxide. Takashi Shimizu, Kenichi Ishii and Eiichi Suzuki; Nanoelectronics Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, Japan.

A supercritical fluid has attracted much interest as an alternative solvent for synthesis and processing of nanomaterials thanks to the high miscibility with gaseous reagents compared with a liquid solvent. It enables a surface-tension-free wet process by the way of temperature- and pressure- control of the solvent. In this work, we propose the noble surface engineering of nano-structured materials, i.e., the surface coatings in a supercritical fluid. Firstly we demonstrate the conformal deposition of a silicon-oxide thin film in supercritical carbon dioxide (scCO₂) where an O₂ gas is miscible as an oxidizing agent. The deposition was carried out on nano-eaves of SiO₂ being 70 nm thick with 450~550 nm in width fabricated using reactive ion etching process. The uniform silicon-oxide film has been deposited even on the backside of the nano-eaves, which is impossible by the conventional physical vapor deposition methods, and is quite hard even by the standard chemical vapor deposition method due to the shadowing effect. Moreover, the filling of a Si-oxide into the horizontal gaps of 70 nm in height and 450~550 nm in depth beneath the nano-eaves has also been successfully achieved. Secondly, we show the deposition of a fluorocarbon in scCO₂. By depositing the fluorocarbon, it was experimentally shown that a hydrophilic SiO₂ surface becomes water-repellent. This surface coating was certified to be effective to prevent the collapse of nano-structures during a liquid-drying process. From these results, the developed surface engineering in the supercritical fluid is promising technology in nanoscale devices fabrication and MEMS.

Y8.15

Application of polyimide sacrificial layers for the manufacturing of uncooled double-cantilever microbolometers. Shusen Huang, Biao Li and Xin Zhang; Boston University, Brookline, Massachusetts.

This paper reports the application of polyimide sacrificial materials in the surface micromachining module of the uncooled double-cantilever microbolometer focal plane arrays (FPAs). This type of microbolometer has the potential of reaching a noise-equivalent temperature difference approaching the theoretical limit and thus has gained increasing interest. The microbolometer thermal imaging system employs arrays of thermally sensitive micro-machined bimaterial elements. Each pixel in the arrays consists of two overlapping bimaterial SiN_x/Al cantilever beams that bend in opposite directions as their temperature rises due to absorption of incident infrared radiation. In this paper, the microbolometer FPAs

were fabricated using a low-temperature surface micromachining technique with a commercial PI2610 polyimide as sacrificial materials. The use of this spin-on polyimide allowed an all-dry final release step overcoming stiction problems, which are often encountered in wet sacrificial etching processes. Polyimide was spun on 4-inch silicon wafers at a spin speed of 2200rpm for 30s and then cured on a hotplate at 90C and 150C, both for 30min, followed by further curing in N₂ atmosphere at 350C for one hour. The cured polyimide had a thickness of about 2.5μm, which is designed to form a quarter-wavelength resonant cavity between the cantilever and the substrate to enhance the infrared absorption in the wavelength of 8-12μm. For the patterning of the polyimide, a 500nm-thick plasma-enhanced chemical vapor deposited (PECVD) SiO_x layer was deposited and then patterned by reactive ion etching (RIE) using a mixture of SF₆ and He. The advantage of using SiO_x as an etching mask is that it is easy to remove the SiO_x in a buffered oxide etcher that does not attack the polyimide. The anisotropic etching of the polyimide layer was then accomplished by RIE. In this RIE process an O₂ flow of 40sccm, a power of 300W and a pressure of 100mTorr were selected, resulting in an etch rate of about 870nm/min. After the stripping of the SiO_x, a 200nm-thick SiN_x layer was deposited with a PECVD unit at a rate of 0.18nm/s. Then the deposition of a 200nm-thick SiN_x layer was carried out with an electron beam evaporator at a rate of 0.20nm/s. The Al was then patterned by phosphorous acid, followed by the patterning of the SiN_x by RIE. After that, the second sacrificial polyimide was spun on the surface at a spin speed of 4000rpm for 30s. After the curing process, the second polyimide had a thickness of less than 1μm. The second polyimide layer was then patterned by RIE. After that, the second Al was deposited, followed by the deposition of the second SiN_x. Following the patterning of the second bimaterial SiN_x/Al cantilever, the double-cantilever microbolometer FPAs were released upon the removal of the both polyimide sacrificial layers by isotropic dry etching in low-pressure and high-density O₂ plasma.

Y8.16

Processing of Through-Wafer Openings in SOI-based Structures for 3-D MEMS Miniaturizing and Packaging Applications. Vladimir Vasilyev, J. Robert Reid and Webster T. Richard; The US Air Force Research Laboratory, Hanscom AFB, Massachusetts.

A fabrication process for through-wafer vias in silicon on insulator (SOI) structures used in packaging microelectromechanical systems (MEMS) switches is presented. The vias are formed under a bonding ring to ensure that a sealed cavity is maintained. This approach allows the die size to be reduced when compared to the die size using traces on a single wafer side. For the Radant MEMS switches that the process was demonstrated with, the die size could be reduced by over 30%. The resulting vias are quite short (10-30 micrometers) allowing low loss from DC to microwave frequencies while maintaining the MEMS devices in a sealed environment. The multi-step fabrication process includes wafer bonding and a series of operations to remove a sequence of the SOI layers. First, HF - HNO₃ - HAc (HNA) was used to etch away the thick Si layer on the back of the SOI wafer, until the remaining Si was approximately 50 micrometers thick. This remaining layer was removed by gaseous XeF₂, that selectively etches Si, stopping when the buried SiO₂ layer is exposed. Photoresist patterns were then formed on the SiO₂ layer, and a buffered oxide etch was used to etch through the SiO₂ layer, stopping on the top Si layer of the SOI wafer. A TMAH wet etch was used to etch through this thin Si layer, stopping on an Al₂O₃ layer used to isolate metal traces from the Si surface. Finally, the Al₂O₃ layer was etched in a dilute HF, stopping on the predefined metal contacts of the switch. After the process was done, the stack had approximately the same thickness as a standard Si wafer, with the MEMS devices enclosed in a cavity below the surface. DC testing was used to verify switch operation. This process has significant advantages over more conventional wafer level packaging approaches. First, the SOI wafer can be used to replace a standard Si wafer without any significant process modification. Second, backside thinning is done through low cost chemical etching. Further, the thickness of the final via is precisely defined by well controlled thickness of the top Si layer of the SOI wafer. Third, a wide variety of wafer bonding techniques are easily supported. Thus the method used for wafer bonding can be chosen to meet any specific device requirements. Fourth, the vias can be formed compactly and when compared to the use of single side feed throughs, allowing the total die area to be decreased. And fifth, the resulting package can be integrated into larger circuits using a flip chip bonding approach.

Y8.17

The Properties of Nanocomposite TiAlN Coatings Prepared by Filtered Arc Ion Plating Process. Kyoung Il Moon¹, SangJin Lee², Yongha Jun² and Sung Wan Kim¹; ¹Plasma Enhanced Technology Development Team, Korea Institute of Industrial Technology, Incheon, South Korea; ²J&L Tech Co., Sicheung City, South Korea.

TiAlN coatings with various nanostructures were produced by filtered arc ion plating methods. The ratio of Ti:Al composition, the pressure and the flux of nitrogen were changed during the deposition. The effects of third elements such as Si, Cr, B on the formation of nanocomposite were also studied. The resulting microstructures were multilayered structure with the layer thickness less than 50 nm, intra/inter type and nano/nano type nanocomposites with the grain size less than 50 nm. The microhardness of nanocomposite coating was over 40 GPa. The thermal stability, oxidation resistance and mechanical properties were characterized in terms of their phase composition, nanostructure. The proper nanocomposite coatings were deposited on the tungsten carbide end mills and their cutting performance and tool life were estimated.

Y8.18

Thermal stability of nc-Cr_{1-x}Al_xN/a-SiN_y coatings with medium and high aluminum content prepared by arc evaporation. Pavla Karvankova¹, Ayat Karimi¹, Olivier Coddet², Marcus Morstein² and Tibor Cselle²; ¹IPMC-FSB, Swiss Federal Institute of Technology Lausanne (EPFL), CH-1015, Lausanne, Switzerland; ²PLATIT AG, CH-2540, Grenchen, Switzerland.

The thermal stability of Cr_{1-x}Al_xN and nc-Cr_{1-x}Al_xN/a-SiN_y nanocomposite coatings with different composition x, silicon content and phase structure has been investigated. The coatings were deposited in an industrial unit by the cathodic arc evaporation method, using rotating cylindrical cathodes. Further sets of coated hardmetal plates were subjected to an annealing step in forming gas (92% N₂/ 8% H₂) atmosphere for several hours at a given temperature (maximum 1000°C). Chemical composition, microstructure and mechanical properties of the coatings were investigated by the RBS, XRD, TEM, SEM, XPS and nanoindentation techniques. As-deposited nc-Cr_{1-x}Al_xN/a-SiN_y coatings with an Al contents x in the range of 0.4 ≤ x ≤ 0.6 showed a single-phase cubic CrAlN structure and a maximum hardness of 38 GPa. With increasing the Al content to x = 0.95 - 0.96, a two-phase films made of hexagonal Al(Cr)N and cubic Al(Cr)N structure with hardness about 31 GPa, were obtained. The hardness of all nc-Cr_{1-x}Al_xN/a-SiN_y coatings increases during annealing at temperatures in the range of 800-1000°C by about 1-4 GPa, even though the residual compressive stress in the coatings was found to relax considerably during this procedure. The addition of silicon into Cr_{1-x}Al_xN coatings improved the thermal stability of the coatings.

Y8.19

Stability of the Diamond (001) surface under different hydrogen and oxygen termination scenarios: a quantum mechanical approach. Daniel Petrini and Karin Larsson; Material Chemistry, Uppsala, Sweden.

Diamond surfaces are extremely interesting for electrical, optical, bio sensor and apprehensive applications due to the unique properties of diamond. The CVD grown diamond films can easily be both hydrogen and oxygen terminated, but the exact termination situation is not yet fully outlined. Theoretically calculated stabilization energies of the 2x1 reconstructed diamond (001) surfaces under different hydrogen and oxygen termination scenarios, have here been studied. The currently investigated oxygen species are: oxygen (bridge), oxygen (radical, on-top) and OH group. The termination ranged from a pure H-terminated surface to a perfectly oxygen terminated, with a mixture in-between. The theoretical method used was a density function theory (DFT) technique, based on a numerical basis set and periodic boundary conditions. The results show that OH coverage up to 50 percent gives an almost identical energetic stability, although slightly endothermic, when compared to a totally H-terminated surface. A diamond surface terminated with small amount (below 35 percent) of O (radical) will on the other hand display large exothermal stabilization energies. Obridge termination show the least stabilization energy, and a mixture of OH groups, ranging from 17 to 33 percent, and hydrogen, must also be present for the surface to be energetically stable compared to an H-terminated surface.

Y8.20

Influence of surface roughness on adhesion and friction. Bruno Zappone, Kenny Rosenberg and Jacob Israelachvili; Univ. of California Santa Barbara, Santa Barbara, California.

Experiments on the adhesion and friction of rough polymer surfaces have been carried out using a Surface Forces Apparatus to determine the role of surface roughness and texture (i.e., ordered versus disordered roughness, and different types of roughness) on adhesion and friction. The aim is to establish how different parameters affect adhesion and, if possible, establish possible universal trends and quantitative scaling relations. Rougher surfaces adhere more weakly, but the deformability (stiffness) of a material plays an important role in addition to the texture and surface energy. Preliminary friction

results are in agreement with the trend that smoother surfaces show higher friction. Of equal interest to the adhesion force is the effective stiffness of a rough surface (e.g., under compression), this being the repulsive component of the overall interaction force between two rough surfaces. This repulsion is not linear, i.e., the effective stiffness is not a single valued number, but closer to an exponential, and it appears to follow certain scaling laws, which may be important for understanding the compaction of dense colloidal suspensions.

Y8.21

Melting Point Measurement of Crystalline Polymer Thin Films Using Optical Methods. Clive Song Li, Jonathan Sokolov and Miriam Rafailovich; Materials Science, SUNY-STONY BROOK, Stony Brook, New York.

Optical birefringence of thin films is measured by a high frequency modulation method using a photoelastic modulator (PEM), laser and polarizers. We applied the method to measurement of melting points of the polymer polycaprolactone. (PCL) The birefringence difference between the crystal state and the melted state was obtained directly by this method. We found the optical birefringence change at about 59°C for films of various thicknesses. Another method, shear modulation force microscopy technique (SMFM), is also used for comparison. The SMFM method, in contrast, shows a depression in melting point as the film thickness decreases. Possible explanations for the differences are discussed.

Y8.22

Selective protein adsorption on highly hydrophilic surface modified with combined V-UV photon and plasma irradiation. Yuji Sato² and Masataka Murahara¹; ¹Electrical Engineering, Tokai Univ., Hiratsuka, Japan; ² Tokyo Institute of Technology, Integrated Research Institute, Solution Research Organization, Yabe Laboratory, Tokyo, Japan.

A highly hydrophilic surface, with a water contact angle smaller than 10 degrees, was rendered to a poly-methylmethacrylate (PMMA) by Xe₂ excimer lamplight and plasma treatment. In result, the implant material that was highly biocompatible and adhesive to soft tissue was developed. The PMMA, poly-ethyleneterephthalate (PET), and poly-tetrafluoroethylene (PTFE) are employed as a soft tissue implant material or cell culture substrate, for they have excellent characteristics of machinability and bioinertness. These polymers, however, have low adhesion to tissue because of their water repellency. Development of a biocompatible material that has an affinity to soft tissue is desired. Thus, we have photo-chemically substituted the amino functional groups on the PMMA surface with V-UV photon irradiation to generate a hydrophilic property. The PMMA surface, which had been pretreated by ammonia plasma, was irradiated with Xe₂ excimer lamplight in the presence of hydrazine as a reaction solution. The hydrazine was photo-dissociated to produce H and N-H radicals. At the same time, the C-H bond was also photo-dissociated by lamplight photon, as the Xe₂ lamp photon energy is higher than the C-H bond energy in PMMA. With these reactions taking place simultaneously, the -NH₂ groups were substituted on the PMMA surface to render it hydrophilic. In order to evaluate the wettability of the modified sample, the contact angle with water was measured. The contact angle was decreased from 83 degrees for untreated PMMA to 60 degrees when irradiated the Xe₂ lamplight for 30 minutes. With the ammonia plasma pretreatment, the contact angle of the treated sample became to 7 degrees at the 1 minute Xe₂ lamp irradiation. Moreover, the change with passage of time was observed for the treated samples. In case of ammonia plasma treatment only, the contact angle returned to 60 degrees from 3 degrees on the plasma treated sample after 30 hours. The sample, however, which was modified by the Xe₂ excimer lamp irradiation after ammonia plasma pre-treatment, was keeping its contact angle at 7 degrees even after 50 hours. The protein adsorption of the sample before and after treatments was also evaluated by scanning electron microscope (SEM) and infrared spectroscopy analysis (FT-IR), using fibrin (FIB) as a protein index in biocompatibility test. From the results, it was confirmed that the protein adsorption increased with the increase of the amino functional groups density. The quantity of FIB adsorption became 3.2 times larger than that of the untreated PMMA.

Y8.23

Abstract Withdrawn

Y8.24

Substrate Effect on the Melting Temperature Depression in the Polyethylene Thin Films. Yantian Wang¹, Miriam Rafailovich¹, Jonathan C. Sokolov¹, Dilip Gersappe¹, Tohru Araki², Ying Zou², Harald Ade², A. David Lewis Kilcoyne³, Gad Marom⁴ and Arnold Lustiger⁵; ¹Materials Science and Engineering, SUNY at Stony Brook, Stony Brook, New York; ²Department of Physics, NCSU, Raleigh, North Carolina; ³Advanced Light Source, LBNL,

Berkeley, California; ⁴Department of Applied Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel; ⁵ExxonMobil Research and Engineering Company, Annandale, New Jersey.

Polyethylene thin films with various thickness (10-250 nm) spun cast onto different substrates were studied by the atomic force microscopy (AFM), transmission electron microscopy (TEM) and shear modulus force microscopy (SMFM). The crystal orientation, morphology and melting temperature (T_m) were found to depend strongly on the substrate materials. The T_m decreases with the film thickness decrease when the film is below a certain critical thickness, and the magnitude of the depression increases with increasing surface interaction. We proposed that the large T_m depression was attributed to the decrease in the overall free energy on melting due to the substrate attraction to the polymer chains.

Y8.25

Depinning of Fluctuating Steps in Vicinal Surfaces from a Meandering Scratch. Eleni Katifori and David R. Nelson; Physics, Harvard University, Cambridge, Massachusetts.

We study the interaction of a thermally fluctuating step on a vicinal surface with a meandering line defect, e.g., an etched groove or raised barrier, in the dilute step limit. The probability density describing the equilibrium step location is derived analytically by mapping the problem to a straight line defect in the presence of a space and time varying tilt field. The consequences of both rapid and slow changes in the orientation of the defect, as well as finite size effects, are discussed. A sudden deflection in the defect direction leads to a delocalization transition, accompanied by a divergence in the trapping length, near a critical angle.

Y8.26

Surface alloy formation of Co-Al system at the early stage of thin-film deposition. Jae Young Park¹, Sun Kyo Jung¹, Chung

Nam Whang¹, Kwang Ryeol Lee² and Seung Cheol Lee²; ¹Institute of Physics and Applied Physics, Yonsei University, Seoul, South Korea; ²Future Technology Research Division, Korea Institute of Science and Technology, Seoul, South Korea.

The surface diffusion and the incorporation of adatoms that occur at an early stage of thin-film multilayer fabrication was investigated by using low-energy ion scattering (LEIS) and density functional theory (DFT) calculation. When 0.5 monolayer (ML) Al atoms have been deposited on the Co(0001) surface at room temperature, it is found that Al adatoms could not penetrate Co surface but occupy a surface adsorption site (named hollow site) because of the relatively small displacement of Co atoms. The height of adsorbed Al atom from the Co(0001) surface is (1.80 ± 0.05) Å. On the Al(001) surface, 0.5 ML Co adatoms preferred incorporation to surface diffusion. After the incorporation process was complete, adsorbed Co and Al substrate atoms are configured a B2-like structure by forming seven Co-Al bonds. The present work shows that the formation of CoAl surface alloy should be considered even at the low substrate temperature and the low incidence energy of deposited Co adatoms.

Y8.27

Low-temperature Preparation of Crystallized Zirconia Films by ECR Plasma MOCVD. Hiroshi Masumoto and Takashi Goto; Institute for Materials Research, Tohoku University, Sendai, Japan.

It is known that zirconia (ZrO_2) has excellent thermal and chemical stability, and oxide ion conduction. Therefore, YSZ is expected to be used as oxide ion conducting materials, optical mirror materials, catalytic materials and heat-resistant materials. Zirconia films have been fabricated by PVD (ex. sputtering and laser-ablation), chemical vapor deposition (CVD) and sol-gel methods. CVD is capable to prepare high quality zirconia films with excellent conformal coverage; however, deposition temperature of conventional CVD was usually high than PVD. On the other hand, an electron cyclotron resonance (ECR) plasma is high-activity plasma and high quality crystalline films can be obtained at low temperature by using ECR plasma. In the present study, zirconia thin films were prepared at low temperatures on quartz, polycarbonate and polyimide substrates by ECR plasma MOCVD. Zr-hexafluoroacetylacetonato [$Zr(HfAc)_4$] solution was used as a precursor. The source, which was placed in a glass bubbler, was carried into a reactor by Ar gas. A microwave (2.45 GHz, 500 W) was introduced into the ion chamber through a rectangular wave guide. A magnetic field (875 Gauss) was applied to the ion chamber to satisfy the ECR condition. A mirror-type magnetic field (450 Gauss at the substrate stage) was applied in order to raise a plasma density, which results in an increase of the deposition rates of films. Substrate temperature (T_s) was from 30 to 700 °C by water-cooling holder and infrared lamp heater. Microwave power was changed from 0 to 900 W. The deposition time was from 30 to 120 minutes. Cubic, monoclinic and tetragonal zirconia films were obtained over $T_s=400$ °C, and cubic and monoclinic zirconia films

were obtained below $T_s=400$ °C. Cubic and monoclinic zirconia films were also obtained at no heating. The deposition rate increased from 10 to 20 nm/min with increasing T_s from no heating to 600 °C. Crystallized zirconia films were obtained on polycarbonate and polyimide substrates at no heating. The ECR plasma was significantly effective to prepare crystallized zirconia films at low temperatures.

Y8.28

Comparative Study of Barrier Layers in Copper Interconnect for Ultra Large Scale Integration Interconnects. Kai Wang^{1,2}, Isaiah O. Oladeji², Alton B. Horsfall¹, Anthony O'Neill¹, Steve J. Bull³ and Alan Cuthbertson²; ¹Electrical, Electronics and Computer Engineering, University of Newcastle upon Tyne, Newcastle Upon Tyne, Tyne and Wear, United Kingdom; ²Technology and Development, Atmel North Tyneside, Newcastle Upon Tyne, Tyne and Wear, United Kingdom; ³School of Chemical Engineering & Advanced Materials, University of Newcastle upon Tyne, Newcastle Upon Tyne, Tyne and Wear, United Kingdom.

Physical vapour deposited (PVD) Ta, TaN, or dual TaN/Ta barriers are conventionally used as the copper (Cu) barrier in advanced VLSI interconnects. However, these barriers together with the PVD copper seed will not meet the demands of future IC metallization. The latter requires thinner and continuous copper barrier/seed with no overhang and good step coverage for excellent electroplated copper gap fill; hence, a need for conformal chemical vapour deposited (CVD) alternative. In this work the comparison is made between the physical properties of CVD tungsten (W) based barrier with the conventional Ta based barriers. Using W barrier offers an attractive alternative, since integrating W and Cu as the W-Cu-contact/W-Cu-first-metal-layer (FML) instead of W-Contact/Ta-Cu-FML will substantially reduce the overall interconnect resistance in advanced integrated circuit which is currently dominated by W-Contact resistance. Further advantages of W barrier layer, includes the ability to directly electroplate the copper on it, removing the requirement for the growth of a copper seed layer.

Y8.29

A Study of Transitions in Electrodeposited Copper using Differential Scanning Calorimetry and Atomic Force Microscopy. Shafaat Ahmed, D. Noel Buckley and Shohei Nakahara; Dept. of Physics and Materials and Surface Science Institute, University of Limerick, Limerick, Ireland.

Previously, we have reported dramatic spontaneous morphology changes (SMC) during room temperature aging in electrodeposited copper metallization observed by AFM. The phenomenon involves the formation, usually quite suddenly, of new features smaller than the existing features on the surface. We have shown that this occurs in copper films electrodeposited under many different conditions and is quite reproducible. An incubation period is observed between the end of electrodeposition and the onset of SMC. The length of the incubation time is found to depend on the temperature. A systematic investigation of the effect of annealing time and temperature on the incubation process gave a value of 0.48 eV for the activation energy in 660 nm copper films on a silicon wafer with a Ti barrier layer. In this paper we present results of a differential scanning calorimetry (DSC) study to further investigate the effect of temperature on such microstructural changes. Copper was galvanostatically electrodeposited from an acidic $CuSO_4$ bath at 15 mA cm^{-2} on polished stainless steel substrates. The resulting films were peeled off and cut into 6 mm diameter disks, a suitable size for the sample pan of the DSC. A series of experiments was carried out at various scan rates ranging from 10 K min^{-1} to 80 K min^{-1} . In these DSC experiments the sample was held at room temperature for 600 s followed by 60 s at 35 °C. An endothermic peak was obtained in each case and it was found that the peak height increased with increasing scan rate. The temperature at the peak also shifted to higher values with increasing scan rate: values ranged from 65 °C at 10 K min^{-1} to 93 °C at 80 K min^{-1} . A series of experiments was carried out in which films were electrodeposited and held at room temperature for various periods of time before carrying out the DSC analysis in the normal manner. If the holding time was less than 5400 s then a peak was observed in the subsequent DSC while if it was greater than 5400 s no peak was observed. This behavior suggests that the process occurring corresponds to the SMC process observed by AFM. In this case there appears to be an incubation period $t \approx 5400$ s. This compares with a value of ~ 5100 s for the incubation time in AFM experiments on films electrodeposited under similar conditions on a polished stainless steel substrate. The detailed results will be discussed and a model, based on the SMC behavior observed by AFM, will be presented to quantitatively explain the DSC results.

Y8.30

Viscosity Measurements of Very Thin Polymer Films.

Chunhua Li¹, Tadanori Koga¹, Clive Li¹, Jun Jiang¹, Suresh Narayanan², Laurence Lurio³, Sunil Sinha⁴, Miriam Rafailovich¹ and

Jonathan Sokolov¹; ¹Department of Materials Science and Engineering, State University of New York at Stony Brook, Stony Brook, New York; ²Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois; ³Department of Physics, Northern Illinois University, DeKalb, Illinois; ⁴Departments of Physics, University of California San Diego, La Jolla, California.

We demonstrate the design of a viscometer, which uses the fundamental theories of bilayer dewetting for in situ measurements of the viscosity of ultra thin polymer films. Liquid/liquid dewetting was measured from polystyrene (PS) and poly(methyl methacrylate) (PMMA) bilayer samples where the bottom PS layer is less viscous than the top PMMA layer. The viscosity, as deduced from the dewetting velocity, was compared with the values obtained using X-ray Photon Correlation Spectroscopy (XPCS) where the viscosity of a single layer is determined from the relaxation rate of thermally induced surface roughness and Dynamic Secondary Ion Mass Spectroscopy (DSIMS) where the viscosity is derived from the measurements of the tracer diffusion coefficient. The results from three different techniques are in good agreement with each other. The scaling relationship, $\eta \sim Mw^{PS}$, yielded $\alpha = 3.3 \pm 0.3$ and $\alpha = 3.2 \pm 0.1$ from dewetting and XPCS measurement, respectively, which was in excellent agreement with the bulk scaling of 3.4 and the prediction from reptation theory. Supported in part by the NSF-MRSEC

Y8.31

Melt Fracture of Polymer Thin Film at Strongly Attractive Surfaces. Chunhua Li, Jun Jiang, Miriam Rafailovich and Jonathan Sokolov; Department of Material Science, State University of New York at Stony Brook, Stony Brook, New York.

In this study, we report an interesting phenomenon of "melt fracture" which was observed to occur when a high viscosity film dewets from a film of lower viscosity. We propose that this phenomena is similar to the "melt fracture" or "shark skin" that is observed when extruding bulk polymer. We hypothesized that the "melt fracture" occurs as a result of shear imposed by the dewetting layer on the visco-elastic lower layer. The dewetting layer is adhered to the lower layer via entanglements across the polymer/polymer interface. When the other interface of the liquid film is adsorbed to an attractive substrate interface, a velocity gradient occurs in the film. Since the films are very thin, an extremely large shear gradient can result given by $\gamma = V/L$. We found that when this shear rate exceed the natural reptation time, melt fracture resulted. Screening the substrate interaction by first deposition a very thin layer of immiscible polymer such as poly (vinyl-pyrrolidone) PVP reduced the degree of melt fracture. A DI 3000 Atomic Force Microscopy (AFM) was used to quantify the depth and the dynamics of the melt fracture process. We found that the depth increased in proportion to time, which indicated that it was a diffusion limited process, and hence was also inversely proportional to the viscosity of the lower film. Supported in part by the NSF-MRSEC

Y8.32

Abstract Withdrawn

Y8.33

Stress Induced Phase Transition in a Monomolecular Perfluoroalkylsilane Film Self Assembled on Aluminium Surface. Sanjay Kumar Biswas and D. Devaprakasam; Mechanical Engineering Department, Indian Institute of Science, Bangalore, Karnataka, India.

We use a dual double cantilever based "surface force" type apparatus to dynamically (sinusoidally; 5Hz, <0.5nm amplitude) probe perfluorooctyl trichlorosilane monolayers self assembled (SAM) on aluminum and silicon substrates of 1nm and 0.7nm RMS (root means square) roughness respectively, using a 1.12 mm diameter ruby sphere of 0.25nm RMS roughness. We record stiffness and damping constant as a function of compression load and deconvolute the elastic modulus using contact mechanical formulations. When mechanical intervention is limited to the terminal end of the molecule there is a strong viscous response and a low level of elastic response in consonance with the ability of the molecule to generate conformation defects freely. When the intervention penetrates into the molecular backbone the damping disappears dramatically and the molecule registers a monotonic and steep rise in elastic resistance in response to further intervention by the probe. We deconvolute changes in free volume and relaxation time to suggest that at a critical applied pressure the monolayer undergoes transition from a liquid like to a solid like phase. The work is specifically directed towards development of solid lubricants for forming of aluminium components.

Y8.34

An Analysis Of Surface Temperature Rise At Small Scale Sliding Contacts. Sudipto Ray¹ and S. K. Roy Chowdhury²;

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Kharagpur, West Bengal, India; ²Mechanical Engineering, Indian Institute of Technology, Kharagpur, West Bengal, India.

A great deal of work has been carried out in recent years on temperature rise at the contact between sliding bodies with engineering scale roughness. However, as surfaces become smoother and loading decreases, in applications such as MEMS and NEMS devices and other such applications measurement of contact temperature rise become increasingly difficult due to the nanometer scale asperity interactions. The analysis of surface temperature rise is no less difficult and it must consider the small-scale asperity height distributions and the surface forces those may be operating at small separations. The paper attempts to predict surface temperature rise at sliding contacts with small-scale roughness considering the influence of relevant parameters. The results in general show that the contact surface temperature steadily increases with surface forces and under certain combinations of load and material parameters extremely high contact temperature rise is predicted, under certain other parametric combinations extremely low temperature rise may occur. The later parametric combination is certainly of much practical importance.

Y8.35

Friction Force Measurements Relevant to Deinking of Waste Paper Determined by Means of the Atomic Force Microscope. Robert John Pugh, Katarina Theander and Mark Rutland; Institute for Surface Chemistry, Stockholm, Sweden.

In the pulping step of the deinking process, the ink detaches from the fibres due to shear and physical chemical interactions. In order to improve the understanding of the forces involved between cellulose and ink, the atomic force microscope and the colloidal probe technique have been use in the presence of a model chemical dispersant (hexa-ethylene glycol mon-dodecyl ether). A cellulose bead was used as the colloidal probe and three different lower surfaces have been used, an alkyl resin, mica and a cellulose sphere. The normal and lateral forces have been measured and it was found that the lateral sliding friction forces decrease with increasing surfactant concentration for both the alkyl resin and mica while no differences were observed for the cellulose. In addition, only small changes in normal force could be detected for the alkyl surface as the concentration changed.

Y8.36

Abstract Withdrawn

Y8.37

Micro-Raman Evaluation of Polycrystalline Silicon Optical MEMS Devices. Justin R. Serrano, Leslie M. Phinney and Sean P. Kearney; Sandia National Laboratories, Albuquerque, New Mexico.

Optical MEMS devices are commonly interfaced with lasers for communication, switching, or imaging applications. Moreover, optical-based actuation of MEMS devices has been demonstrated to be a viable alternative for powering devices under harsh environments in which electrical signals might not be feasible. The miniature size of these devices can often lead to overheating, structural deformation, and damage of the component being irradiated. Laser irradiation of MEMS components can also lead to changes in the material at the microstructure level which is detrimental their performance. The evaluation of these changes is crucial to asses the reliability of laser-irradiated MEMS devices. In this study we present the effects of long-term irradiation of surface micromachined polycrystalline silicon (polysilicon) MEMS structures, designed and fabricated using Sandia National Laboratories' SUMMiT-V process. Previous studies of laser-induced damage on polysilicon MEMS actuators identified two regimes to the damage formation on the surface of the device irradiated with 808 nm CW laser light: immediate damage, which occurred at higher laser powers, and prolonged exposure damage which occurred at lower powers and longer exposure times. Long-term exposure damage is attributed to microstructural changes in the polysilicon leading to increased absorption and heating of the part. We have used micro-Raman spectroscopy to characterize the test devices before and after irradiation with powers and exposure times below the threshold for immediate damage. We have also used micro-Raman spectroscopy to measure surface temperature during irradiation and correlate observed changes to laser heating temperatures. 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.

Y8.38

Role of Fe and Ni Nanoparticles on Mechanical Properties of Alumina Thin Films Deposited by Laser Ablation.

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North Carolina; ²Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina.

This paper reports our recent work on the improved mechanical properties of alumina thin films embedded controllably with Fe and Ni nanoparticles with uniform particle size distribution and interparticle separation. The Fe/Ni nanoparticles-alumina composite thin films have been fabricated using a multi-target pulsed laser ablation technique. The evidence in favor of uniform particle size distribution (~5 nm) and inter-particle separation (2-4 nm) have been obtained using a high resolution transmission electron microscopy and other structural characterization techniques such as AFM and grazing incidence XRD. The mechanical properties measurements, performed by nanoindentation in continuous stiffness mode and applying Nix-Bhattacharya and King's model for film-only properties, have shown that metal nanoparticle-alumina thin film composite samples fabricated at 500 C have superior mechanical properties (31 GPa and 365 GPa with Fe and 33 GPa and 380 GPa with Ni) compared to pure alumina thin films (15 GPa and 190 GPa), deposited under similar conditions. These results are taken to suggest that metal nanoparticles have a catalytic effect on the growth of alumina thin films with enhanced crystallinity. A proof in favor of this argument is obtained by depositing the pure alumina thin films at two different temperatures (500 and 600 C). The elastic modulus and hardness values of pure alumina films are 15 GPa and 190 GPa (500 C), and 32 GPa and 320 GPa (600 C) respectively. A simple comparison of these values shows that pure alumina films deposited at 600 C possess the same mechanical properties as metal embedded alumina thin films deposited at 500 C that supports catalytic role of metal nanoparticle on the growth of films with improved crystallinity.

Y8.39

Bio-inspired design of microstructures by Laser Interference Metallurgy. Frank Muecklich¹, Claus Daniel^{1,2} and Andres Lasagni¹; ¹Dept. Materials Science, Functional Materials Lab, Saarland University, Saarbruecken, Saarland, Germany; ²Oak Ridge National Lab, Oak Ridge, Tennessee.

Tailoring of microstructures is a basic tool of materials development in order to reach higher performance as well as smaller scattering of the microstructure geometry. The consideration of biological microstructures teaches us to solve the task by creating "the right property at the right place" by means of geometrically designed microstructural patterns. Line or dot like patterns as well as lattices might be geometries to combine properties of different phases, grain sizes, defects, textures in micro or nano dimensions. Since additional geometrical degrees of freedom for the tailoring are available with such patterns the consequence of superior microscopic and macroscopic properties might be achieved. The precondition for that is a fast structuring technique on relevant surface areas. The Laser Interference Metallurgy uses the possibilities of short pulse Laser material interactions and scales that down to the microstructures by applying the interference theory. Combining that with careful thermal simulations opens the way to a new kind of direct microstructure design with very high precision and efficiency. Examples from metallic as well as non metallic systems will be presented. The paper gives an introduction into the principle and various possibilities of this technique and is related to two more specific papers from C.Daniel et al. and A.Lasagni et al.

SESSION Y9: Tribology

Chair: Paul Chalker

Thursday Morning, December 1, 2005

Back Bay A (Sheraton)

8:00 AM *Y9.1

Nanoscale Design and Engineering of Carbon Films and Related Microstructures for Advanced Manufacturing Applications. Ali Erdemir, Argonne National Laboratory, Argonne, Illinois.

Recent advances in carbon films and related microstructures (i.e., diamond, diamondlike carbon, carbon nitride, boron, carbide, and carbide-derived carbon) may have significant positive impact on demanding machining and manufacturing applications. These films may provide not only excellent wear resistance but also much needed lubricity under the very stringent operating conditions of these applications. In particular, disordered and nanocomposite carbon films (with two or more distinct phases) can favorably react with gaseous or aqueous species in their surroundings and hence provide extremely low friction and wear coefficients to sliding surfaces. Some of these nanocomposite films may be formulated in such a way that they can substantially increase the load-bearing capacity of sliding surfaces and hence improve their resistance to scuffing and wear. It is also possible to design such coatings to provide self-replenishing and

-lubricating secondary films on sliding contact surfaces and thus further enhance the overall lubricity of these surfaces. In this presentation, an overview of recent advances in disordered and nanostructured carbon films and related microstructures will be presented and the emphasis will be placed on their potential applications in various machining and manufacturing operations. Specific examples will be given to demonstrate the superior performance and durability of such novel films under various conditions. The fundamental tribological mechanisms that control their exceptional friction and wear behaviors under dry and marginally lubricated sliding regimes will also be discussed.

8:30 AM Y9.2

Tribological Properties of MoS₂ Films Containing Ti and Carbon. James Krzanowski and Dyumani Nunna; Mechanical Engineering, University of New Hampshire, Durham, New Hampshire.

Molybdenum disulphide (MoS₂) is a solid lubricant that performs well in vacuum and low humidity environments, but its tribological performance degrades at higher humidity levels. Improving high humidity tribological performance can potentially be achieved by either adding small amounts of certain metallic elements or producing multiphase composite films containing MoS₂ and another solid lubricant compound. In this work, we have examined the properties of MoS₂ films containing Ti, C and both Ti and C. The films were deposited by RF magnetron co-deposition, and were evaluated at low (~25-30%) and high (55-65%) relative humidity levels. Pin-on-disc tests using a 440C steel counterface were conducted to determine the friction coefficients and coating life. Film compositions and structure were evaluated using XPS, SEM, XRD, and electron microprobe analysis. The films were deposited at room temperature and were generally found to be amorphous. The addition of small amounts of Ti to the MoS₂ films improved high-humidity performance, with a minimum average friction coefficient (for the first 2000 cycles) of 0.15 for films with 1.6% Ti, but then increased to 0.35 for films containing 18% Ti. For MoS₂ films co-sputtered with TiC, optimal friction coefficients were 0.05 at low humidity levels and 0.17 at high humidity levels. Films with carbon only as an additive did not demonstrate any significant improvements in tribological performance. It is proposed that the presence of high levels of water vapor act as a catalyst resulting in the conversion of MoS₂ to MoO₃ which then causes high wear rates and rapid erosion of the film.

8:45 AM Y9.3

The Enhancement of Thermal Stability in Nano Structured PVD Coatings. Ghassan El Nayal, Department of Engineering Materials, Institute of Materials Research, Sheffield, United Kingdom.

The mechanical and tribological behavior in TiAlN/VN, TiAlYN/VN, TiAlN/VN/CrN, TiAlYN/VN/CrN, and TiAlN/CrN nano-structured coatings was investigated in the 25-700 °C temperature range. All coatings were processed in an industrial sized multi arc/ unbalanced magnetron sputtering Physical Vapor Deposition (PVD) unit. The control of coating composition, structure and properties was attained using a variety of process operating parameters. This included the magnetron power (0-10kW), the constitution and the composition of the coupling target material (Ti_{0.5}Al_{0.5}, Ti_{0.48}Al_{0.48}Y_{0.04}, Ti_{0.47}Al_{0.47}Y_{0.06}, V and Cr). Characterizing techniques used during this investigation included TGA, X-RD, WDX, SEM, TEM, heated pin-on-disc tribometer and nano-hardness tester. In the lower temperature range (25-300 °C), a superior tribological behavior was associated with TiAlN/VN coatings. At higher temperatures (≥ 500 °C), on the other hand, the latter coatings experienced a sharp fall in mechanical strength which had dramatic consequences on their tribological properties, namely the coefficient of friction and sliding wear. This was attributed to the formation of a semi molten transfer phase consisting mainly of Vanadium oxide and was evident on the tribological track of tested coatings. The rapid deterioration in thermo-mechanical, hence, the thermo-tribological behavior of the coating material was significantly delayed to higher temperatures when the Vanadium was substituted with Chromium and/ or Yttrium. In other words, the thermal stability of the coating material was significantly enhanced when TiAlN/VN coatings were replaced with TiAlYN/VN, TiAlN/VN/CrN, TiAlYN/VN/CrN, or TiAlN/CrN coatings. In this investigation, a synchronized type of correlation between the coating thermo-tribological and thermo-mechanical behavior was observed. Both the tribological and mechanical behaviors at high temperatures were linked to the tendency of the coating material for oxidation and in particular its oxidation kinetics.

9:00 AM Y9.4

High-Pressure Hydrogen Effect on Sliding Contact Surfaces. James D. Holbery¹, Russ Jones², John Abrefah¹, Laura Riester³ and Peter J. Blau³; ¹Pacific Northwest National Laboratory, Richland, Washington; ²Exponent Inc, Bellevue, Washington; ³Oak Ridge National Lab, Oak Ridge, Tennessee.

Developing a thorough understanding of hydrogen diffusion service materials is critical to the long-term performance of functioning hardware. Hydrogen produces two primary effects on the structural integrity of materials: 1) classical embrittlement where the ductility and hence the fracture toughness is decreased and 2) time-dependent cracking at stresses below those needed for fracture. When hydrogen interacts with materials at elevated temperatures, one effect is the development of gas bubbles either near the surface called blisters or as bubbles at the grain boundaries. The development of hydrogen bubbles at grain boundaries, as a result of hydrogen damage, causes embrittlement and reduced structural integrity. Understanding absorption and diffusion is critical to predicting any hydrogen effect on a material. From a hydrogen gas this requires dissociation of the hydrogen molecule, and absorption through an oxide film found on most metals, diffusion of the hydrogen to key sites in the material such as grain boundaries and particles and ultimately a linking up of micro-cracks induced by the hydrogen. Predicting the friction between two sliding materials poses the additional challenge of resolving several mechanisms affecting the overall sliding friction coefficient. In this study, we utilize several techniques to quantify the surface effects of several material due to hydrogen penetration. Specifically, we have focused on the resulting change in friction coefficient due to the hydrogen service environment that will be experienced within a hydrogen-powered internal combustion engine. Our results indicate significant changes in friction coefficient for sliding material pairs under these conditions that could have long-term effects on performance including significant changes in surface topography due to facet formation.

9:15 AM Y9.5

Mechanical Properties and Tribological Behavior of Contaminate Nanoparticles on Micromachined Surfaces. Frank William DelRio^{1,3}, Maarten P. de Boer¹, Brad L. Boyce² and Martin L. Dunn³; ¹MEMS Device Technologies Department, Sandia National Laboratories, Albuquerque, New Mexico; ²Microsystem Materials, Tribology and Technology Department, Sandia National Laboratories, Albuquerque, New Mexico; ³Department of Mechanical Engineering, University of Colorado at Boulder, Boulder, Colorado.

Carbon-based fullerene and inorganic fullerene-like nanoparticles have been shown to improve the tribological behavior of contact surfaces when added to conventional lubricant fluids. While these nanoparticles are intentionally added to shearing interfaces, other types of particles are inadvertently deposited during the microelectromechanical system (MEMS) fabrication process. These particles hinder the analysis of interfacial adhesion as a function of surface roughness and relative humidity (RH) by changing the equilibrium separation of the contacting surfaces. This paper reports on the characteristics of these nanoparticles and their effect on the adhesion of micromachined surfaces. The nanoparticles were initially discovered during adhesion measurements using microcantilevers fabricated by standard surface micromachining techniques. Different samples show a large difference in the adhesion energy of the polysilicon surfaces. We measured the ground polysilicon layers by tapping-mode atomic force microscopy (AFM) and showed a correlation between the number of nanoparticles on the surface and the measured adhesion energy (i.e., more particles correlate with a lower adhesion energy). The size and shape of the particles were found using scanning electron microscopy (SEM); typical particles range in diameter from 30-100 nm. At low particle densities, the intrinsic surface roughness controls the adhesion under dry conditions. We suspect that the reaction moment at the crack tip interface, which can be calculated by finite element method (FEM) simulations, induces a force sufficient to crush individual particles. Therefore, it becomes important to determine their individual load-displacement curve. We used a nanoindenter with a dull Berkovich tip (400 nm diameter) to image the particles and directly measure this curve. A comparison of the FEM and experimental results confirms the intrinsic surface roughness and not the particles control the interfacial adhesion below a threshold density. This work is critical in assessing the performance and reliability of real MEMS interfaces. Acknowledgement: 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.

9:30 AM *Y9.6

Surface Engineering for Protection Against Combined Wear and Corrosion. Robert J. K. Wood, Surface Engineering and Tribology Group, School of Engineering Sciences, University of Southampton, Highfield, United Kingdom.

The operation of modern fluid handling systems increasingly demands for low costs with increased reliability and longevity along with no loss of fluid containment. These can not be achieved without minimising the material damage caused by the combined surface degradation mechanisms of wear and corrosion, termed tribo-corrosion, when systems are handling solids or are cavitating.

This paper will review the performance of bulk and treated surfaces as well as a variety of coated systems and the complexities encountered when these surfaces are exposed to environments which contain sand particles or cavitation in a corrosive marine medium. The erosion and erosion-corrosion performance of a variety of offshore and marine coatings and bulk surfaces will be discussed using volume loss rate versus sand impact energy maps. Recent research into the erosion-corrosion HVOF aluminium and nickel aluminium bronze coatings will be reviewed as candidates to be selected for erosion-corrosion resistant surfaces. Oilfield abrasion-corrosion of sintered and HVOF tungsten carbides as well as CVD boron carbide coatings will also be discussed. Electrochemical techniques designed to monitor the erosion-corrosion mechanisms and coating integrity will be presented and used to quantify the synergistic terms present when both erosion and corrosion act concurrently.

10:30 AM *Y9.7

Coatings for Extreme Environments in Industrial Applications. Alejandro Sanz, Materials, SKF Engineering & Research Centre, Nieuwegein, Netherlands.

There are a large number of industrial processes in which great demands are made on the surface behavior of several components. The types of surfaces in industrial machinery are very large and a technology supplier has to carefully analyze the complex value chain of a coating technical solution in order to properly set the sequence and timing of a surface engineering business strategy. The surface quality is measured in two different ways: a) the influence of surface properties on the quality of the products being manufactured or b) the weight of the component replacement cost in the unit economical equation and on the plant productivity. The present paper describes different coating applications for both the steel industry and the bearing manufacturing. Rolling bearings and related products such as ball and roller screws are experiencing increased load demanding and are required to be operational in more and more difficult conditions or extreme environments. Furthermore, environmental concern and related government legislation require the use of less mineral lubricant oil and toxic additives. Lubrication free is a technology/market trend where surface engineered components will play an increasing role. A successful design of coated components requires detailed knowledge on materials, tribology and contact mechanics. The present paper presents a series of coatings and engineered surface solutions for bearings working in extreme environments and or with limited or non-existing lubrication. The deposition techniques covered in this articles include PVD, CPVD, IPVD, reactive magnetron sputtering and others applied to the domain of wear, false brinelling, smearing, lubricant life and contamination resistance under extremely high loaded rolling contact fatigue conditions. An overview on several high temperature coating applications in the steel mills will illustrate the service life and productivity enhancement of coated components. Coated parts (if correctly designed and properly coated) last longer and allow a more flexible and more accurate maintenance planning. New advanced steel production methods and more rigorous operating conditions are opening the possibilities for new coating techniques and new coating materials. Coatings seem to offer a diversification opportunity with innovative, flexible and performing solutions that will lead to an ever-increasing role of surface engineering in the quest for higher industrial efficiency.

11:00 AM Y9.8

Friction-Induced Phase Transformation in Nickel-Titanium Thermal Spray Coatings. Sudeep P. Ingole¹, Sharmili Datta¹, Pranay Asthana¹, Pravansu S. Mohanty² and Hong Liang¹; ¹Mechanical Engineering, Texas A&M University, College Station, Texas; ²Mechanical Engineering, University of Michigan, Dearborn, Michigan.

Thermal-spray coated amorphous nickel-titanium (NiTi) coatings have shown great potential in tribological applications. The NiTi coatings are superior over many existing surfaced coatings due to its increased strength and hardness. In this research, we conducted tribological investigation of thermal sprayed NiTi amorphous coatings using a pin-on-disk tribometer. The wear mechanisms were studied using an atomic force microscope (AFM) and a scanning electron microscope (SEM). It was found that under a few locations on the wear track the hard coatings actually underwent martensite transformation from amorphous. This indicated the potential instability of amorphous coatings. In this presentation, we discuss about the frictional behavior and wear mechanisms.

11:15 AM Y9.9

Integrated Tribo-SPM for Nanotribology. Antanas Daugela, Norm Gitis and Alex Meyman; Center for Tribology, Campbell, California.

Quantitative nanometer resolution metrology tools have become a standard in semiconductor, data storage and other hi-tech industries,

where products have to be tested for thin-film properties. Though it is critical to characterize advanced thin films and coatings, today's off-line nanoscale metrology tools can capture only a limited number of parameters. There is an immediate need for process control instruments capable of in-situ nanometer scale quantitative characterization at different stages of manufacturing process. A novel quantitative nano+micro-tribometer with integrated SPM and optical microscope imaging has been developed to characterize numerous physical and mechanical properties of liquid and solid thin films and coatings, with in-situ monitoring their changes during micro and nano indentation, scratching, reciprocating, rotating and other tribology tests. Both the materials properties and surface topography can be assessed periodically during the tests. An example of blind nanoindentation characterization of silicon wafer based coatings is provided. DLC coated magnetic media disk is characterized by means of a microscratch technique on the same instrument.

11:30 AM Y9.10

Surface modification through sonochemistry for tribological applications. Sudeep P. Ingole¹, Orlando Patricio¹, Catherine

Leonida¹, Pranay Asthana¹, Srinivas Guruzu¹, Hong Liang¹ and George Totten²; ¹Mechanical Engineering, Texas A&M University, College Station, Texas; ²Mechanical Engineering, Oregon State University, Portland, Oregon.

Among recently developed surface modification techniques, sonochemistry has emerged as a promising method due its simple and cost-effective nature. The advantage of using high intensity ultrasound is the localized heating, high pressure, and short lifetime when bubbles generated through acoustic cavitation collapse. In this research, we investigated the surface interactions between boron-boron nanoparticles and boron particle-aluminum flat surface. Using surface characterization techniques such as the atomic force microscopy (AFM), scanning electron microscopy (SEM), and the transmission electron microscopy (TEM), we found that the nanoparticles of boron fused with each other while the boron particle and aluminum surface exhibited chemical reactions and phase transformations. During the presentation, we discuss about mechanisms of interfacial interactions as well as potential tribological applications.

11:45 AM Y9.11

Electrical Conduction in Thermally Sprayed Metal Coatings.

Atin Sharma, Richard J. Gambino and Sanjay Sampath; Materials Science and Engineering, Stony Brook University, Stony Brook, New York.

The process of thermal spray is conventionally employed to make thick (~1mm) protective coatings such as thermal barrier or wear resistant coatings. However, in the recent past, attempts have been made to prepare functional coatings for electrical and electronic device applications that require relatively thinner ($\leq 150 \mu\text{m}$) coatings. In order to make such thin-coating devices, it is important to understand the coating properties in the low thickness regime. In the present work, the properties of a set of air plasma sprayed (APS) molybdenum coatings, sprayed to different thicknesses, was studied as a function of coating thickness. The apparent density of the coatings was found to increase with thickness until a *saturation* density ($\sim 80\%$ of the bulk density of molybdenum) was achieved. This increase in the density was attributed to the increased volume fraction of the metallic component (or decreased porosity volume) in the composite coatings. The in-plane electrical conductivity was measured as a function of the volume fraction of the metal and the results were analyzed using a two-layer model of the coating. The top layer which was composed of coating roughness was assumed to have fixed thickness and conductivity whereas the conductivity of the bottom layer was assumed to vary with thickness (density). A fit to the data obtained from the above model showed that the conductivity of the bottom layer obeys a power law relationship of the type $\sigma(f) \propto (f - f_c)^t$ throughout the composition range (with $t=1.72$ and $f_c=0.09$). These results are interesting because the critical exponent found in our system falls within the range predicted by many theories (1.65-2.2) for a three-dimensional percolation system[1] whereas a relatively low value of threshold volume fraction indicates the inherent anisotropy of thermally sprayed coatings[2]. This analysis also elucidates some of the fundamental aspects of the initial stages of the coating build-up in the plasma spray process and should be generally applicable to thin coatings made by a variety of materials. This research was supported by the MRSEC program of the National Science Foundation under award number DMR 0080021. [1] D. Deptuck, J.P. Harrison, and P. Zawadzki, Phys. Rev. Lett. 54, 913 (1985) [2] L.N. Smith and C.J. Lobb, Phys. Rev. B 20, 3653 (1979)