Monday Morning, October 2, 2000

Surface Engineering Room 201 - Session SE+TF-MoM

Hard and Superhard Coatings

Moderator: A. Inspektor, Kennametal Inc.

8:20am SE+TF-MoM1 Plasma Deposition of Hard and Thermal Resistant Coatings in the System Si-B-C-N, D. Hegemann, C. Oehr, Fraunhofer Institute for Interfacial Engineering and Biotechnology, Germany; R. Riedel, Technical University Darmstadt, Germany; H. Brunner, Fraunhofer Institute for Interfacial Engineering and Biotechnology, Germany

As a result of covalent bonding, the four elements boron, carbon, nitrogen and silicon can form superhard materials. Considering the well-known diamond-like and cubic boron nitride films, which are limited by their temperature resistance and adhesion, respectively, further research in the as before mentioned system is required. Thus, BCN and SiBCN thin films are very promising candidates which are therefore investigated. A capacitive rf discharge in an asymmetrical but confined geometry is chosen for the deposition experiments to sustain well defined plasma conditions. The bias voltage depending on delivered power and pressure is taken as control parameter. Due to the use of single-source precursors - pyridine borane and (PB) triazaborabicyclodecane (TBBD) for BCN, tris(dimethylamino)silylamino-bis(dimethylamino)borane (TDADB) for SiBCN - relative low substrate temperatures (300°C) can be applied yielding amorphous films. Ar or N@sub 2@ in an excess of 50:1 serves as carrier gas. Both with BCN and SiBCN film deposition, several regimes of different chemical composition become apparent increasing the bias voltage. An influence of the used precursor is merely observed at low biases. At moderate bias voltages films comparable to thermal CVD processes are obtained. Further increasing the bias yields hard coatings up to 13.5 GPa and 30.8 GPa measured by microindentation for BCN and SiBCN, respectively. It is found that the hardness scales mainly with the carbon content of both films, analogously. Annealing the films for 5 h in argon or air exhibits a thermal and oxidation resistance of the SiBCN films exceeding 1200°C. On the other hand, BCN films start to decompose at about 1000°C in argon and 800°C in air. Moreover, the SiBCN films show lower internal stresses (1-2 GPa) compared to BCN, which is attributed to a stabilization effect of sp@super 3@ hybridized carbon by silicon incorporation.

8:40am SE+TF-MoM2 Structure and Mechanical Properties of Ti-Si-C Coatings Fabricated by Sputtering and Pulsed Laser Deposition, S.H. Koutzaki, J.E. Krzanowski, University of New Hampshire; J. Nainaparampril, Systran, Inc.; A.R. Phani, University of New Hampshire

Nano-structured coatings consisting of mixtures of carbide compounds can provide a useful route to developing super-hard materials. Heterogeneous nano-structured coatings can be obtained by either deposition of multilayer structures or by depositing film compositions that undergo a natural phase separation due to thermodynamic immiscibility. In the present work, we have taken the latter approach, and deposited films by RF co-sputtering from dual carbide targets, as well as by pulsed-laser deposition (PLD) using ternary carbide targets. We have examined a number of ternary carbide systems, and to date the most promising coatings have been obtained in the Ti-Si-C system. In this system, the TiC and SiC phases are highly immiscible and phase separation on deposition is likely to occur. We first examined sputter-deposited TiC coatings with varying SiC content. It was found that the nano-indentation hardness increased with SiC content, with a maximum hardness nearly twice that of the sputtered-deposited TiC films at a SiC content of 15 at. %. We further analyzed these films using high-resolution TEM, XPS and X-ray diffraction. Since cubic SiC has an X-ray pattern almost identical to that of TiC, the extent of phase separation could not be determined by that method. However, XRD did demonstrate a general disordering of the films with increasing SiC content. High-resolution TEM also revealed that films of higher SiC content exhibited a mottled structure and nano-scale phase separation within the grains. Further studies were conducted comparing PLD TiC and TiC-12 at.% SiC films (the latter made using a ternary target). The Ti-Si-C coatings exhibited about 25% higher hardness levels in comparison to TiC alone.

9:00am SE+TF-MoM3 Hard and Superhard Coatings - A Review, W.D. Sprou¹, Reactive Sputtering, Inc. INVITED

Hard coatings such as titanium carbide deposited by the high temperature chemical vapor deposition (CVD) process first made their commercial appearance in the late 1960s. The single layer coatings were soon supplanted with multilayer CVD coatings, but it was difficult to apply these coatings to high speed steel (HSS) tooling or steel alloys without damaging the metallurgical properties of the steel. In the early 1980s, several physical vapor deposition (PVD) techniques became available for depositing hard coatings such as titanium nitride or titanium aluminum nitride onto HSS. One of the driving forces in the PVD coatings business has been a desire to increase the hardness of the coatings with the ultimate goal of matching or exceeding the hardness of diamond. Today superhard (hardness greater than 40 GPa) coatings exist. The hardening mechanisms for achieving superhardness fall into two categories, intrinsic and extrinsic. Intrinsic materials such as diamond, cubic boron nitride, and some ternary compounds rely on high bond energies and short bond lengths to achieve superhardness whereas the extrinsic nanostructured multi-layer and nanocrystalline materials rely on the microstructure to restrict dislocation movement to achieve superhardness. A hardness exceeding that of diamond has been reported for a nanocomposite of titanium nitride and silicon nitride. Coating hardness is only one property that should be considered when engineering a surface. Coating toughness should also be factored in especially in situations where impact loading will occur. Today advances are being made in high-density plasma (HDP) PVD techniques that will have a direct impact on future PVD hard coatings. The high degree of ionization in HDP systems will allow new compounds synthesis at temperatures well below the thermodynamic equilibrium point. Perhaps in the near future crystalline alpha alumina will be deposited below 500 degrees C by HDP PVD techniques.

9:40am SE+TF-MoM5 Unbalanced Magnetron Sputter Deposition of Al-Ti Ceramic Coating for High Speed Milling Application, *X. Zeng*, Gintic Institute of Manufacturing Technology, Singapore

Hard coatings for high speed machining consist of multiple layers because of the requirements for high adhesion strength to the substrate, high thermal stability, high hardness and low friction coefficient and good compatibility. Traditionally used coatings like TiN, CrN and their alloyed nitride coatings have high hardness and good adhesion on common tooling materials used in industry. However, these coatings usually have poor performance in high speed machining applications, especially in the cutting of hardened tool steels, because of phase transition (oxidation) at high temperatures. Ti-Al alloyed nitrides seem to be one of the most promising coatings for this application due to its high thermal stability, low friction coefficient and high hardness. This paper reports the development of a multilayered Ti-Al ceramic hard coating on tunsten carbide ballnose endmills for high speed milling using an unbalanced magnetron sputtering system @footnote 1@. The process parameter dependence of the coating properties was studied. X-ray diffractometry, x-ray photoelectron spectroscopy, nanoindentation and scratch test were used to characterize the structural, compositional and mechanical properties of the coatings. High hardness, up to 40 GPa, good adhesion strength, up to 100 N in scratch critical load, and high oxidation resistance were achieved, leading to excellent performance in high speed milling on hardened tool steel at a machining speed of 260 m.min@super -1@. The results show that the tool life with this coating is improved by a factor of 4 or better, under the testing conditions used, compared to the uncoated WC tools. The surface finish of the machined steel achieved with this coating is also significantly better. @FootnoteText@ @footnote 1@ X.T. Zeng, J. Vac. Sci. Technol., A 17, (1999) 1991

10:00am SE+TF-MoM6 Thermal Stability and Mechanical Properties of Nano-scale W/ZrN Multilayers, A. Madan, Northwestern University; J. Ji, S.A. Barnett, Applied Thin Films, Inc.

Nanolayered thin films show an enhanced hardness and improved mechanical properties as compared to the individual layer components. The high-temperature stability of these films is important for various technological applications e.g. dry-cutting. We report on the thermal stability and mechanical properties of polycrystalline, immiscible W/ZrN nanolayered films. W/ZrN multilayers of bilayer periods 2 to 40 nm were sputter deposited in a dual-opposed-cathode unbalanced-magnetron sputtering system. The W fraction was varied from 0.3 to 0.8 by adjusting the relative power on the two targets. The 1 micron films were annealed at

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temperatures from 750°C to 1000°C in inert atmospheres. The as-deposited and the annealed films were characterized using x-ray diffraction, crosssectional transmission electron microscopy (XTEM), and nanoindentation. The as-deposited films showed an enhanced hardness in comparison to the rule-of-mixtures values irrespective of the bilayer period or the layer composition ratio. High- and low-angle x-ray diffraction (XRD) showed that the layered structure was stable after annealing at 1000°C for 1 h. XTEM results for as-deposited and annealed films will be presented. The annealed films show hardnesses as high as 44 GPa. The excellent high-temperature stability of the W/ZrN nanolayered structures arises because W and ZrN are mutually immiscible.

10:20am SE+TF-MoM7 Growth and Characterization of ZrN/ZrB@sub 2@ Nanolayered Coatings for High Temperature Applications, K Martin, J. Ji, I. Kim, S.A. Barnett, Applied Thin Films, Inc.; A. Madan, Northwestern University; P. Hedge, A. Inspektor, Kennametal, Inc.

There is a great need for cutting tool coatings that perform well at elevated temperatures, both because of the desire to cut at higher rates and to eliminate coolant fluids. However, current cutting-tool coating materials fail rapidly under these conditions because of poor high-temperature properties. The ZrN/ZrB@sub 2@ nanolayered system is expected to provide a unique combination of properties including high hardness, excellent stability at elevated temperatures, low chemical solubility in Fe and good thermal expansion match with cemented carbide tools. In this investigation, ZrN/ZrB@sub 2@ nano-layered coatings were deposited using a dual-cathode magnetron sputtering system. The key properties including hardness, adhesion, and residual stress were evaluated as a function of composition, bilayer period, and substrate bias. The hardness values for as-deposited coatings ranged from 30-38 GPa and increased to 49 GPa after annealing at 1000°C. Low and high angle XRD revealed that the superlattice structure was stable at elevated temperatures. The increase in hardness after annealing is attributed to the transition of the soft amorphous ZrB@sub 2@ to the crystalline form. Adhesion testing verified that the coatings adhered well on cemented carbide inserts even after annealing at 1000°C.

10:40am SE+TF-MoM8 Fabrication of Al-Pt Coating on Ni Base Superalloys and Studies of Their Structure, *M. Ghoranneviss, H. Parchamy Aragy,* Islamic Azad University, Iran; *A. Sedghi,* International Iran Khomani University, Iran; *A. Shokohi,* Islamic Azad University, Iran

Thin film coating are formed on the enginneering materials to improve their physical and mechanical properties these coating are used mainly in different fields of industrial application and in these respect many research conducted to improved their properties.In projects this research, therefore, the formation of Al-Pt(Aluminum/Platinum) alloys coatings on nickel based super alloys has been studied.Sputtering-ion beam technique under Argon plasma and subsequent heat treatment is been used to fabricate these coating.Ion implantation is applied the Aluminum-Platinum alloys coatings. The main goal of this work is increasing erosion and consequently erosion-corrosion resistance of these coating. Scan Electron Microscope, Glow discharge Spectrometers and X-Ray Diffraction techniques is used to investigate the structure of fabricated coatings. These results correlates with other investigations and these method can be presented as a industrial method for fabrication of these coating.lon implantation improved these properties but the results not very appreciable.Details will discus in full paper.

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Surface Engineering Room 201 - Session SE-MoA

Coatings for Extreme Environments: Wear Resistant, Lubricious, Anti-corrosive, High Temperature Coatings Moderator: W. D. Sproul, Reactive Sputtering Inc.

2:00pm SE-MoA1 Coatings and Surface Engineering for Tough Applications, A. Inspektor, Kennametal Inc. INVITED

A functional surface is an engineered system consisting of substrate and coating designed to work together. From a 50 µm thick diamond layer on cutting tools to a few atoms thin protective barrier on hard drives, a functional surface is a critical component in many new high technology products. It is the first line of defense of the coated part and thus, it is absolutely vital to the performance and to the reliability of the part in tough applications. This paper will present and critically review principles of surface engineering for cutting tools and wear parts. An emphasis will be on the design and preparation of the working surface as illustrated by case studies from diamond-coated cutting tools, thermal barriers for automotive and aerospace engines, concepts in cBN deposition, and recent developments in the field of nano-layer and nano-composite superhard films.

2:40pm SE-MoA3 Influence of the Interface Composition on the Corrosion Behavior of Unbalanced Magnetron Grown Niobium Coatings on Steel, C. Schönjahn, H. Paritong, W.-D. Münz, Sheffield Hallam University, UK; I. Petrov, R.D. Twesten, University of Illinois, Urbana

In general niobium is well known as a chemically extremely stable material. However the corrosion performance of 0.5 to 1 μm thick , unbalanced magnetron (UBM) grown niobium coatings on steel substrates depends significantly on the in vacuo etching pretreatment of the substrates prior to coating and on the chemical composition of the steel substrate. Corrosion tests, TEM and STEM analyses have shown that a dense fine grained partially implanted 5-10 nm thick niobium interface layer formed during the metal ion etching pretreatment is paramount to protect the steel substrate thoroughly against corrosion in chlorine containing aqueous electrolytes, whereas the pretreatment with Ar @super +@ and Cr @super +@ ions leads to inferior corrosion results. Moreover the energy of the impinging Nb @super +@ ions used during the etching process plays an important role. Maximum pitting potential and minimum corrosion currents were found for bias voltages between -600 and -900 V. In summary the results suggest that the UBM deposited Nb coatings are not completely dense although no evidence for the presence of voids has been found by TEM analysis and that the major justification for niobium as corrosion barrier depends on the existence of the thin interface layer generated by high energetic ion bombardment during the etching step. The UBM deposited coating (U@sub s@=-75V) acts therefore only as an itself chemically stable mechanical spacer protecting the thin interface layer against mechanical damage.

3:00pm SE-MoA4 Oxidation Resistance of NiAl and NiAl-AlN Coatings Deposited by Magnetron Sputtering, *D. Zhong*, Colorado School of Mines; *A.M. Peters*, Los Alamos National Laboratory; *J.J. Moore, G.G.W. Mustoe*, Colorado School of Mines; *J. Disam, S. Thiel*, Schott Glas, Germany

It is well known that NiAl exhibits excellent oxidation resistance and it shows improved cyclic oxidation resistance when NiAl-AlN composite is used. In this work, NiAl and NiAl-AlN coatings have been deposited from a NiAl compound target by using RF magnetron sputtering technique. The oxidation behaviors of NiAl and NiAl-AlN films were studied using a Netzsch Simultaneous Thermal Analyzer (STA409C) and Rutherford Backscattering Spectrometry (RBS). Their structures and microstructures were characterized using x-ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM). It was shown that they are excellent oxidation resistant coatings. In this paper, their oxidation rates and mechanisms will be discussed together with their structure observations as well.

3:20pm SE-MoA5 Aspects of Surface Engineering in the Automotive Industry, Y.T. Cheng, General Motors R&D Center

The manufacturing of an automobile is to a large extent the making of engineered surfaces on several length scales using a variety of processing techniques. In this presentation, we will summarize aspects of our recent work related to surface engineering. Examples include the preparation and characterization of nanocomposite thin films consisting of metal-metal and metal-ceramic materials; their tribological properties and potential application as low-friction and wear resistant coatings for electrical connectors will be discussed. Other examples include the investigation of thin films for sensors, battery electrodes, and catalysts. We will also review our work on modeling indentation measurements. Although significant progress has been made in surface engineering, it is still largely a "trial-and-error" process. We will illustrate with examples the needs for: (1) reducing the cost and improving the reproducibility of tribological coatings, (2) better characterization techniques for mechanical property measurements at the nano- and micro-meter scales, and (3) design guidelines and models based on the fundamental understanding of the relationships between the structure, property, and performance of engineered surfaces.

3:40pm SE-MoA6 Tribological Performance and Initial Finite Element Modeling of Reactively Sputtered Single and Multi-layer Chromium Nitride Thin Films, S.L. Rohde, L. Olson, S.M. Aouadi, University of Nebraska; D.M. Mihut, Multi-Arc Scientific Coatings; B. Neville, Iowa State University; D.M. Hornyak, University of Nebraska

Tribological properties of Cr-N based single- and multi-layer thin films are compared with FEA modeled stress fields under similar loading, to evaluate the feasibility of "building-in" load support, with alternating hard/soft film layers to optimize performance on both traditional tool steels and more compliant substrates. The first phase involved the deposition and evaluation of coatings on substrates of both hardened A2 tool steel and 2024-alloy aluminum. Next, the wear behavior was assessed using pin-ondisk (PoD) tests, performed unlubricated at 40 to 50% humidity using alumina and/or tungsten carbide 'pins'. The wear was reduced in most cases, with the multi-layered structures performing best on all substrate materials. PoD tests on the A2 tool steel substrates, favored the hardest thin film structures; however, these same films did not perform as well on the more compliant Al-substrates. For the Al-substrates, neither the stiffest nor the most compliant films excelled, instead multi-layer films with alternating hard/soft structures designed to provide a more graded compliance from the substrate up to the rigid top layer yielded the best results. In this case, wear rates were reduced by as much as much as three orders of magnitudes over uncoated 2024 Al. In the final stage, finite element modeling studies have been initiated to try to understand the behavior of these multilayered coating/substrate combinations under specific loading conditions. First generation models are matched to their respective wear systems and the results compared. These models will then be used to guide the development of second generation coatings, that will be used to verify and improve the efficacy of the models. The goal of the modeling program is thus to facilitate specification and optimization of application specific coating structures into the original component designs.

4:00pm SE-MoA7 Tribological Performance of a Novel High Wear Resistant 390 Al Alloy Overlay, *R.D. Ott, C.A. Blue, M.L. Santella, P.J. Blau,* Oak Ridge National Laboratory

A novel process has been developed at Oak Ridge National Laboratory (ORNL) for the production of high silicon (Si) containing aluminum (AI) alloy surface layers (overlay) on Al alloys. The main purpose of the overlay is to improve the wear resistance of the underlying alloy. The process is versatile enough to place the overlay only in critical areas, thus, greatly reducing the cost of a component. Instead of manufacturing a component from expensive high Si content 390 Al alloy, the component could be manufactured from an inexpensive alloy, such as 319 Al alloy, and the 390 Al alloy overlay could be placed in essential areas were high wear resistance was required. Test specimens comprising of 390 Al alloy overlays on 319 Al alloy have been processed to mimic bulk 390 Al alloys. Pin-ondisk wear tests have been performed, following ASTM standards, to quantify the wear resistance of the 390 Al alloy overlay with that of bulk 390 Al alloy. Wear tests have also been performed on bulk 319 Al alloy as a baseline. Lubricated and non-lubricated pin-on-disk wear tests were conducted utilizing 440C stainless steel and 52100 steel balls as the pin material. Also evaluated were the frictional forces during the wear tests, scratch hardness, microhardness, and the Hertzian contact pressures. From the tests conducted, the 390 Al alloy overlay shows potential as a replacement of bulk 390 Al alloy for high wear resistant applications.

4:20pm SE-MoA8 Mechanical and Tribological Properties of Substoichiometric Oxide and Superstoichiometric Carbide Coatings for Wear Reducing and Lubricating Applications, St. Bärwulf, E. Lugscheider, K. Bobzin, University of Technology Aachen, Germany

The tungsten and vanadium oxides are promising to be usable as solid lubricants at elevated temperatures because of their ability to form non stoichiometric Magnéli-phases with reduced shear strength. So far they

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were mainly investigated as powdery material or as a component of ceramics for tribological or machining applications. As a matter of fact metal-oxides are interesting for tribological insets at atmospheric conditions because of their expected oxidation stability, hardness and low adhesion against the counterbody. For low temperature insets carbon containing coatings are meanwhile widely spread in numerous applications. Because of their phase generation / transition the zircon- and hafniumcarbon systems offer a very interesting possibility to deposit graded coatings with self-adapting properties in dependance on the external mechanical load and the contact conditions. This self-adapting effect will be shown exemplarily for a hydraulic component after an inset under load in relative motion. The presentation will report about the mechanical and tribological properties of these coatings. Further possible ranges of applications will be deduced from the fundamental characterization and results of concrete insets (e.g. machining) shown. Therefore the coatings were analyzed by various testing methods to characterize the tribological, mechanical and structural properties, like contact angle measurements, SEM, scratch testing, nanoindentation, XRD and pin on disk.

4:40pm SE-MoA9 Thin Film Disk Contact Start/stop Durability Failure Model: Subcritical Interfacial Crack Growth, *R.L. White*, *V. Raman*, IBM Corporation

Analogous to fatigue failure in bulk materials, contact start/stop (CSS) failure of thin film disks is modeled as the progressive growth of interfacial cracks resulting from the cyclic tractions applied by intermittent slider-disk contact. Interfacial cracks eventually reach a critical dimension, resulting in film fracture or spallation and catastrophic failure of the head-disk interface. There are two bodies of evidence which support such a model. The first derives from scratch adhesion testing of mechanically textured disk media. The scratch data demonstrate that the same weibul statistics that can be fitted to CSS failures also describe the distribution of critical loads necessary to produce delamination of the disk metallurgy. Furthermore, a number of cases can be cited in which the critical loads can be correlated to start/stop durability, including the effects of hydrogenation on the start/stop durability of CHx overcoats. Secondly, this model provides for the semi-quantitative prediction of the effects of headdisk interface parameters which are in general agreement with empirical studies. The tractions applied at the head-disk interface are predicted to diminish with distance from the interface with a 1/d dependence. Since subcritical crack growth rate follows a power law relationship to stress intensity, start/stop failure statistics would be expected to show a power law dependence on carbon thickness. Data are presented demonstrating CSS life is proportional to the 3rd power of carbon thickness. The effects of CSS test temperature and slider size can also be rationalized based on the above model for CSS failure.

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Surface Engineering Room 201 - Session SE-TuM

Interface Engineering and Graded Films: Structure and Characterization

Moderator: I. Petrov, University of Illinois, Urbana

8:40am SE-TuM2 Epitaxial Growth of Metastable B1-NaCl-Structure TaN@sub x@ on MgO(001) by Ultrahigh Vacuum Reactive Magnetron Sputter Deposition, C.-S. Shin, D. Gall, J.E. Greene, I. Petrov, University of Illinois

Metastable B1-NaCl-structure TaN@sub x@ (x = 1-1.3) layers, with thicknesses 0.25 to 0.5 @micro@m, were epitaxially grown on MgO(001) at temperatures T@sub s@ between 600 and 700 °C by ultra-high-vacuum reactive magnetron sputtering in N@sub 2@/Ar mixtures. X-ray diffraction and transmission electron microscopy results show that the epitaxial relationship is cube-on-cube, (001)@sub TaN@||(001)@sub MgO@ with [100]@sub TaN@||[100]@sub MgO@. TaN@sub x@ layers grown at T@sub s@@>=@ 700 °C undergo a transition from the metastable NaCl structure to the thermodynamically-stable hexagonal phase. NaCl-structure TaN@sub x@ layers with x = 1-1.22 exhibit a nearly constant resistivity of 225 @micro@@OHM@-cm with hardness (H) and elastic modulus (G) values, determined by nanoindentation, of 31±0.9 and 457±16 GPa, respectively. Higher N/Ta ratios lead to an increase in @rho@ and a decrease in H and G. All cubic TaN@sub x@ layers exhibit negative temperature coefficients of resistivity between 20 and 400 K due to weak carrier localization. TaN@sub x@ is superconducting with the highest critical temperature, 8.45 K, obtained when x is close to 1.

9:00am SE-TuM3 Stress Evolution in TiN and TaN Layers and Multilayers Prepared by Reactive Magnetron Sputtering and Studied with in-situ Laser Reflection Curvature Technique, *T. Joelsson, J. Birch, P. Sandström, L. Hultman,* IFM Linköping University, Sweden

TiN and TaN are interesting materials for an industrial purpose both as hard coatings and as contact materials and diffusion barriers in microelectronics. Control and understanding of the stress evolution in these films is of importance since problems such as delamination and cracking may occur due to compressive and tensile stresses. We have used time-resolved insitu curvature technique to measure the stress evolution during UHV magnetron reactive sputter deposition onto Si wafers. 800 nm thick individual layers of TaN and TiN have been studied at different nitrogen partial pressures during growth. For TaN at low nitrogen partial pressures, the stress evolution is first tensile with a maximum level of around 0.5 GPa then after 30 nm it turns compressive. At higher nitrogen partial pressures the TaN layers are always compressive. For TiN the layers starts to grow compressive and then turns tensile. For TiN in multilayer and at low nitrogen partial pressure (0.45 mTorr) first a tensile stress is developed then a compressive and finally a tensile stress. This can be correlated with the coalescence stages. The initial compressive state seen in the TiN films is probably correlated to heating of the sample due to bombardment of energetic species (approximately 40° C). When TiN and TaN are deposited sequently to form a multilayered structure the overall residual stress is determined by the thickness of the individual layers and the eventual thermal relaxation time between the different layers. TaN also exhibits phase transformations as a function of layer thickness in a multilayer stack, which in turn offsets the stress evolution.

9:20am SE-TuM4 The Compressive Coating Stresses in the Scratch Adhesion Test, Y. Xie, H.M. Hawthorne, National Research Council Canada, Canada

Despite the widespread use of the scratch adhesion test, there is no model available to determine the critical coating stress for initiating interfacial failure, so that ranking the coating-substrate adhesion of coated systems with different mechanical properties is impossible. In this study, a mathematical model is developed to calculate the distribution of compressive stresses in a thin coating induced by a scratch indenter. For ease of use in practice, a simple equation, @sigma@@sub cm@ = 0.15 (P@sub c@H@sub f@/H)@super 0.5@ E@sub f@@super 0.3@ E@super 0.2@/R, is then derived from the model, where @sigma@@sub cm@ is the critical mean compressive stress in the coating for interfacial failure, P@sub c@ is the critical normal load measured from the scratch adhesion test, H@sub f@ and E@sub f@are the hardness and Young's modulus of the substrate, and R is the indenter radius. This equation is useful for ranking

the coating-substrate adhesion of different coated systems, or, for estimating the critical mean coating stress for interfacial failure.

9:40am SE-TuM5 Interface Engineering and Graded Films: Structure and Characterisation, S.J. Bull, University of Newcastle, U.K. INVITED The properties and performance of most bulk materials and coatings are controlled by interfaces. For bulk materials the surface is the most important interface, though grain and phase boundaries may also play a role in dictating performance. However, when developing coating systems there is the possibility of using many interfaces to control behaviour. As well as the surface, the coating/substrate interface will be important and in multilayer coating designs the number and properties of the individual layer interfaces will also play a role. It has often been observed that multilayer coatings offer enhanced hardness and fracture resistance compared to comparable single layer coatings though the reasons for these improvements are not always well understood. This paper will review the effect of interfaces on the mechanical properties and tribological performance of bulk materials, single and multilayer coatings highlighting the importance of engineering interfaces with high strength if coatings with optimum properties are to be achieved. A simple model will be introduced which enables the effect of such interfaces to be more fully appreciated. The possibility of using graded compositions to improve performance will be discussed in light of this model.

10:20am SE-TuM7 Characterization of Cr@sub 2@N/CrN Multilayer Coatings Produced by Ion-Assisted Reactive Magnetron Sputtering, S.M. Aouadi, University of Nebraska; K.C. Wong, K.A.R. Mitchell, University of British Columbia, Canada; S.L. Rohde, University of Nebraska

A series of monolithic and multilayer coatings of chromium nitride with various compositions and architectures were deposited at low temperatures (<200°C) on silicon substrates using ion-assisted reactive magnetron sputtering. Real-time in-situ ellipsometry was used to control the deposition process. The multilayer coatings were fabricated with a CrN to Cr@sub 2@N ratio in the range from 1 to 12. In addition, the deposition parameters were altered to obtain interfacial geometries that varied from sharp to various levels of grading. The deposited coatings were characterized post-deposition using X-ray diffraction (XRD), Rutherford backscattering (RBS), X-ray photoelectron spectroscopy (XPS), and ex-situ spectroscopic ellipsometry (SE). The crystal phases and textures were identified using XRD. The film composition, the periodic structure of the multilayers and the interface type were determined from RBS, XPS and SE measurements. To compare the mechanical properties of the coatings, their hardness was evaluated using a nanoindenter. Most coatings gave hardness values in excess of 20 GPa.

10:40am SE-TuM8 Optimization of In Situ Substrate Surface Treatment in a Cathodic Arc Plasma: A Plasma Diagnostics and STEM-EDX Study, C. Schönjahn, A.P. Ehiasarian, W.-D. Münz, D.B. Lewis, R. New, Sheffield Hallam University, UK; R.D. Twesten, I. Petrov, University of Illinois, Urbana It has been shown previously that the in situ substrate cleaning step prior to PVD deposition affects the interface formation which influences the adhesion of the coating on the substrate. Most promising results were obtained for Cr ion bombardment where the Cr ions are extracted from a cathodic arc source by negatively biasing the substrates with U@sub s@=-1200V. The main objective of the current project is a further optimization of the in situ substrate surface pre-treatment with respect to reduced process costs and lower risk for local substrate overheating. Langmuir probe measurements show that the presence of Ar leads to a two-fold increase of the speed of the cathode spot thus reducing the amount of macro particles emitted by the cathodic arc source. The presence of Ar leads to an increased ion current density of j = ~30 Am@super -2@ for P@sub Ar@ = 8x10@super -2@ Pa compared to j = 6 Am@super -2@ at background pressure of P@sub tot@ = 7x10@super -4@ Pa due to the ionization of Ar in the cathode spot and in charge exchange reactions with Cr ions as observed by Optical Emission Spectroscopy. Although the mean energy of bombarding species decreases the higher ion flux suggests a more effective removal of substrate material. This is indeed observed by measuring an effective etching rate of 4 nm.min@super -1@ at P@sub tot@ = 7x10@super -4@Pa compared to 8 nm.min@super -1@ at P@sub Ar@ = 8x10@super -2@Pa. However, owing to the loss of high energy Cr ions, metal ion implantation, which was shown to be beneficial for adhesion, is reduced. The implantation profiles were studied by STEM-EDX analysis on electron transparent cross sections. Based on these results a two stage ion bombardment procedure is proposed. The first stage is Cr bombardment at an Ar pressure of 8x10@super -2@ Pa for intensive cleaning. This is followed by pure Cr ion bombardment for enhanced ion

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implantation due to the higher portion of multiply charged Cr ions to achieve enhanced adhesion.

11:00am SE-TuM9 Laterally Graded Multilayers and their Applications@footnote 1@, C. Liu, A. Macrander, Argonne National Laboratory; J. Als-Nielsen, Copenhagen University, Denmark; K. Zhang, Illinois Institute of Technology

Laterally graded multilayers consisting of uniform W layers and wedgeshaped C layers have been made at the Advanced Photon Source (APS) deposition lab for tunable x-ray double-monochromator applications. The double monochromator has two identical graded multilayers in series, as in the conventional double-crystal monochromator arrangement. By letting the x-ray beam hit slightly different (bilayer) d spacing on each multilayer, one can adjust the bandpass and peak energy of the transmitted beam. Also, since that the Bragg angles of the two multilayers are not constrained to be the same, the angle of the transmitted beam can be varied in the vertical plane. This option may be an attractive alternative to the conventional way for studying liquid surfaces in reflectivity and grazing incidence diffraction measurements. The graded multilayer comprised 60 bilayers of W and C on 100 x 25 x 3 mm float glass with a d spacing varying from 35 to 60 Å and an average gradient of 0.27 Å/mm along the long direction. The films were made by DC magnetron sputtering with the sputtered atoms passing a contoured mask while the substrate was moving. Two different masks were designed to produce either a uniform (for W) or graded (for C) thickness profile. The multilayer and graded multilayers have many other novel applications. Potential applications in xray fluorescence detection and x-ray standing wave experiments will be discussed. @FootnoteText@@Footnote 1@This work is supported by the U.S. Department of Energy, BES, under contract no. W-31-109-ENG-38

11:20am SE-TuM10 A Novel Interface Modification Technique Applied from the Top of a Coated Layer, *M. Yoshitake*, *Y.-R. Aparna, K. Yoshihara*, National Research Institute for Metals, Japan

A technique to modify interface after the formation of interface is desired either from a process requirement or because of the change of material use with time. A novel technique to form an intermetallic compound at the interface between coated layer and substrate by depositing a chosen metal film on the top of a coated layer is presented. Based on the property of the intermetallic compound, an interface is modified. Experimentally, the diffusion and interfacial reaction of specimens with top-film/middlefilm/substrate structure were investigated. With proper choice of top-film element, top-film element diffuses inside without detectable reaction with middle-film and concentrate at the interface between middle-film and substrate followed by intermetallic compound formation. We discuss conditions for obtaining above phenomena and general guide for a choice of top-film element is presented. Key factors are (1)segregation tendency of top-film element on middle-film metal, (2)activation energy of diffusion of top-film element in middle-film and in substrate and (3)formation of intermetallic compound between top-film metal and substrate in phase diagram. The examples of intermetallic compound formation by the diffusion of top-film element are given in Ti-film/Nb-film/Cu-substrate, Fefilm/Nb-film/Ti-substrate and other combinations.

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Surface Engineering Room 201 - Session SE-TuA

Surface Engineering: Surface Preparation to Postcoating Surface Finishing

Moderator: Y.-W. Chung, Northwestern University

2:00pm SE-TuA1 Surface Engineering by Plasma Immersion Ion Processing, M.A. Nastasi, Los Alamos National Laboratory INVITED Ion beam processing, including ion implantation and ion beam assisted deposition (IBAD), are established surface modification techniques which have been used successfully to synthesize materials for a wide variety of tribological applications. In spite of the flexibility and promise of the technique, ion beam processing has been considered too expensive for mass production applications. However, an emerging technology, Plasma Immersion Ion Processing (PIIP), has the potential of overcoming these limitations to become an economically viable tool for mass industrial applications. In PIIP, targets are placed directly in a plasma and then pulse biased to produce a non-line-of-sight process for intricate target geometries without complicated fixturing. If the bias is a relatively high negative potential (20-100kV) ion implantation will result. At lower voltages (50-1200V), deposition occurs. Potential applications for PIIP are in low-value-added products such as tools used in manufacturing, orthopedic devices, and the production of optical coatings. This talk will focus on the technology and materials science associated with PIIP.

2:40pm SE-TuA3 The Surface Modification of Wear Resistant HSS Cutting Tools with Adapting Engineered Coatings, *G.S. Fox-Rabinovich*, McMaster University, Canada; *A.I. Kovalev*, SPRG, Russia

The friction parameter, wear resistance, phase and chemical compositions, atomic structure of multi-layered surface engineered coating for cutting tools were studied. A number of fine structure analysis methods including AES, SIMS, EELS, EELFS were applied. The surface engineered coatings being investigated was formed by duplex surface treatment technology including ion nitriding of high-speed steel and by hard PVD (Ti, Cr) N coating cathode arc deposition. Top protective layer of the multi-layer coating was formed by lubricant coating consists of Perfluoro-popyethers (PFPEs) with hydroxyl end groups (known by the brand name Z-DOL). This lubricant has the following chemical structure: (HO-CH2-CF2)-(C2F4O)6-(CF2O)290-CF2-CH2OH. Evolution of atomic structure at PFPE was investigated by vibration spectroscopy. Such adapting coating makes it possible significantly - by factor of 2.0-2.5 increase the wear resistance of cutting tools by surface damage prevention during running-in stage of wear. The mechanism of Z-DOL influence on wear phenomenon as a lubricant is discussed.

3:00pm SE-TuA4 Enhanced Passivity of Austenitic AISI 304 Stainless Steel by Low-Temperature Ion Nitriding, S. Rudenja, Tallinn Technical University, Estonia; I. Odnevall Wallinder, C. Leygraf, Royal Institute of Technology, Sweden; P. Kulu, V. Mikli, Tallinn Technical University, Estonia Low-temperature ion-nitriding introduces interstitial nitrogen into the austenitic stainless steel matrix. The passivity and anodic oxidation of a nitrided AISI 304 stainless steel have been studied by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) in 0.1 M H@sub 2@SO@sub 4@ + 0.05 M HCl solution. The chemical composition of the oxidized surface film on the stainless steel was analyzed by X-ray photoelectron spectroscopy (XPS), including angle-resolved spectra of the elements. The distribution of the chemical elements beneath the oxidemetal interface was studied with Auger depth profiling. Defects of crystalline structure nearby the surface were studied with transmission electron microscopy (TEM). An enhanced passivity of the nitrided stainless steel was detected by anodic polarization. Capacitance measurements by EIS revealed a 3-4 nm thick oxide film on the surface of nitrided specimens, that is 2-3 times thicker than on blank specimens. XPS analyses and Auger depth profiles indicate increased chromium uptake into the oxide film on nitrided surface, supposedly through the kinetically stable oxide-metal interface enriched with nitrogen and nickel. Several possible mechanisms influencing passivation of the nitrided stainless steel may operate simultaneously. Among these mechanisms, austenite strengthening by interstitial nitrogen near the oxide/alloy interface and associating with structural defects like dislocation branches are most likely explanation for the enhanced passivity of the nitrided stainless steel.

3:20pm SE-TuA5 CVD Diamond Nucleation under Extreme Conditions, K.-A. Feng, Institute of Physics, CAS, China; J. Kang, University of Michigan; Z. Lin, Institute of Physics, CAS, China

It is well known that the diamond is an outstanding material for a wide range of applications. The synthesis of the diamond films using various methods of CVD (chemical vapor deposition) have received significant in recent years. In order to enhance the density of diamond nucleation, abrading the substrate surface with diamond paste and adding negative bias to the substrate are two routine pretreatment methods. Here, we propose a new method to greatly enhance the nuclei density. Under extreme low pressure and ultra pure hydrogen, high-density nucleation of diamond is achieved on mirror-polished silicon in a hot-filament chemical vapor deposition (HFCVD). The diamond film are studied by Scanning Electron Microscopy (SEM) and Raman Spectrum. The enhanced nucleation at very low pressure should be attributed to an increased mean free path, which induces a high density of atomic hydrogen and hydrocarbon radicals near the silicon surface. Atomic hydrogen can effectively etch the oxide layer on the surface of silicon and so greatly enhance the nucleation density. The residual oxygen in the hydrogen (not ultra pure) is shown a very obvious negative effect on the nucleation of diamond, that is, oxygen atoms possess opposite effects in the nucleation stage and the growth stage of the diamond.

3:40pm SE-TuA6 Large-area Nitrogen-doped SiO@sub 2@ Films Deposition in a Large-scale Integrated RF PSII/PVD System, L. Wu, D. Manos, College of William and Mary

A large-scale integrated implantation/deposition system was used to deposit large-area, high quality nitrogen-doped SiO@sub 2@ films. With a 0.61 m I.D. chamber, 0.57 m I.D. quartz window, and 0.43 m I.D. RF antenna, the system is capable of large-area, uniform surface materials processing. The nitrogen-doped SiO@sub 2@ films were produced by simultaneous sputter deposition of SiO@sub 2@ and nitrogen ion implantation by the plasma. At an RF power of 750 watts, the deposition rate of SiO@sub 2@ over an approximately 20 inch area was 5-10 Å/min. The films were characterized by AES and SIMS depth profiling, and variable angle spectroscopic ellipsometry (VASE). The films were highly transparent, with refractive indexes around 1.5 throughout the visible spectrum and zero extinction coefficients. The films were stoichiometric SiO@sub 2@ with an implanted nitrogen concentration of around 10%. The level of nitrogen doping is easily controllable by adjusting the implant pulse frequency and pulse voltage. N-doped SiO@sub 2@ films have been deposited on Si, Ti, and stainless steel substrates with good adhesion and uniformity. The nitrogen implantation improved properties of the interface between the film and the substrates. This method shows promise for depositing SiO@sub 2@ at low temperature, on a variety of substrates, allowing a range of dopant combinations to produce variable dielectric constants. The low-temperature process preserves small feature dimensions when performed on a masked substrate. The process was modeled using MAGIC and Profile Code to compare to the measured lateral and depth profiles of various features.

4:00pm SE-TuA7 Cleaning, Etching and Oxidation of W films for Microelectronics Applications, P. Cao, M.-S. Lim, S.S. Perry, University of Houston; *E.J. Mitchell*, D.C. Koeck, H.C. Galloway, Southwest Texas State University

During the fabrication of integrated circuits with tungsten plugs, the tungsten surface undergoes chemical mechanical planarization (CMP). It is important to characterize the effects of any pre- or post-processing cleaning steps on the tungsten surface. To investigate this, we have examined tungsten films prepared by chemical vapor deposition (CVD) to carefully characterize how they respond to common cleaning and etching procedures. Topography changes were examined by atomic force microscopy and surface chemistry was characterized by X-ray photoelectron spectroscopy (XPS). Cleaning and etching procedures investigated in this study include solutions of KNO@sub 3@ and H@sub 2@O@sub 2@, KOH, a buffered solution of KIO@sub 3@ and NaOH as well as the RCA SC-1 clean. The relative ability of these cleaning treatments to remove residual hydrocarbons from the W surface has been evaluated. In addition, the influence of these treatments on the native tungsten oxide layer has been measured as well. The XPS results show a general increase in the oxidation state in W for most solutions, specifically entailing an increase in W@super 6+@ and a corresponding decrease in W@super 4+@. These results are relevant to both material removal during the CMP process and the effectiveness of cleaning procedures. A correlation of the

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results shows that weakly oxidizing solutions are not as effective in removing organic contaminants as strongly oxidizing solutions.

4:20pm SE-TuA8 Reactions of Fluorocarbon Polyatomic Ions with Polymer Surfaces, M.B.J. Wijesundara, L. Hanley, University of Illinois at Chicago 25 - 100 eV, mass-selected CF@sub 3@@super +@ and C@sub 3@F@sub 5@@super +@ ions are used to deposit fluorocarbon films on polystyrene surfaces. Monochromatic x-ray photoelectron spectroscopy and contact angle measurements are used to quantify the effect of the unique chemistry and structure of the incident ions on the fluorocarbon film. Oxidation and other aging processes are also examined for these films, following air exposure for several weeks. Fluorination efficiency of the film increases with ion size and energy. The fluorocarbon components vary with ion size, energy, and fluence. These ions deposit largely intact at 25 eV and undergo partial decomposition at 50 or 100 eV. Overall, CF@sub 3@@super +@ and C@sub 3@F@sub 5@@super +@ behave as covalently bound polyatomic precursors or fragments that can react and become incorporated within the polystyrene surface. The size and structure of the ions affect polymer film formation via differing chemical structure, reactivity, sticking probabilities, and energy transfer to the surface. Overall, the different reactivity of these two ions with the polymer surface supports the argument that larger species contribute to the deposition of polymeric films from fluorocarbon plasmas. These results further indicate that complete understanding and accurate computer modeling of plasmasurface modification requires accurate measurement of the identities, number densities, and kinetic energies of higher mass ions and energetic neutrals.

4:40pm SE-TuA9 An Aging Study of Fluorocarbon Plasma Polymers Deposited on Si-C Plasma Polymer Films Using XPS, C.E. Moffitt, D.M. Wieliczka, University of Missouri, Kansas City; Q.S. Yu, C.M. Reddy, H.K. Yasuda, University of Missouri, Columbia

Thin films (~<3nm) formed from D.C. plasma polymerization of C@sub 2@F@sub 6@ deposited on trimethylsilane-based D.C. plasma polymers have proven to tremendously enhance adhesion of subsequent organic coatings. This enhancement in adhesion was observed to be restricted to coatings deposited within the first 5 days after deposition. An XPS study of the aging of these films during exposure to atmosphere was carried out on polished aluminum alloy samples. It was ascertained that extended exposure to x-ray flux degraded the samples, so an optimized scheme was employed to limit the exposure and collect data quickly. The results of this time study indicate that a decrease in fluorine concentration correlates with the time frame of the decrease in adhesion promotion. The decrease in a high binding energy fluorine peak component is the dominant evolution of the fluorine spectra. This is accompanied by a decrease in CF@sub x@ levels and increases in C-C and C-CF bonding during the continued oxidation of the films. The thin nature of the films allows for the observation of the underlying silicon signal, which appears virtually unchanged throughout the oxidation process, indicating a stable interface with little change in the overlayer thickness. Partial support for this project was provided by DARPA under U.S. Air Force contract # AF F33615-96-C-5055.

5:00pm SE-TuA10 An XPS Investigation into the Role of Oxygen in the Structural Formation of Methylated Silane Plasma Polymers, C.E. Moffitt, D.M. Wieliczka, University of Missouri, Kansas City; T.M. El-Agez, Islamic University of Gaza, Palestine; Q.S. Yu, C.M. Reddy, H.K. Yasuda, University of Missouri, Columbia

Films formed from plasma polymerization of carbon containing, silanebased monomers have shown great promise as intermediate adhesion and anti-corrosion promoters on a number of substrates. Incorporation of oxygen in the deposition process has been shown to modify the surface energy of deposited films, yielding a fully variable range of surface wettability from hydrophobic to hydrophilic. A photoemission investigation of films formed with several monomers and various plasma ignition techniques was carried out. It yields insight regarding the chemical changes at the interface with oxidized surfaces, the surface structure of postdeposition plasma treated films, and the mechanism responsible for elemental bonding changes between types of deposition. Aging of a D.C. trimethylsilane plasma polymer was observed to primarily involve the oxidation of Si sites with a loss of carbon bound to silicon sites, which is correlated to spectroscopic ellipsometry data indicating the tendency for a more silica type index of refraction as the film ages. The aging/oxidation study then further correlates to the observed effects of the incorporation of oxygen with the monomer during deposition. Partial support for this

project was provided by DARPA under U.S. Air Force contract # AF F33615-96-C-5055.

Tuesday Evening Poster Sessions, October 3, 2000

Surface Engineering Room Exhibit Hall C & D - Session SE-TuP

Poster Session

SE-TuP1 General Rule to Predict Under-layer Segregation on Film Surface, M. Yoshitake, Y.-R. Aparna, K. Yoshihara, National Research Institute for Metals, Japan

Film deposition with multi-layer structure is widely utilized in many industrial fields such as electronic device and magnetic film. Diffusion and reaction of under-layer metal sometimes cause troubles and considerable efforts are made to prevent diffusion and reaction. In catalysis field, on the other hand, surface segregation of one component in alloys or bi-layer thin film is decisive factor for its catalytic ability. We studied surface segregation of under-layer metal on the top of a film in a vacuum with Auger electron spectroscopy (AES) and/or X-ray photoelectron spectroscopy (XPS). When surface segregation of under-layer metal was observed, no significant interfacial reaction between under-layer and top layer was detected. Metallic films of sub-micron or micron order thickness were deposited on polished metallic substrates. Al, Ti, Cr, Ni, Cu, Nb and Fe were used as a substrate material, and Al, Ti, Cr, Cu, Zr, Nb and Fe were used as a film material. More than 25 combinations of film-substrate materials have been investigated. From the viewpoint of phase diagram, three types of combinations are included in those combinations, i.e., two elements in solid solution, two elements in separation, and two elements in an intermetallic compound. General rule to predict under-layer segregation on film surface is discussed based on adsorption energy. This rule is quite different from that for segregation in bulk alloy.

SE-TuP3 Role of Surface Condition in Diamond Nucleation during Biasenhanced Nucleation, N. Ali, W. Ahmed, Manchester Metropolitan University, UK; Q.H. Fan, University of Aveiro, Portugal; C.A. Rego, Manchester Metropolitan University, UK

Thin polycrystalline films of diamond have been deposited on copper substrates using hot-filament chemical vapour deposition (HFCVD) system. It is known that substrate surfaces require some form of pre-treatment prior to diamond CVD. Substrate biasing has been extensively used to enhance diamond nucleation density. Majority of the work published, to date, relating to diamond nucleation by means of bias-enhanced nucleation (BEN) looks at either negatively or positively biasing substrates such as silicon where the surface biased is smooth. However, there is very little work been carried out which investigates the effect of surface roughness and surface impurities on diamond nucleation during the BEN process. We negatively bias polished copper substrates, where the polishing materials used were diamond paste, diamond powder and silicon carbide. Our preliminary results have shown that by amalgamating surface polishing with biasing there is a definite enhancement in the overall nucleation density with all the commonly used polishing materials. We observed that both surface roughness and polishing material residues seeded into the copper substrates play a critical role in diamond nucleation during the BEN process. The nucleation densities were calculated from SEM images and the surface roughness values were obtained from AFM analysis. Furthermore, the quality of the diamond grains was gauged using Raman spectroscopy.

SE-TuP4 High Rate Sputtering for Ni Films by r.f.-d.c. Coupled Magnetron Sputtering System with Multipolar Magnetic Plasma Confinement, K. Kawabata, T. Tanaka, Hiroshima Institute of Technology, Japan; A. Kitabatake, K. Yamada, Y. Mikami, Hiroshima Sanyo Vacuum Industries Co., LTD., Japan; H. Kajioka, K. Toiyama, Western Hiroshima Prefecture Industrial Institute of Technology, Japan

It is difficult to prepare ferromagnetic films such as Ni with the conventional magnetron sputtering at a low pressure and at a long substrate-target distance. Ni films were prepared by an r.f.-d.c. coupled magnetron sputtering with a multipolar magnetic plasma confinement (MMPC) at the low pressure of 6.7x10@super -2@ Pa and at the long distance of 120 mm, where the permanent magnets were placed around a Ni target (200mm, 5mm thick) outside the chamber. R.f. power and d.c. bias were applied simultaneously to the target where an r.f. power of 60W was utilized to stabilize the plasma discharge. The deposition rate of Ni films significantly increased with the increasing target d.c. bias voltage (V@sub T@) because the target current increased with the V@sub T@. The highest value of the deposition rate was about 250 nm/min at V@sub T@=-850V. The increase in the deposition rate with V@sub T@ might be

attribute to enhanced gas ionization due to a strong magnetic confinement of the plasma. It was found that the high rate sputtering for Ni films is possible at the Ar gas pressure of 6.7x10@super -2@Pa. The resistivity for all the films deposited at different d.c. bias voltages was 7.1- $8.2\mum@ohm@cm$ whose values were close to the bulk value of $6.9\mum@ohm@cm$. The intensity of the Ni (111) plane observed from X-ray diffraction patterns markedly increased with the V@super T@ and the value of the grain size estimated from the plane was 32-75nm. Therefore, it is shown that the sputtering system with MMPC has some advantages, in comparison with conventional magnetron sputtering, such as high deposition rate, plasma discharge stability, and the preparation of high quality magnetic thin films.

SE-TuP5 The Properties of the Wettability and Corrosion Resistance of Surface Preparation and PVD Coatings on Mold Steel, *S.-M. Chiu*, *C.-H. Lin*, *W.-C. Lo*, *Y.-C. Chen*, Metal Industries Research & Development Centre, Taiwan

During the production of IC components, packaging process is used for protection IC chips from harmful environments.Molding,trimming,and forming stages are three sequential works of packaging process. There are many factors affect moldability including molding die, mold condition, EMC, package design, and operator status. The function of molding die is to capsulate IC chips with thermosetting epoxy molding compound(EMC). The EMC is composed of many additives will abrade and corrode the molding die. It is important to extend the duty life of molding die for upgrading the production rate. In this study we compare several mold steels such as high-speed steel, stainless steel, tungsten carbide, and ceramics.Electrical discharging machining(EDM) and shot peening processes prepare the different surface roughness of mold steels. Some commercial surface treatment are preformed for comparing the surface characteristics of treated mold steels. There are including electroplated hard chromium, plasma nitriding, PVD coatings, and PCVD coatings. The contribution of these factors and their interactions to the contact angle, salt spray test, and wear test are determined. In the research of wettability shows, the influence of surface roughness on contact angle is to effect an increase in the contact angle from 77° to 110° as the roughness increases from an Ra value of 0.05µm to 2.0µm. The surface treatment can obviously reduce the influence of surface roughness on the contact angle.PVD Crbased coatings show the highest contact angle value, above 120°, even better than PTFE polymer material.PVD Cr-based coatings and plasma nitriding can effectively improve corrosion resistance of molding steels. To optimize the surface charactristics of PVD Cr-based coatings on molding die and be used in the IC packaging production lines. It shows that about 50% of production shots, comparing with electroplated hard chromium coating, before needing to clean the molding die.

SE-TuP6 On the Shielding Influence of Charged Particles on the Kinetics of the Oxide Film Growth, D.G. Mukhambetov, O.V. Chalay, Karaganda Metallurgical Institute, Kazakhstan

The object of this work was to investigate kinetics of the two phase oxide film growth on the @alpha@-Fe surface at the temperatures of 650 - 750 K. It is experimentally attained that film thickness h - time oxida- tion @tau@ relationship in the range denoted above is logarithmic function, whereas Kabrera and Mott's theory gives square law of the film growth. In our work analytical treatment of obtained data was made on the basis of this theory, but we suppose that self-deceleration of the film growth is caused not by attenuation of the electric intensity in the film because of increase of h but by shielding influence of the space charge of diffusing ions and elec- trons in that oxide film. With that aim in view the Debye shielding distance for plasma substance state in the oxide film was taken into consideration. Logarithmic law of the oxide film growth was derived. Estimating calcula- tions of this law parameters quantitatively corresponding with the literature data were made . The obtained results were used in the development of the surface oxidation technology of the electric steel.

SE-TuP8 Characterization of Plasma-nitrided Iron by SEM, XRD and XPS, L.C. Gontijo, Centro Federal de Educacao Tecnologica do Espirito Santo, Brazil; P.A.P. Nascente, R. Machado, Universidade Federal de Sao Carlos, Brazil; E.J. Miola, L.C. Casteletti, Universidade de Sao Paulo, Brazil

Plasma nitriding technique has been used to improve the tribological and mechanical properties of materials, specially iron-based alloys. In this work, the Pulsed Glow Discharge (PGD) technique was used for nitriding pure iron. Four samples were nitrided in a gas mixture of 80 % H@sub 2@ and 20 % N@sub 2@ under a pressure of 400 Pa, discharge frequency of 9 kHz, and temperature of 853 K. Samples 1, 2 and 3 were nitrided for 30, 60 and

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90 minutes, and then quenched in situ. The fourth sample was nitrided for 90 minutes and then quenched in air. The nitrided iron samples were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). SEM micrographs showed differences in the surface morphologies for the samples which were quenched inside the chamber. However, when the results for samples 3 and 4 were compared, it was noticed an even more significant change in the surface morphology, which demonstrates the importance of the cooling rate on the formed layer. XRD identified the Fe@sub 4@N phase in all samples. Besides this phase, also the Fe@sub 3@N, Fe@sub 2@O@sub 3@ and Fe@sub 3@O@sub 4@ phases were detected in the sample quenched in air. XPS was employed to obtain chemical-state and quantitative information of the plasma-nitrided iron surfaces.

SE-TuP9 Surface Charge Assisted Ion Deposition: A New Possibility of Film Structure Control, *I.G. Levchenko*, Kharkov State Aerospace University, Ukraine; *M. Keidar*, University of Michigan

The method proposed namely Surface Charge Assisted Ion Deposition consists in using the surface electrical charge as a tool for thin film microstructure and characteristics control. It was shown that the substrate electrical charge provides the powerful and convenient possibilities of nuclei distribution function control resulting in thin film growth with the required characteristics. Using the specified surface charge - film thickness function it is possible to influence the nuclei distribution function. Criterions of electrical controllability were determined on the basis of nucleus electrical balance. It was shown that the method can provide realization of the time-divergent and time-convergent distribution functions. Interesting are the modes provides the equalization of distribution function following by the uniform growth. The possibility to create composite films consisting of bearing very hard matrix such as TiN or TiC filled with the solid-state lubricant such as Cu is shown. The Surface Charge Assisted Deposition provides formation of high-uniform bearing matrix characterized by the high hardness and tensile strength. Other filling matters can be used to provide the wide range of thin film characteristics such as high thermal conductance, temperature conductivity etc. Experimental data on comparative tests of films deposited by the Surface Charge Assisted Deposition and films deposited with the usual methods are given. The friction test shows the film wear resistance increase by factor of 1.25 due to high wear resistance and low friction coefficient of the films applied with the controlled surface charge. The experiment set-up and test conditions are shown.

SE-TuP10 Formation and Dynamic of Nuclei Distribution Function in Ion Deposition. Theoretical and Numerical Investigation, *I.G. Levchenko*, Kharkov State Aerospace University, Ukraine; *M. Keidar*, University of Michigan

The defining role of nuclei distribution function in thin film structure formation is now proved. The present paper is intended to develop the complete model of distribution function formation covering the whole set of the most important factors influencing the film growth. In particular, the following processes were taken into account: adsorbed particles diffusion about the substrate surface; nucleus diffusion causing the distribution function change; nuclei collisions; nuclei coalescence accompanied with the transitional guasi-liquid layer formation; etc. The study was carried out on the basis of the continuity equation for nucleus distribution function and equation for adatoms concentration in the nucleus area. Dynamic of distribution function formation was studied in the various conditions of deposition namely in high and low external flow intensity, high and low diffusion mobility, etc. The numerical simulation was performed using the above model in the most complex conditions: high rate of adsorbed particles and nuclei migration, high intensity of external flow, high substrate temperature, various ionization coefficients. The program developed provides both distribution function calculation and surface ensemble visualization in the form of series of the screen shots. The nuclei ensemble consisting 1000 particles was investigated, and surface concentration fields were calculated in the area of non-continuous film being formed. Comparisons with experimental data are shown justifying the accuracy of the model proposed.

SE-TuP11 Effect of Annealing on the Microstructure and Mechanical Property of TiN/AIN Multilayer Films Prepared by the Ion-beam Assisted Deposition, *D.G. Kim*, Kwangju Institute of Science and Technology, Korea; *Y-.J. Baik*, Korea Institute of Science and Technology, Korea; *T.Y. Seong*, Kwangju Institute of Science and Technology, Korea

Nano-scale nitride multilayers are considerable research interests because lattice and composition modulation induces outstanding mechanical

properties. Since the microstructure of nanolayered films is metastable both mechanically and thermodynamically, the thermal effect can be an important issue. In this study, we investigated the mechanical property and the thermal stability of the TiN/AIN multilayer films. TiN/AIN multilayers were prepared on (100) Si wafer by ion-beam assisted deposition (IBAD), evaporating alternatively Ti and Al metals with nitrogen and Ar ions bombardment. The multilayers were designed to have layer sequences in different bilayer periods (I) from 3.6 to 50 nm. In addition, the samples, having 3.6 and 20 nm periods, were annealed at temperatures between 800 @super o@C and 1100 @super o@C. Nano indentation hardness was employed to acquire the mechanical property of the samples. X-ray diffraction and cross-sectional transmission electron microscopy were also used to investigate the microstructural changes of the TiN/AIN multilayers with bilayer periods. The hardness for the multilayer films with ¥ë @>=@ 6 nm was around 22 GPa, whilst the hardness for the samples with ¥ë@<=@ 4 nm showed higher than 30 GPa. For the sample with ¥ë@<=@ 4 nm, a strong and narrow superlattice (111) peak was observed. However, the peaks of the hexagonal AIN and TiN were absent in this diffraction pattern. This result showed that the (111) oriented multilayer film composed of the TiN and cubic AIN was formed and these coherently bonded superlattice made the hardness with ¥ë@<=@ 4 nm sharp increase. There was no observable change in the micro-structure of the samples annealed at lower than 900 @super o@C, which preserved the discrete layered structure. But the interdiffusion of the multilayer was perceived at the higher temperature and led to deterioration of the mechanical property.

SE-TuP12 Impression of High Voltage Pulses on Substrate in Pulsed Laser Deposition, T. Ikegami, T. Ohsima, M. Nakao, Kumamoto University, Japan; S. Aoqui, Sojo University, Japan; K. Ebihara, Kumamoto University, Japan

DLC film coatings are of technological interest for enhancing wear resistance and corrosion resistance of metals. Pulsed laser deposition (PLD) can deposit hydrogen-free DLC films, those are expected superiority in hardness and adhesion to the substrate, by graphite ablation in vacuum ambient. In PLD, controllable parameters, laser fluence, pressure and kind of ambient gas and bias voltage to a substrate, are limited. In this research, negative high voltage (HV) pulses are applied to a substrate holder synchronously with the plasma plume to modify carbon plasma plume in the similar way to plasma immersion ion implantation. Here, a carbon plasma plume produced by laser ablation is used as a high-density plasma source. High energetic carbon ions and excited atoms can be expected to improve film properties and its adhesion to the substrate. Effect of HV pulses on the plasma plume was investigated by optical emission spectrometry, laser induced fluorescence meth od and their effect on DLC films was examined using FTIR, AFM and Raman analyses. By applying HV pulses emission from C@super +@ increased and modification was found in film properties.

SE-TuP13 Characterization of Chromium Nitride Coatings Deposited by A Hybrid PVD and Metal Plasma Ion Implantation Process, D.-Y. Wang, K.-W. Weng, National Chung-Hsing University, Taiwan

Chromium nitride coatings were deposited using a hybrid PVD and metal plasma ion implantation (MPII) process. MPII is a plasma-based ion implantation process, which supplies low energy (10-80 keV) metal ions with multiple charge states. At the initial coating stage, low dosage of MPII ion flux helps in effective surface activation and ion mixing. The interface adherence is significantly improved. A subsequent ion bombardment by MPII in conjunction with a conventional cathodic arc evaporation process provides apparent advantage of film densification and stress relaxation. The influence of ion energy of MPII source upon film properties will be conducted using mechanical and tribological tests.

SE-TuP14 Energy and Angular Distributions of Deposition Flux in Magnetron Sputtering Systems, R.I. Erickson, J.R. Doyle, Macalester College

The substrate energy and angular distribution of atoms sputtered in a magnetron glow discharge in argon is studied using Monte Carlo simulations and deposition profiles in cavity substrates. The simulation uses the TRIM code for the nascent sputter atom energy and angular distribution. The gas phase collisions are modelled using Thomas-Fermi-Dirac potentials for the higher energies and Lennard-Jones potentials for near thermal energies. Comparison of experimental deposition profiles on cavity substrates with the predicted angular distribution of arriving flux yields good agreement. The simulation results predict that the average energy of arriving atoms exhibit a dependence Bexp(-apd) down to thermal energies where p is the pressure, d is the target-substrate distance, B is the average energy of the nascent sputter atoms, and a is a constant

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independent of p and d. The constant a can be considered the inverse of a characteristic pd value for thermalization, and is parameterized by the atomic number of the target atom yielding a universal relation for arbitrary targets sputtered in argon.

SE-TuP15 The Corrosion Resistance of the Chromium Nitride on Carbon Steel by Cathodic Arc Deposition, S. Han, National Chung Hsing University, Taiwan, ROC; J.H. Lin, National Tsing Hua University, Taiwan, ROC; S.C. Chung, Industrial Technology Research Institute, Taiwan, ROC; S.H. Tsai, National Tsing Hua University, Taiwan, ROC; F.H. Lu, National Chung Hsing University, Taiwan, ROC; H.C. Shih, National Tsing Hua University, Taiwan, ROC, Taiwan,ROC

The electrochemical behavior of CrN coating on steel is investigated. The CrN coatings are deposited using a reactive cathodic arc plasma deposition technology in an industrial scale. The microstructure and crystalline of chromium nitride have been investigated using XRD, XTEM and SAD. The CrN coatings exhibit microcolumnar morphologies. The aqueous corrosion behavior of the coatings was studied in a saline (3% NaCl solution) environment by OCP and EIS measurements. The OCP measurements indicated that the CrN coatings are nobler than the uncoated substrate. The R @sub p@ of the CrN coatings is at least an order of magnitude larger than the uncoated alloy steel. Moreover, the R @sub p@ of the CrN coatings tends to decrease with immersion duration, showing that the corrosion changes from charge transfer to diffusion control process especially when the immersion time is long enough.

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Incorporating Principles of Industrial Ecology Room 304 - Session IE+PS+MS+SE-WeM

Environmentally Friendly Process Development Moderator: D.R. Baer, Pacific Northwest National Laboratory

8:20am IE+PS+MS+SE-WeM1 CVD Films as Directly Patternable Low-k Dielectrics, K.K. Gleason, H.G. Pryce Lewis, Massachusetts Institute of Technology; G.L. Weibel, C.K. Ober, Cornell University INVITED As microelectronic feature sizes decrease to 100-nm and below, major advances in both interconnect and lithographic technologies are necessary. Novel low-k candidates being assessed include fluorine- and siliconcontaining materials produced by chemical vapor deposition (CVD). Fluorine- and silicon-containing polymeric materials are also ideal resist candidates for 157-nm photolithography, as conventional photoresists are opaque at this wavelength. In this paper, we present a collaboration aimed at merging the role of sacrificial resist and low-k dielectric. Specifically, we are investigating a direct dielectric patterning process in which a low-k fluorocarbon or organosilicon material is deposited by CVD, exposed, and developed using no wet processing. In our scheme, a film is deposited using hot-filament CVD, a non-plasma technique which offers the ability to tailor film chemistries. The film is masked and exposed using e-beam or a 157-nm source, and developed using supercritical CO@sub 2@ as a dry developing medium. The patterned film then serves as a low-k material compatible with metallization schemes such as the damascene process. This technology would greatly simplify future device manufacture by reducing the number of steps involved in patterning. The CVD process and the use of dry development also offer environmental, safety and health advantages over solvent-based spin-on coating and aqueous development. Positivetone contrast has been demonstrated in fluorocarbon CVD films and fullydeveloped images of 0.25-micron have been demonstrated from e-beam exposure. We are presently working to enhance sensitivity and optimize image resolution.

9:00am IE+PS+MS+SE-WeM3 Characterization of Remote Plasma Clean Process for Plasma CVD Chamber, *T. Tanaka*, *T. Nowak*, *M. Seamons*, *B.H. Kim, K. Lai, M. Cox, P. Loewenhardt, D. Silvetti, S. Shamouilian*, Applied Materials Inc.

Remote plasma cleaning of CVD process chambers has proven to be more efficient than conventional in-situ plasma cleaning in terms of higher throughput and higher gas breakdown efficiency. It is still important, however, to maximize the efficiency of the remote plasma clean process because of the potential environmental impact and the cost of process gases. The remote clean process involves three steps: generation of reactive species (mostly fluorine atoms) in a remote plasma source, transport of the reactive gas, and the cleaning reaction in the CVD chamber. We studied the efficiency of the process in each step. Since accurate direct measurement of the atomic fluorine concentration in the various parts of the CVD reactor is difficult, we used etching of thermal oxide wafer coupons to estimate the relative distribution of atomic fluorine within the reactor. Source dissociation efficiency was studied using an indirect technique based on correlation of pressure to effluent composition. We found that it requires approximately 24eV to break down each NF@sub 3@ molecule. This translates to 1.7W/sccm of NF@sub 3@ flow. This was seen to be approximately the same for both a microwave discharge operating at 2.45GHz and an inductively coupled plasma at 13.56MHz. Results characterizing the transport step demonstrate the importance of system design on minimizing recombination losses of the reactive species which, for a parallel plate reactor, can be as high as 50% of the atomic fluorine generated in the remote plasma source. The experimental results are compared with a simple model, which describes the general behavior of the cleaning process.

9:20am IE+PS+MS+SE-WeM4 Silicon Oxide Contact Hole Etching Process Employing Environmentally Harmonized Technique, K. Fujita, M. Hori, T. Goto, Nagoya University, Japan; M. Ito, Wakayama University, Japan

Etching process of SiO@sub 2@ contact holes in ULSI has been developed by using high-density plasmas employing stable PFC gases. PFC gases, however, cause a serious environmental problem, namely global warming and hereby the uses of fluorocarbon gases would be restricted in the near future. Recently, we proposed environmentally harmonized technique replacing stable PFC gases for preventing global warming, where polytetrafluoroethylene (PTFE) is evaporated by a CO@sub 2@ laser and the generated fluorocarbon species (C@sub x@F@sub y@) are injected into ECR plasma reactor from externally. This technique, therefore, enables us to achieve a novel plasma process with new gas chemistries. In this study, this system has been successfully applied to ECR plasma etching of SiO@sub 2@ contact hole and the behavior of CF@sub x@ (x=1-3) radical densities in the plasma were evaluated by infrared diode laser absorption spectroscopy (IRLAS). The high SiO@sub 2@ etching rate of 780 nm/min was obtained at a microwave power of 400 W, a pressure of 2.7 Pa, a total flow rate of 80 sccm and a bias voltage of -450 V. Dependence of contact hole etching characteristics on Ar dilution and pressure has been investigated. Anisotropy of contact hole etching was improved with increasing the Ar dilution ratio and decreasing the pressure because the fluorocarbon polymer deposition was suppressed at the higher Ar dilution and the lower pressure. IRLAS measurements indicate CF@sub 2@ radicals and higher radicals (C@sub x@F@sub y@) have the good relation with the polymer deposition. The anisotropic contact hole etching was achieved at an Ar dilution ratio of 90 %, a pressure of 0.4 Pa and the etching rate of SiO@sub 2@, selectivity of SiO@sub 2@ to Si and selectivity of SiO@sub 2@ to resist were 340 nm/min, 31 and 6.4, respectively. These results indicate that this environmentally harmonized technique will propose the alternative etching system replacing PFC gases.

9:40am IE+PS+MS+SE-WeM5 Photocatalytic, Anti-fogging Mirror, K. Takagi, ULVAC Japan, Ltd., Japan; H. Hiraiwa, T. Makimoto, T. Negishi, ULVAC Japan, Ltd.

Recently, environmental pollution is growing more serious everyday, and it is urgently required to develop resource-saving and non-chemical products, which may save and even purify the nature. In such circumstances, titanium dioxide (TiO@sub 2@) thin coating film has come into the spotlight as a savior of the environmental problems. Because of its attractive photocatalytic natures, such as anti-bacterial, self-cleaning, decomposition of organic substances, and super-hydrophilic natures, TiO@sub 2@ has been studied and developed energetically in these days. Already, its super-hydrophilic and self-cleaning natures are applied to automobiles' anti-fogging side mirrors, which are now in practical use, and ULVAC Japan is one of the top makers for manufacturing vacuum deposition system for anti-fogging mirrors. The film architecture of this mirror is the double layer of SiO@sub 2@ / TiO@sub 2@ on the substrate coated by E/B evaporation or sputtering. The photocatalytic natures are as follows; 1. The contact angle of water on this surface is less than 10@Ao@ after irradiation of Blacklight, on which the engine oil is spreaded and cleaned by washing. 2. The contact angle keeps less than 10@Ao@ when this sample is preserved in the dark room. This report describes current developmental status of vacuum deposition system for TiO@sub 2@/SiO@sub 2@ thin film coating that is applied to automobile-mounted photocatalytic mirrors and is useful for environment saving and purification.

10:00am IE+PS+MS+SE-WeM6 Low-k Materials Etching in Magnetic Neutral Loop Discharge Plasma, Y. Morikawa, S. Yasunami, ULVAC JAPAN Ltd.; W. Chen, T. Hayashi, ULVAC JAPAN Ltd., Japan; H. Yamakawa, T. Uchida, ULVAC JAPAN Ltd.

Many low-k materials, like Si containing inorganic / organic compounds, purely organic compounds and porous silicate glass, are proposed and examined as the interlayer dielectric one. The magnetic neutral loop discharge (NLD) plasma is very useful for very fine pattern etching process, because the NLD plasma has high density and low temperature characteristics and tends to form uniform density distribution on the substrate, at lower pressure region than 1 Pa under 13.56 MHz oscillating induction field.@footnote 1-3@ So we adopted the NLD plasma to etch organic low-k materials, with very high etch rate over 900 nm/min by using NH@sub 3@. An etching issue for the purely organic low-k materials is bowing in the hole smaller than 200nm in diameter, probably caused by reaction of the hole-wall surface with hydrogen atoms. Based on this consideration, we carried out the etching by using nitrogen gas mixed with a low concentration of hydrogen gas in low pressures below 1 Pa. The etch rate increased abruptly at hydrogen addition of a few quantity and approached gradually to a constant value at 20%. But the bowing size became larger above hydrogen mixed ratio of 20%. So we measured mass spectra of ion species produced in the plasma to know the mechanism. It was found that intensity of N2H+ also increased abruptly and then was close to a constant value at 20%. The other species did not show similar tendency. It is deduced from this result that N2H+ ion may participate in main etching reaction to obtain the conformal etched profile. Etching characteristics for OSG, pure organic low-k materials and porous silicate glass will be shown. @FootnoteText@@footnote 1@W.Chen, T.Hayashi, M.Itoh, Y.Morikawa, K.Sugita, H.Shindo and T.Uchida : Jpn. J. Appl. Phys.,

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38 (1999) 4296 @footnote 2@W.Chen, T.Hayashi, M.Itoh, Y.Morikawa, K.Sugita and T.Uchida : Vacuum, 53 (1999) 29 @footnote 3@W.Chen, T.Hayashi, M.Itoh, Y.Morikawa, K.Sugita, H.Shindo and T.Uchida : J. Vac. Sci. Technol. A17(5), (1999) 2546.

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Plasma Science and Technology Room 310 - Session PS1+TF+SE-ThM

Fundamentals of Plasma Enhanced Chemical Vapor Deposition

Moderator: A. von Keudell, Max-Planck-Institut für Plasmaphysik

8:20am PS1+TF+SE-ThM1 Analysis of Pulsed O@sub 2@/TEOS Helicon Plasmas by Time-resolved Optical Spectroscopy, *A. Granier*, Institut des Materiaux de Nantes, France; *A. Rousseau*, Laboratoire de Physique des Gaz et des Plasmas, France; *L. Le Brizoual*, Institut des Materiaux de Nantes, France

The use of pulsed plasmas instead of continuous plasmas in Plasma Enhanced Chemical Vapor Deposition is known to improve film quality and adherence, due to the reduction of stress. Here, pulsed low pressure (2 mTorr) helicon oxygen/tetraethoxysilane (TEOS) plasmas are investigated by time-resolved optical emission spectroscopy in order to monitor the kinetics and lifetime of radical species in the plasma-off and plasma-on periods. The 300W rf power is 100% modulated and the duty cycle is varied from 1 to 500 Hz. The time behavior of Ar (750 nm), O (844 nm), H (486 nm), OH (306 nm) and CO (296 nm) emissions in the diffusion chamber are studied. The Ar line takes less than 100 microseconds to reach its equilibrium. The H. OH. O and CO intensities take significantly greater times to equilibrate due to the relatively long lifetime of their ground states, and it was necessary to go to a duty cycle of 1 Hz, including a 130 ms plasma-on time and a 860 ms plasma-off time to reach the stationary state. Under the plasma conditions investigated (a 2 mTorr pressure including a TEOS partial pressure of 0.2 mTorr) the OH, O, H intensities take about 1ms, 40ms and 80 ms, respectively to reach their equilibrium. In addition, their intensities normalized to the Argon line intensity increase from a value close to zero at the ignition time, which indicates that the excited states of OH, O, H radicals are created by electron impact excitation on their ground-states and that these radicals have completely disappeared after 860 ms. In contrast, the normalized CO intensity increases from almost zero but has not yet reached its equilibrium after 130 ms, which is consistent with the fact that CO is a stable molecule which is lost by convection to the pump. Additional results obtained in pure oxygen plasmas are also presented and compared to those obtained in O@sub 2@/TEOS plasma.

8:40am PS1+TF+SE-ThM2 Aluminum Oxide Deposition in an Ionized PVD System, N. L¹, D.N. Ruzic, University of Illinios, Urbana-Champaign; A. Paranjpe, CVC Inc.; J.E. Norman, J.P. Allain, University of Illinios, Urbana-Champaign

An Aluminum target of a planar magnetron system is powered by a pulsed DC plasma generator to deposit AlOx film using a mixture of Ar and O2. Compared with the conventional sputtering magnetron system, the pulsed directed current (DC) bias is able to discharge the accumulated ions on the insulating AlOx film surface effectively during the positive duty cycle. The chamber also contains a secondary radio-frequency (RF) plasma source to ionize the sputtered metal neutral flux, and generate oxygen atoms and radicals. The directionality of the ion flux can be important for high aspect ratio features. The deposition rates of AI and AIOx films as a function of O2 partial pressure vs. Ar are examined with and without the RF plasma. The deposition rate of AlOx with 400 Watts RF is actually much higher than the deposition rate of Al without the RF at the same total pressure of 25mTorr. Hysterisis curves showing the transition point from metallic mode to poison mode at a certain partial pressure are presented. The presence of a secondary plasma producing ionization makes the metallic sputtering mode possible at a higher O2 partial pressure. A gridded energy analyzer and a guartz crystal microbalance (QCM) are embedded in the substrate plane to allow the ion and neutral deposition rates to be determined. Electron density and electron temperature changes caused by the RF power are measured by a Langmuir Probe. SEM photos of deposited films show differences in film quality as a function of RF power.

9:00am PS1+TF+SE-ThM3 Surface Transport Kinetics in Plasma Deposition of Hydrogenated Amorphous Silicon, K.R. Bray, A. Gupta, G.N. Parsons, North Carolina State University

The concept of dynamic scaling was developed to help understand the role of kinetic phenomena that occur on surfaces during non-equilibrium processes (such as film deposition). Plasma deposition of a-Si:H is particularly intriguing because it is well known that over a wide

temperature range, kinetic growth process results in very smooth (nonrandom) surface texture indicating significant surface species transport, but the growth rate is not thermally activated. We have used rf plasma deposition to form a-Si:H films with both helium and argon diluted silane, and used dimensional and frequency analyses to analyze surface topography obtained from AFM images. Surface fractal scaling parameters, including static (a) and dynamic (b) scaling coefficients, Fourier index, saturation roughness, and lateral correlation length (Lc), were determined as a function of film thickness and temperature. After film coalescence (15-20 s) the scaling coefficients are consistent with the surface topology being described as a self-similar structure; a is constant with growth time and is ~1.0, b is ~4.0, and the saturation roughness value increases exponentially with time as tb/a. Based on Herring's models of surface transport, the scaling coefficient values are consistent with surface smoothening being driven by diffusion. In this picture, the lateral correlation length can be equated with the surface diffusion length. We find that Lc ranges from ~50 to 200nm, and is thermally activated, corresponding to a diffusion activation energy of ~0.2eV. This result has important implications for current growth models, where diffusion length is proposed to decrease with increasing temperature because of increasing density of diffusionterminating dangling bond sites. Possible modifications to current models, consistent with our observed data, will be discussed and presented.

9:20am **PS1+TF+SE-ThM4 Hydrogenated Amorphous Silicon Fractal Growth and its Relation to the Growth Mechanism**, *A.H.M. Smets*, Eindhoven University of Technology, The Netherlands; *D.C. Schram*, Eindhoven University of Technology, The Netherlands, Netherlands; *M.C.M. van de Sanden*, Eindhoven University of Technology, The Netherlands

The roughness evolution of the anorphous hydrogenated amorphous silicon (a-Si:H) growth has been studied using in situ HeNe ellipsometry. The a-Si:H depositions are performed using expanding thermal plasma (ETP) deposition technique. With the ETP technique it is possible to grow a-Si:H under dominantly SiH@sub 3@ flux conditions with growth rates ranging over two orders magnitude (1-100 Å/s). The roughness evolution can be divided in an initial growth phase corresponding to a nucleation phase followed by a post initial phase in which the a-Si: H bulk is grown. The post initial growth phase can be described following the universal scaling law, i.e. the roughness scales as t@super beta@ where t is the time and @beta@ the dynamic scaling exponent which depends on the surface relaxation mechanism. The measured scaling exponent @beta@ for growth rates equal or smaller than 22 Å/s is temperature dependent and drops from 0.5 at 100 Celsius down to 0.06 at 500 Celsius. A simple solid on solid (SOS) model is introduced, based upon an activated site at which growth can occur and which can diffuse with a site dependent surface diffusion. With this model the temperature dependent @beta@ can be simulated and the activation energy of the diffusion mechanism can be deduced without the knowledge which process is really responsible for the surface relaxation. The obtained activation energy is equal to ~ 1.0 eV on a terrace site, much higher then what would be expected from physisorbed SiH@sub 3@ dominated a-Si:H growth. At higher growth rates (70 Å/s) the @beta@ shows a maximum around 300 C Celsius. The obtained @beta@ at low temperatures and high deposition rates corresponds to a phase in which the roughness evolution tends more to ballistic fractal growth. Possible relaxation mechanism to explain the high diffusion activation energy will be discussed.

9:40am PS1+TF+SE-ThM5 Interactions of Chemically Reactive Radicals with Si Growth Surfaces during Plasma Deposition of Si Thin Films, S. Sriraman, University of California, Santa Barbara, U.S.A; S. Ramalingam, E.S. Aydil, D. Maroudas, University of California, Santa Barbara

Hydrogenated amorphous silicon (a-Si:H) thin films grown by plasma deposition from SiH@sub 4@ containing discharges are widely used in photovoltaic and flat-panel display technologies. The structural quality and electronic properties of the deposited films depend on the identities and fluxes of chemically reactive species that originate in the plasma and impinge on the growth surface. Atomic-scale simulations of radical-surface interactions are of utmost importance in understanding the fundamental mechanisms of the deposition process. In this presentation, moleculardynamics (MD) simulations of radical-surface interactions during deposition of a-Si:H from chemically reactive radicals, SiH and SiH@sub 2@, are analyzed. The simulations reveal a broad class of reaction mechanisms and predict surface reaction probabilities that are in good agreement with experimental measurements. The growth of a-Si:H films starting from an initial H-terminated dimerized Si(001) surface is studied through MD simulations of repeated impingement of the individual radical precursors. Special emphasis is placed on the identification of the

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elementary surface chemical reactions that govern the deposition process. Effects of the reactions on the growth surface are examined by analyzing local structural configurations and surface chemical reactivity in the vicinity of the surface reaction sites. Evolution of the films' structure, surface morphology and roughness, surface reactivity, and surface composition are analyzed in detail and comparisons made with similar films deposited from individual SiH@sub 3@ precursor. The resulting surface hydride compositions in the deposited films are compared with experimental data. The comparisons are used to discuss our current understanding of the deposition process and implications for plasma deposition of a-Si:H.

10:00am PS1+TF+SE-ThM6 SiH@sub x@ Radical Densities in a Remote SiH@sub 4@ Plasma for High Rate Deposition of a-Si:H, W.M.M. Kessels,

J.P.M. Hoefnagels, M.G.H. Boogaarts, Eindhoven University of Technology, The Netherlands; D.C. Schram, Eindhoven University of Technology, The Netherlands, Netherlands; M.C.M. van de Sanden, Eindhoven University of Technology, The Netherlands

The ground state densities of SiH@sub x@ radicals in a remote Ar-H@sub 2@-SiH@sub 4@ plasma used for high rate deposition of device quality a-Si:H (up to 100 Å/s) have been investigated in detail by cavity ring down absorption spectroscopy (CDRS) and threshold ionization mass spectrometry (TIMS). SiH@sub 3@ has been measured by CRDS using the broadband à @super 2@A@sub 1@ <- @td X@ @super 2@A@sub 1@ absorption peak at 200 - 260 nm and revealed very good agreement with the TIMS measurements on SiH@sub 3@. SiH@sub 2@ has been measured by TIMS and SiH and Si by CRDS on the transitions A @super 2@@DELTA@ <- X @super 2@@PI@ (~414 nm) and 3p4s <- 3p@super 2@ (~251 nm), respectively. The generation and loss processes for the silane radicals have been investigated thoroughly for different plasma conditions and the contribution of the radicals to film growth has been determined. It is shown that for optimum a-Si:H film properties, the contribution of SiH@sub 3@ is approximately 90%, of SiH@sub 2@ is smaller than 5%, of SiH is ~2%, and of Si is 0.2%. For these conditions, the spatially resolved axial and radial SiH@sub 3@ densities in the plasma are compared with 2-D axisymmetric fluid dynamics model calculations using Phoenics CVD, in which the basic gas phase and surface reactions are taken into account. Furthermore, the first time-resolved silane radical measurements in a modulated rf biased plasma for the determination of the radicals' surface reaction probability will be presented.

10:20am PS1+TF+SE-ThM7 Fundamentals of Plasma Enhanced Chemical Vapor Deposition, J. Meichsner, Ernst-Moritz-Arndt-University Greifswald, Germany INVITED

Applications of non-isothermal plasmas for chemical vapor deposition and plasma surface modification imply the understanding of the fundamental problem: the plasma-surface interaction. From the plasma physics point of view the transition between the gas plasma and the solid state is characterized by the plasma sheath in front of the surface which controls the flux and kinetic energy of the charged particles. Additionally, in a reactive molecular plasma the complex chemical reactions must be taken into account in the gas phase and at surfaces. Depending on nature of molecular gases, surface material and plasma properties the modification of a thin surface layer, etching or thin film deposition may be found simultaneously on electrodes, immersed samples or surrounding walls. Insitu diagnostic tools are preferably qualified to provide detailed information about processes in the gas plasma and at surfaces. The experimental investigations involved plasma diagnostics by means of optical spectroscopy (OES, LIF) and mass spectrometry (energy selective ion analysis, electron attachment mass spectrometry) as well as surface and thin film characterization using special methods of FTIR-spectroscopy (IRRAS, ATR, fiber based), ellipsometry and microgravimetry. In a low pressure rf-discharge of Hexamethyldisiloxane the chemical conversion of the monomer gas into new stable gas molecules and deposition of a thin organic film were investigated in dependence on characteristic process parameters. The changed atomic composition and molecular structure of the organic films were connected with varied film properties interesting for semipermeable membranes, photo-conducting films, optical or protective coatings. In fluorocarbon plasmas the investigation of the Polyethylene and Polystyrene surface modification as well as thin film deposition revealed the dynamics between incorporation of atoms/molecules and etching of surface material.

11:00am PS1+TF+SE-ThM9 Thin Film Growth via Surface Reactions of CH@sub 3@, C@sub 2@H@sub 2@ and H as Investigated by Radical Beam Experiments, *M. Meier*¹, *A. von Keudell*, Max-Planck-Institut für Plasmaphysik, Germany

The knowledge about surface reactions of hydrocarbon radicals is a key element for the understanding of thin film growth in low temperature plasmas using hydrocarbons as precursor gas. Besides the formation of hard coatings by using an additional ion bombardment during growth, it is possible to deposit polycrystalline diamond at elevated substrate temperature from a methane discharge diluted in 99 % hydrogen. The dominant species which are believed to be responsible for diamond formation are atomic hydrogen together with either CH@sub 3@ or C@sub 2@H@sub 2@. In our experiment, we employ particle sources for the production of quantified beams of the radicals CH@sub 3@ and H and for C@sub 2@H@sub 2@ molecules to study the interaction of these species with a hydrocarbon film surface. The emitted fluxes of these beam sources are quantified by using angular resolved ionization threshold mass spectrometry. Recently it has been shown that the sticking coefficient of CH@sub 3@ increases from 10@super -4@ to 10@super -2@ if atomic hydrogen reacts simultaneously with the growing film surface at a low substrate temperature of 320 K. A similar experiment using C@sub 2@H@sub 2@ and H revealed no significant growth via C@sub 2@H@sub 2@ adsorption at the film surface. The variation in the film composition during the synergistic growth is monitored via in situ real time infrared spectroscopy. From the interpretation of these spectra a growth synergism for the simultaneous interaction of CH@sub 3@ and C@sub 2@H radicals with the film surface is observed. This demonstrates that the various synergisms between the growth precursors have to be taken into account for a consistent description of thin film growth via radical adsorption.

11:20am PS1+TF+SE-ThM10 Deposition Kinetics in Methane rf Glow Discharges: A Combined Experimental and Modeling Study, J.R. Doyle, D. Cole, B. Magocsi, Macalester College

Methane rf glow discharges are commonly used for diamond-like carbon deposition, but in spite of many experimental and theoretical studies, the details of the plasma chemistry, and in particular the identity of the dominant film precursors, are still debated. In this work we present a comprehensive model of the film deposition using a "semi-empirical" approach. Optical emission measurements and measured electrical properties of the discharge are combined with a Particle-in-Cell/Monte Carlo (PICMC) simulation, which is then used to calculate ion and neutral radical production rates and profiles. Diffusion-reaction-drift (fluid) equations are then solved for stable gas production and ion and radical transport to the electrode surfaces. The model is corroborated by mass spectrometry measurements of the stable gas partial pressures. Film growth rates are calculated from the model and are compared to measured growth rates as a function of pressure and power on both the grounded and powered electrode. The results suggest that C@sub n@H@sub m@ radicals and ions with n > 1 are the dominant sources of mass deposition under conditions used to produce diamond-like films.

11:40am PS1+TF+SE-ThM11 Using Plasma Energetics to Influence Silicon Nitride Step Coverage, K.L. Seaward, Agilent Technologies; M.L. Jezl, University of Wisconsin, Madison

PECVD silicon nitride is widely used in the fabrication of electronic and optical devices, integrated circuits, and display devices. An important characteristic of PECVD silicon nitride is step coverage, which describes how well the deposition conforms to features that are being coated. Both high and low step coverage are technologically important. In the present work, we investigate altering the plasma energetics to change the amount of PECVD silicon nitride deposited on the underside of structures. Models that predict such step coverage suggest that the precursor sticking coefficient is the dominant factor. Accordingly, different inert gases were added to the deposition plasma to either increase or decrease sticking coefficients by way of increasing or decreasing the plasma electron energy. Depositions were run with 4% ammonia, 1% silane, and 95% He, Ar, Xe, or N@sub 2@. Deposited films were characterized by etch rate, stress, FTIR, Auger, and SEM. Deposition plasmas were characterized by optical emission and rf tuning parameters. The only characteristic related to step coverage was the ratio of N-H bonds to Si-H bonds in the films. Since PECVD silicon nitride films have between 10% and 30% hydrogen content, it is expected that hydrogen plays a large role in film properties. What appears to happen for step coverage is a change in bonding configuration from nitrogen being primarily three-fold coordinated to silicon (high step

¹ PSTD Coburn-Winters Student Award Finalist

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coverage) to nitrogen being primarily two-fold coordinated to silicon with the third bond being to hydrogen (low step coverage). This latter material, called silicon diimide, is a chemical analog of SiO@sub2@ which, when plasma-deposited with silane, also has low step coverage. This analogy with SiO@sub2@ deposition suggests that precursor sticking coefficients are high during formation of silicon diimide, and this occurred most prominently with mixtures of He and N@sub2@ present in the plasma.

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