Surface Engineering
Room 132 - Session SE-MoM

Nanocomposites, Multilayers, & Nanostructured Materials

Moderator: G.J. Exarhos, Pacific Northwest National Laboratory

9:40am **SE-MoM1 Magnetron Sputtered W/C Films with C@sub 60@ as Carbon Source***, **J.-P. Palmquist**,* Uppsala University, Sweden*; M. Oden, Zs. Czigany, J. Neidhart, L. Hultman,* Linköping University, Sweden*; U. Jansson,* Uppsala University, Sweden

Thin films in the W-C system have been prepared by magnetron sputtering of W with co-evaporated C@sub 60@ as carbon source. We have previously demonstrated epitaxial growth of several binary and ternary metal carbides as well as superlattice structures and gradient films at very low deposition temperatures (100-500 oC). In this study, we present the first results of epitaxial deposition of several phases in the W-C system. In addition, nanocrystalline tungsten carbide films can be deposited. At low C@sub 60@/W ratios, epitaxial growth of @alpha@-W with a solid solution of carbon was obtained on MgO(001) and Al@sub 2@O@sub 3@(0001) at 400 oC. The carbon content in these films (10-20 at%) was at least an order of magnitude higher than maximum equilibrium solubility and gives rise to an extreme hardening effect. Nanoindentation measurements showed that the hardness of these films increased with the carbon content and values as high as 35 GPa were observed. At high C@sub 60@ /W ratios, films of the cubic @beta@-WC@sub 1-x@ (x = 0-0.6) phase was deposited. This phase is not thermodynamically stable at T< 2500 oC but is frequently observed in thin film deposition. The microstructure of the @beta@-WC@sub 1-x@ films was dependent on the deposition conditions. At high deposition rates, nanocrystalline films with a grain size <30 Å were obtained in the temperature range 100-800 oC. The hardness of these films varied from 14 to 24 GPa. Also, for the first time, we have demonstrated epitaxial growth of single-crystalline @beta@-WC@sub 1-x@ films on MgO(001) at very low deposition rates, ~5 Å/min. Finally, at intermediate C@sub 60@/W ratios, epitaxial films of hexagonal W@sub 2@C was deposited on MgO(111), while polycrystalline phase mixtures was obtained on other substrates.

10:20am **SE-MoM3 Synthesis and Characterization of Thermally Stable TiB@sub 2@/TiC Nanolayered Superlattice Coatings for Dry Machining Applications***, **K.W. Lee**,* Northwestern University, US*; Y.H. Chen, Y.-W. Chung, K. Ehmann, L.M. Keer,* Northwestern University

It was demonstrated from previous studies that nanolayered superlattice coatings with the correct choice of components and layer thicknesses have enhanced hardness, due to interfaces providing barriers against dislocation motion and multiplication. We expect superlattice coatings made of two immiscible components to be stable against interdiffusion. Therefore, the layer structure and reasonable hardness for such superlattice coatings should be preserved at high temperatures. These thermally stable coatings are desirable for protection of cutting tools in dry machining applications, which may operate at temperatures in the 800 â€“ 1000 C regime or higher. For this reason, TiB@sub 2@ and TiC were chosen for this investigation. Nanolayered coatings made of these two immiscible components were synthesized by dc dual-cathode magnetron sputtering. Substrate rotation was used to enhance uniformity of the coating. Substrates included silicon, M2 steel and WC cutting inserts. Superlattice coatings with TiB@sub 2@ (001) and TiC (111) preferred orientations on Si (001) were synthesized. Transmission electron microscopy studies showed that the layer structure of the coating was preserved after annealing in vacuum at 1000 C for one hour. Room-temperature hardness of these coatings approaches 50 GPa, far exceeding the rule-of-mixture value. Coatings synthesized using the substrate rotation system have improved surface smoothness and reduced internal stress. Wear and durability tests on coated M2 steel and WC cutting inserts demonstrated the improved tribological performance of these coatings under unlubricated conditions compared with other standard coatings such as TiN.

10:40am **SE-MoM4 Chemical Vapor Deposition and Characterization of TiO@sub 2@ Nanoparticles***, **W. Li**, S.I. Shah, C.P. Huang,* University of Delaware*; O.J. Jung,* Chosun University, South Korea

Chemical vapor deposition (CVD) was used to deposit TiO@sub 2@ nanoparticles with and without metal ion dopants. X-ray photoelectron spectroscopy (XPS) and X-ray energy dispersive spectroscopy (EDS) experiments confirmed the TiO@sub 2@ chemical composition. X-ray diffraction (XRD) patterns showed the polycrystalline anatase structure of TiO@sub 2@. Transmission electron microscopy (TEM) revealed that these particles are nanosized with an average diameter of approximately 20-30 nm. The nanosized particles can provide a large surface to volume ratio and large number of free surface charge carries which are crucial for the enhancement of photocatalytic activity. In order to improve the photocatalysis efficiency, Pd@super 2+@, Pt@super 2+@, Nd@super 3+@ and Fe@super 3+@ transition metal ion were also incorporated as dopants. The effects of dopants on photocatalytic kinetics were investigated by studying the degradation of 2-chlorophenol (2CP) with an ultraviolet light source. The results showed that doped TiO@sub 2@ nanoparticles have higher photocatalytic efficiency than those without dopants with Nd3+ showing the highest efficiency. Time of 90% destruction of 2CP was reduced by one half with Nd3+ doping when compared with undoped TiO@sub 2@.

11:00am **SE-MoM5 Nanocomposite Tribological Coatings with "Chameleon" Surface Adaptation***, **A.A. Voevodin**, J.S. Zabinski,* Air Force Research Laboratory **INVITED**

Composite coatings where hard nanocrystalline grains are embedded in an amorphous matrix provide considerable improvement in hardness, toughness, wear resistance, and friction reduction. A review of their design concepts is provided with a focus on: (1) improvement in toughness characteristics; and (2) adaptive tribological behavior. Embedding small 5-20 nm hard nanocrystalline grains in an amorphous matrix helps to arrest crack development and introduces ductility through grain boundary sliding. Matrix materials may be selected to provide adaptation of the surface chemistry and/or microstructure to variations in environment and loading conditions to mantain tribological properties. Such materials have been coined chameleon coatings. A combination of nanocrystalline TiC and WC embedded into an amorphous diamond-like carbon (DLC) matrix enabled the coatings to adjust their mechanical response from hard to ductile and significantly reduced the danger of brittle failure. A similar concept was used to improve toughness of composite coatings made of nanocrystalline yttria-stabilized zirconia (YSZ) embedded in an amorphous YSZ/Au matrix. In another example, a combination of nanocrystalline WC and WS2 in an amorphous DLC matrix exhibited surface chemical and microstructural self-adjustment in sliding contact when test environment was cycled from humid to dry. This coating could repeatedly adjust its surface from hexagonal WS2 for sliding in dry nitrogen or vacuum environments to graphitic carbon for sliding in humid air, maintaining a low friction coefficient in both environments. The YSZ/Au nanocomposite developed a gold rich surface layer during heating at 500 °C in air, which considerably improved YSZ tribology in temperature cycling. This coating was further doped with MoS2 and carbon to obtain an environmental adaptation similar to that in the WC/DLC/WS2 system. Chameleon coating designs and applications for advanced tribological coatings are discussed.

11:40am **SE-MoM7 Nanometer-size Monolayer and Multilayer Molecule Corrals on HOPG: A TOF-SIMS, XPS and STM Study***, **Y.J. Zhu**, T.A. Hansen, S. Ammermann, J.D. McBride, T.P. Beebe, Jr.,* University of Utah

The surface chemistry of highly oriented pyrolytic graphite (HOPG) bombarded with energetic Cs@super +@ ions was studied using the combined surface analysis techniques of TOF-SIMS, (time-of-flight secondary ion mass spectrometry), XPS (x-ray photoelectron spectroscopy) and STM (scanning tunneling microscopy). Controlled surface modification and defect production were achieved by bombardment of HOPG with Cs@super +@ ions at various energies and at various dose densities. XPS shows cesium implanted into HOPG exists in an oxidized state. The Cs@super +@ bombardment of HOPG enhances oxygen adsorption due to both the dissociative adsorption of oxygen at defect sites produced by Cs@super +@ ions, and by the formation of cesium oxide. The surface coverage of cesium on HOPG increases linearly with increasing Cs@super +@ dose density at low bombardment energies, and decreases rapidly with increasing Cs@super +@ bombardment energy due to cesium implantation below the surface. The thermal stability of cesium in HOPG has a complex behavior at elevated temperatures. Defects created by Cs@super +@ ion bombardment in HOPG were subsequently oxidized at 650 @super o@C in air to controllably produce nanometer-size monolayer and multilayer molecule corrals (etch pits). Multilayer pits can be produced using higher energy Cs@super +@ ion bombardment, and monolayer pits can be produced using lower energy Cs@super +@ ion bombardment. The pit density, pit yield, pit diameter and pit depth can be controlled by varying experimental conditions, and they were studied systematically by STM. The measured depth-resolved growth rates for multilayer pits are in good agreement with the model of the growth rate acceleration by adjacent layers. The results obtained lead to a better understanding of the kinetics and mechanism of the graphite oxidation reaction, and more importantly to the accurate production and control of nanometer-size monolayer and multilayer molecule corrals on HOPG.

Surface Engineering
Room 132 - Session SE-MoA

Surface Engineering I: Graded, Multicomponent, and Complex Coatings

Moderator: A. Inspektor, Kennametal Inc.

2:00pm **SE-MoA1 Multi-Level Control for Reactive Sputtering**, ***W.D. Sproul,*** *B.E. Sylvia,* Reactive Sputtering, Inc.

Pulsed dc power combined with partial pressure control of the reactive gas has made it possible to reactively sputter deposit non-conducting films such as aluminum oxide at relatively high deposition rates. Most reactive sputtering control systems rely on a single feedback signal for process control. However controlling on a single variable can affect the quality and repeatability of the deposited films. For example when the target voltage is used as the feedback signal, it can change for reasons other than a change in the reactive gas partial pressure such as outgassing or a disappearing anode. Another signal is needed to remove the ambiguity in the control process. Similarly if a mass spectrometer is used to provide the primary feedback control signal, the control signal can change with time due to drift in the mass spectrometer. A new system has been built that overcomes the problem of controlling on a single feedback signal. This new system, called IRESS, controls on a primary signal and then makes on-line adjustments to this primary signal based on secondary feedback signals. Examples of how this works for aluminum oxide and aluminum oxynitrides coatings will be given.

2:20pm **SE-MoA2 The Influence of Sputtering Conditions on Microstructure and Mechanical Properties of Zr-Si-N Films Prepared by r.f.- Reactive Sputtering**, ***M. Zhou,*** Osaka University, Japan*; M. Nose,* Takaoka National College, Japan*; Y. Deguchi,* Toyama University, Japan*; T. Mae,* Toyama National College of Technology, Japan*; K. Nogi,* Osaka University, Japan

ZrN and ZrSiN films were prepared in an r.f. sputtering apparatus which has a pair of targets facing each other (referred to as the Facing Target -type r.f. Sputtering). Si content in the ZrSiN films was changed by using different number of Si tips during deposition. Films were deposited on silicon wafer. During the deposition, substrate was heated from room temperature to 473K, 573K and 673K in order to investigate the influence of substrate temperature on the microstructure and properties of transition metal nitride films. The microstructure of the deposited films was studied by XRD. The chemical contents of zirconium, nitrogen and silicon of the films were determined by EPMA with ZAF method. In order to investigate the relationship between mechanical properties and microstructure of films, the hardness and Young's modulus were measured by a nano-indentation system at room temperature. The load was selected to produce an impression depth below 60nm (not more than 5% of film thickness) so that the influence from the substrate can be neglected. The surface morphology of as-deposited films was also observed by AFM. A study of their microstructure and mechanical properties has provided as follows: (1) As-deposited ZrSiN films were consist of nano-crystals and the crystal size was in the range of 5-10 nm; (2) With increasing substrate temperature from room temperature to 673K during deposition, the crystal size of as-deposited ZrSiN films did not show obvious increase; (3) The hardness of ZrSiN films increased with small amount of Si reaching maximum hardness value of 35GPa, regardless of substrate temperature; (4) AFM results show that the surface morphology have obvious change with increasing Si content and substrate temperature.

3:00pm **SE-MoA4 Characterization of Ternary Nitride Films using Spectroscopic Ellipsometry**, ***S.M. Aouadi,*** *T.Z. Gorishnyy,* University of Nebraska - Lincoln*; F. Namavar,* Spire Corporation*; N. Finnegan,* University of Illinois at Urbana-Champaign*; S.L. Rohde,* University of Nebraska - Lincoln

This paper reports on the first attempt to quantitatively analyze the chemical and phase composition of ternary nitride nanocrystalline films using spectroscopic ellipsometry (SE). Coatings of CrBN, TiBN, TiZrN, and TiCrN were deposited at low temperatures (<200 Â°C) on silicon substrates using ion beam assisted deposition (IBAD) and/or unbalanced magnetron sputtering. These coatings were developed for the protective and decorative coating industries, which require very precise compositions to obtain the desired mechanical properties and/or color. The deposited films were characterized post-deposition using x-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), Rutherford Backscattering (RBS), infrared spectroscopic ellipsometry (IR-SE), and visible-light spectroscopic ellipsometry (VIS-SE). The primary phases in the films were identified using XRD. The chemical composition and phase composition of the samples were determined from XPS, AES, and RBS measurements, as appropriate. VIS-SE and IR-SE data were analyzed using two different approaches to obtain the chemical and phase composition of these samples. The first approach relies on the identification of the optical constants for a few samples of known compositions (from RBS, AES or XPS data) and the use of these optical "standards" in the interpolation of the optical constants of unknown materials to deduce the corresponding chemical composition. The second approach is based on the effective medium approximation, which requires the knowledge of the optical constants of each of the constituent phases. The chemical compositions obtained by SE using both the above approaches were compared to the results obtained from traditional chemical analysis techniques (RBS, XPS, and AES).

3:20pm **SE-MoA5 Structural and Chemical Interplays in Hard Coatings Properties: Multinary Transition Metal Nitrides**, ***F. Lévy,*** Swiss Federal Institute of Technology in Lausanne - EPFL, Switzerland*; P. Hones, P.E. Schmid, R. Sanjinés, M. Diserens,* Swiss Federal Institute of Technology in Lausanne - EPFL **INVITED**

Transition metal nitrides are useful as hard, resistant and protective coatings. Both film composition and film morphology have an influence on the functional properties like hardness, wear and corrosion resistance or colour. Physical vapour deposition techniques are flexible enough to allow a control of the chemical and structural characteristics. In turn, targeted or new coating properties can be obtained. In particular new coating chemistries can be explored by reactive sputtering, which is a clean, polyvalent process, compatible with elemental metal sources. Property improvements may be driven by structural and morphological features, as discussed for example in (CrMo)N ternary sputtered thin films. In contrast, the effects of electronic structure and chemical bonding are illustrated in (CrW)N. In single-phase refractory thin films, the hardness often increases with increasing substrate temperature T@sub s@. This effect has been related to an increase of the grain size d (e.g. in TiN, H@sub m@ = 23...35 GPa with d = 300...600 nm for T@sub s@ = 200...650 @degree@C). In CrN@sub y@, however, the increase in hardness from 8 to 19 GPa observed with increasing substrate temperature T@sub s@ = 330...680 @degree@C was not related to the grain size in a straightforward manner. For this material the grain size was always of the order of 40 nm. The porosity of the film, however, was reduced by substrate heating as demonstrated by an increase of the density. In the ternary compounds, for example in Cr@sub 1-x@Mo@sub x@N@sub y@, the grain size increases significantly in comparison with the binary end compounds. This grain size increase is accompanied by a loss of hardness. The morphology of the films remains columnar and the apparently increasing porosity can be held responsible for the deterioration of the mechanical properties. The chemical composition is determining for most properties, even if often masked by the morphological features. Such effects are present in binary compounds (CrN@sub y@) and are amplified in ternary systems ((Cr,M)N@sub y@ with M = Mo, W).

4:20pm **SE-MoA8 Formation of Voids and its Influence on the Thermal Stability of Co Silicide**, ***N.S. Kim,*** *H.S. Cha, N.G. Sung, H.H. Ryu, W.G. Lee,* Hynix Semiconductor, Korea

We investigated the voids formation during Co silicidation and its influence on the thermal stability of CoSi@sub 2@ on boron or BF@sub 2@-doped poly-Si in ULSI device. The sheet resistance of as-formed CoSi@sub 2@ has been slightly higher on BF@sub 2@ doped poly-Si than boron doped poly-Si, but the sheet resistance of CoSi@sub 2@ on boron doped poly-Si after thermal process increased abruptly. Cross-sectional TEM has shown local voids at the interface between CoSi@sub 2@ and BF@sub 2@ doped poly-Si, but no void on boron doped poly-Si. Furthermore, as pre-cleaning time in diluted HF before Co deposition increased, sheet resistance of as-formed CoSi@sub 2@ decreased and void formation on BF@sub 2@ doped poly-Si was suppressed, but thermal stability of CoSi@sub 2@ after following thermal process was aggravated. From those results, It was thought that the thermal agglomeration of CoSi@sub 2@ was suppressed by stress release at the interface with local voids formed by remained oxide and some florine compounds on the surface of BF@sub 2@ doped poly-Si.

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Poster Session

SE-MoP1 Developments in Ammonium-based Solution with Inhibitors and Ionic Carboxylic Acids on Post Cu CMP Cleaning for Removal Colloidal Silica Abrasives*, S.-Y. Chiu,* ***T.-C. Wang****, Y.-L. Wang,* National Chiao Tung University, Taiwan, R.O.C.*; M.-S. Tasi,* National Nano Device Laboratories, Taiwan, R.O.C.*; M.-S. Feng,* National Chiao Tung University, Taiwan, R.O.C.

During the Cu CMP process with colloidal silica based slurry, colloidal slica abrasives would be selectively adsorbed onto copper line. These particle defects will influence the yields of the folloing thin deposition and lithography process. In this study, an approache are proposed to overcome the corrosion problem of copper line and to remove chemisorbed colloidal silica from polished copper surface. The clean solution would be formulated by adding ionic carboxylic acids into ammonium-based solution with inhibitors. We also elucidated the influence of electrostatic interaction between colloidal silica abrasives, copper and silicon dioxide films. Electrochemical polarizatio, zeta potetial, contact angle, AFM, SEM, surface scan, KLA defect mapping, and electro-property analyses are being evaluated for monitoring silicon dioxide (the polish stop layer) and copper films during post Cu CMP cleaning process. By means of these analytical methods, an suitable post Cu CMP cleaning chemistry in alkaline ammonium-based solution with inhibitor and carboxylic acids was developed to effectively remove colloidal abrasives left on the wafer, meanwhile not to cause copper wires corrosion.

SE-MoP2 Mechanical Properties of Polymer-carbon Nanotube Composite*,* ***C. Wei****, K. Cho,* Stanford University*; D. Srivastava,* NASA Ames Research Center

Recently carbon nanotubes are considered as nanoscale fibers which can strengthen polymer composite materials. Nanotube-polymer composite materials can be used for micron scale devices with designed mechanical properties and smart polymer coating to protect materials under extreme physical conditions. To explore these possibilities it is important to develop a detailed atomic scale understanding of the mechanical coupling between polymer matrix and embedded nanotubes. In this work we study the mechanical properties of polymer-carbon nanotubes (CNT) composite using molecular dynamics (MD). We will discuss the contribution of Van der Waals potential to the load transfer from matrix to nanotube. Our MD simulations show that polymer can chemically bonded to CNT. We will discuss about the resulting mechanical coupling between the CNTs and polymer matrix to develop an efficient nano-composite materials.

SE-MoP4 Effect of Pre and Post Surface Modification on Copper (II) Fluoride Formation in the Cu/PTFE System*,* ***J. Torres****,* Johns Hopkins University, US*; C.C. Perry, S.R. Carlo, D.H. Fairbrother,* Johns Hopkins University

Fluoropolymers are attractive materials for devices in the microelectronics industry because of their desirable physical, chemical, and dielectric properties. Copper is best suited for interconnect wiring because of its low resistivity and electro-migration; unfortunately, its adhesion to fluoropolymers is generally poor. In this study we present results of the effect of Ar@super +@ and X-ray pre and post treatment of PTFE surface in terms of CuF@sub 2@ formation. There seems to be correlation between adhesion and chemical reactivity with the surface, thus, any pre or post processes that initiate the formation of Cu-F bonds will enhance adhesion. Although there are studies in the literature that characterize the Cu/PTFE interface, few studies have concentrated specifically on pre- and post surface modification with respect to compound formation. Copper thermally evaporated on unmodified PTFE is chemically inert, forming a metallic overlayer; no Cu-F bond formation in either the F(1s) or C(2p) XPS regions was observed. Pretreatment of PTFE with either Ar@super +@ or X-ray irradiation was found to be ineffective in activating the surface towards Cu-F bond formation during physical vapor deposition of Cu. In contrast, post-surface modification of the Cu/PTFE interface with either Ar@super +@ or X-ray irradiation resulted in the production of CuF@sub 2@. The extent of CuF@sub 2@ production was found to be similar for both Ar@super +@ and X-ray irradiation post-treatment strategies for comparable initial Cu coverages, suggesting a common reaction mechanism for the formation of CuF@sub 2@. AFM images of virgin PTFE show an amorphous surface, composed of globular features, while after Ar@super +@ treatment the surface becomes fibrous. When Cu is deposited on PTFE the surfaces appearance is smooth as a result of the metallic overlayer.

SE-MoP6 Adhesion Enhancement of Thin Film Metals onto Polyimide Substrates by Bias Sputtering*, S.Y. Kim, J.S. Kang,* ***Y.H. Kim****,* Hanyang University, Korea

The adhesion of thin film metals deposited by bias sputtering has been studied. Al, Cr, Ta, and Ti thin films have been deposited onto polyimide substrates using DC magnetron sputter. RF bias of 0 ~ 400 watt was applied to the substrate during DC sputtering. The adhesion was evaluated using a 90 degree peel test. The peel adhesion strength was low when the RF bias was not applied during sputtering. However, it increased with RF bias power in all specimens. Scanning electron microscopy and Auger depth profile indicated that polyimide cohesive failure occurred during peeling and heavy deformation was observed in the metal films peeled from polyimide substrates when RF bias was applied during deposition. Cross-sectional transmission electron microscopy showed the thin implanted layer of metals in the polyimide interface. The implantation layer was likely formed due to the RF bias to the substrate. This implantation effect can explain the adhesion enhancement by bias sputtering.

SE-MoP7 Oxidation Properties of Zn and Ni-Zn co-deposited with Nanometer Diamond Powder*,* ***W.-H. Lee****,* National Taipei University of Technology, Taiwan, ROC

The co-deposition of nickel and zinc with or without reinforcement of nanometer diamond powder were successfully manufactured by the method of electro-plating process on the carbon steel substrate. The variables investigated within this research work include the additions of ZnCl2, anode current density (ACD) and cathode current density (CCD), PH value, plating temperature, and the concentration of nanodiamond powder in nickel sulphamate plating solution. It revealed that g (Zn21Ni5) phase could be plated on the specimen surface with the thickness of 30 ¢Ggm for 1 hour plating time. The diamond powder used in this research work had an average size of 25 nm and concentration of 2 g/l to 20 g/l in the solution. After experiments, the corrosion resistance of these co-deposited plating layers was tested by the salt spray (fog) testing procedure for 0.5 to 30 days. It was found that the pure Ni-Zn alloy without co-deposited with nanometer diamond powder exhibited three times of corrosion resistance than that of with reinforcement of nanodiamond powder. The structure, surface morphology and the cross section of plating layers were examined by the x-ray, SEM, and optical microscope. The distribution of chemical compositions of plating layers was analyzed by the energy despersive analyzer of x-ray (EDAX) as well.

SE-MoP8 The Effect of Cooling Conditions on Plasma-Carbonitrided Iron Surfaces*, L.C. Gontijo, R. Machado, E.J. Miola,* Universidade Federal de Sao Carlos, Brazil*; L.C. Casteletti,* Universidade de Sao Paulo, Brazil*;* ***P.A.P. Nascente****,* Universidade Federal de Sao Carlos, Brazil

Plasma- carbonitriding 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 employed for carbonitriding pure iron. This method is more economical than others because it provides for faster nitrogen and carbon diffusion, which in turn allows for lower processing temperatures and shorter treatment times with satisfactory results. Three sample sets were carbonitrided in a gas mixture of 2 vol. % CH@sub 4@, 20 vol. % N@sub 2@, 78 vol. % H@sub 2@, under a pressure of 400 Pa, discharge frequency of 9 kHz, temperature of 580 °C, during 90 minutes. The first sample set was cooled under vacuum, the second set, under air, and the third set was quickly removed from the furnace and then quenched in oil. The three sample sets were characterized by optical microscopy (OM), scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). For the samples cooled under vacuum, the diffusion zone comprised of enlongated needle-like precipitates and shorter ones, which were identified as @gamma@'-Fe@sub 4@N and @alpha@"-Fe@sub 16@N@sub 2@, respectively. The same phases were also observed in the diffusion zone of the samples cooled under air. However, these phases were not detected in the samples quenched in oil. The compound layer for the three sample sets consisted of @gamma@'-Fe@sub 4@N and @epsilon@-Fe@sub x@(N,C). An austenite (@gamma@) transformed zone was detected in between the compound layer and the diffusion zone.

SE-MoP9 The Temperature Effects on Surface Energy of PVD Coatings*, **S.M. Chiu,*** Metal Industries R&D Centre, Taiwan, ROC, Taiwan*; T.P. Cho, C.W. Chu,* Metal Industries R&D Centre, Taiwan, ROC*; Y.-C. Chen,* Shu-Te University, Taiwan, ROC

There are serious sticking and wear problems in the molds surface during the IC packaging and die casting processes while the operation temperature ranges from 150°C to 800°C.Some surface treatment are performed on high speed steel for comparing the surface energy properties in different temperature and atmosphere condition.The surface energy properties was studied by the contact angle measurement.The surface treatments include electroplated hard Cr,PVD Cr-based and DLC coatings. The films microstructure is examinated by atomic force microscopy,SEM and X-ray defraction .The control of the surface morphology and phase structure of the coatings is most important to obtain low surface energy properties.

SE-MoP10 Effect of Heat Treatment on the Oxidation and Properties of Ion-Plated ZrN Thin Film on 304 Stainless Steel*, **W.-J. Chou,*** National Tsing Hua University, ROC, Taiwan*; G.-P. Yu,* National Tsing Hua University, ROC*; J.-H. Huang,* National Tsing Hua University, ROC, Taiwan

It is a common practice to apply heat treatment processes for improving the structure and properties of thin films. One of the problems during heat treatment process is the contamination and oxidation of the thin film by the atmosphere in the furnace. To solve the problem, using a controlling atmosphere in the furnace, especially lowering down the oxygen partial pressure, is considered to be the most effective method. In this study, an oxygen meter was used to monitor the furnace atmosphere during the heat treatment process, and the oxygen partially pressure was controlled down to 10-15 atm. Zirconium nitride (ZrN) films deposited on 304 stainless steel, by a hollow cathode discharge ion-plating (HCD-IP) technique, was used as the specimen in heat treatment. The thickness and composition of the coated specimen were controlled to be 0.6 mm and N/Zr=1, respectively. The residual stress and preferred orientations of the ZrN films were determined using X-ray diffraction (XRD). Hardness of the films was measured by nanoindentation. Atomic force microscopy (AFM) was used to study the surface roughness of thin film. The extent of surface oxidation and composition of the ZrN film were determined using X-ray photoelectron spectrometry (XPS). The (111) texture coefficient increases with increasing treatment temperature. The hardness of the ZrN film was rapidly increased after heat treatment. The oxidation of the thin film was incapable avoided even in the gas atmosphere with an oxygen partially pressure lower than 10-15 atm.

SE-MoP11 Deposition of Ti(C,N) and Zr(C,N) Thin Films by Plasma Assisted MOCVD and In-situ Plasma Diagnostics with Optical Emission Spectroscopy*, Y.K. Cho, J.S. Yoon, **C.-H. Heo**, J.G. Han, S.W. Lee, J.-H. Boo,* Sungkyunkwan University, Korea

Ti(C,N), Zr(C,N) films are synthesized by pulsed D.C. plasma assisted metalorganic chemical vapor deposition (PA-MOCVD) using metal-organic compounds of tetrakis diethylamido titanium and tetrakis diethylamido zirconium at 200 °C to 300 °C. H@sub 2@ and He+H@sub 2@ gases are used as carrier gases to compare plasma parameter. The effect of N@sub 2@ and NH@sub 3@ gases as reactive gas is also evaluated in reduction of C content of the films. Radical formation and ionization behaviors in plasma are analyzed by optical emission spectroscopy (OES) at various pulsed bias and gases conditions. He and H@sub 2@ mixture as carrier gas is very effective in enhancing ionization of radicals, especially N@sub 2@ resulting is high hardness. However, NH@sub 3@ as reactive gas highly reduces formation of CN radical, there by decreasing C content of Ti(C,N) and Zr(C,N) films in a great deal. The hardness of film is obtained to be 1400 HK to 1700 HK depending on gas species used and bias voltage. Higher hardness can be obtained for H@sub 2@ and N@sub 2@ gas atmosphere and bias voltage of 600 V. Plasma surface cleaning using N@sub 2@ gas prior to deposition appear to increases adhesion of films on cold forming steel. The changes of plasma including radicals and film properties are illustrated in terms of carrier and reactive gases as well as pulsed power variation.

SE-MoP12 A Study of Nitrided Layers of SAE 303 Stainless Steel using a Magnetized Plasma Process*, G.A. Lacerda,* Instituto Tecnologico de Aeronautica - ITA - Brazil, Brazil*; C. Otani, **H.S. Maciel,*** Instituto Tecnologico de Aeronautica - ITA - Brazil*; C. Alves Jr.,* Universidade Federal do Rio Grande do Norte, Brazil

Iron nitride is an important material in metallurgy, especially as constituent of the so-called compound layers generated on the surface of workpieces made of steel and hardened by nitriding and carbonitriding. More recently the iron nitrides reappeared in the literature but now as thin films and as potencial candidates for magnetic recording heads or eventually recording media. Dealing with an investigation of this subject, a series of plasma nitriding experiments has been conducted on SAE 303 austenitic stainless steel samples, using an experimental system based on an ordinary dc glow discharge which was located between the magnetic poles of an electromagnet. In this system the sample is placed on the cathode and the magnetic field (B), which is uniform and perpendicular to the sample surface, can be varied from zero to 1440 Gauss. The nitriding processes were carried out under constant substrate temperature of 430 °C and gas pressure of 5.0 Torr, whereas different N@sub 2@-H@sub 2@ gas mixtures were used. The nitrided layers were characterized by micro-hardness testings, X-ray diffraction, conversion electron Mössbauer spectroscopy and scanning electron microscopy. The results showed a strong influence of the applied magnetic field upon the mechanical properties of the samples surface as consequence of different nitride phase growing. A decrease in the surface hardness with the increase of the magnetic field strengh was observed for all the conditions tested. For certain gas mixtures, as for example 50%N@sub 2@-50%H@sub 2@, a noticeable effect occurred, i.e., at low and high B field, in the range provided by the electromagnet, the prevalent structure of the nitrided layer is dominated by the Fe@sub 3@N, but it changes to Fe@sub 4@N based structure for B field in the middle range of (260-770) Gauss.

SE-MoP14 Microscopic Polishing of Cu Thin Films using Atomic Force Microscopy*, K.M. Fishbeck, M.D. Arthur, J.S. McDonald, K.L. Muessig, D.C. Koeck, **H.C. Galloway**,* Southwest Texas State University*; M.-S. Lim, S.S. Perry,* University of Houston

Chemical Mechanical Planarization of microelectronic wafers in multiple stages of fabrication is an important process in creating efficient multilayer devices in the modern semiconductor industry. The CMP process uses a rotating pad to apply pressure to a wafer surface exposed to a polishing slurry composed of both a corrosive solution and suspended abrasive particles. In order to study the fundamental mechanisms of CMP, an Atomic Force Microscope is used in conjunction with a liquid cell to simulate the CMP process. Copper thin films grown on Si wafers are exposed to chemicals of variable composition in the liquid cell, with the force of the AFM tip itself providing the mechanical component of the CMP process. A sputtering process is used to coat the AFM cantilever tips with a thin film of alumina to more closely model a single abrasive particle in a CMP slurry. The solutions used in the liquid cell are of varied concentrations and consist of both a corrosive agent(HNO@sub 3@ or NH@sub 4@OH) and a suitable corrosion inhibitor. The materials used for both the samples and the tip coating were chosen for their relevance to current microelectronic fabrication applications, as were the solution components used in the liquid cell. In this way it is possible to study the localized effects of CMP on the exposed samples as a functions of force, solution chemistry, and exposure time. In situ AFM imaging at varying time intervals allows analysis of both material removal processes and surface topography changes.

Surface Engineering
Room 132 - Session SE-TuM
Surface Engineering II: Cleaning, Modification, and Finishing

Moderator: L.-Q. Wang, Pacific Northwest National Laboratory

8:20am **SE-TuM1 PVD Surface Engineering Utilising Combined Steered Cathodic Arc and Unbalanced Magnetron Sputter Deposition**, **INVITED**

The application of combined steered cathodic arc evaporation and unbalanced magnetron sputtering utilising closed magnetic field conditions generated by electromagnets raises a broad field of opportunities to surface engineering of metallic substrate materials. Low pressure plasma nitriding (5.10@super -1@ Pa) as well as low energy metal ion implantation (U@sub s@-1200 V) with steered arc discharge as ion source allow the synthesis of substrate/ coating interfaces specifically tailored to the demands of the actual application. Nitriding as deep as 20µm and Cr ion implantation to a depth of 20nm create a surface chemistry, which enhances the adhesion and encourages localised epitaxial growth of the reactively magnetron sputter deposited nitride films. Alternatively semi-implanted micro-crystalline Nb deposits may be formed, which represent an excellent pre-treatment for corrosion and wear resistant hard coatings. Due to the outstanding adhesion and the graded film architecture, including a stress gradient inducing base layer, superhard- superlattice coatings with a period of approximately 3.5 nm based on TiAlN (TiAlN/CrN, TiAlN/VN, TiAlN/ZrN) and CrN (CrN/NbN) showing Hp values > 40 GPa have been produced exhibiting comparable coating productivity to monolithically grown nitrides like TiAlN and CrN. Despite residual stresses in the coatings up to -7 GPa critical load values L@sub c@ > 50N and HRC indentation class "1" were achieved. Finally, TiAlN coatings with layered Y incorporation have been especially designed for dry high speed cutting of HRC>60 die steel and coating of hot forging tools for working temperatures >900°C.

9:00am **SE-TuM3 Surface Processing of Large-scale FEL SS Test Electrodes by PSII/PVD to Suppress Field Emission**, ***L. Wu***, *D.M. Manos,* College of William and Mary*; F. Dylla, C. Sinclair, T. Siggins,* Thomas Jefferson National Accelerator Facility

Large-scale highly polished stainless steel test electrodes for FEL electron injection gun have been processed by an integrated PSII/PVD system to suppress field emission. Hand polishing, which is very time-consuming and difficult, has been the main technique used to reduce field emission from these large 3-D electrode structures. Even after extensive polishing, the performance of the electrodes has been found to be unpredictable, with turn-on voltages varying by factors of 2 or more for similarly prepared electrodes. Prior to this work, the maximum practical operating field gradient was 3-6 MV/m, with a dark current of several nA. With a 0.61 m I.D. chamber, 0.57 m I.D. quartz window, and 0.43 m I. D. RF antenna, the PSII/PVD system used in this study is capable of large-area plasma source ion implantation and also of PVD of high purity SiO2 films over stainless steel, with adjustable nitrogen concentrations. Both the PSII and PVD processes are performed at low substrate temperatures, critical to keeping the original electrode surface profile and surface finish. Two recipes were developed, using DC glow discharge cleaning prior to HV pulse implanting to condition the electrode surface and to prevent arcing during implantation. In addition to the test electrodes, witness samples processed under similar conditions were studied by AES depth profiling, SIMS, variable angle spectroscopic ellipsometry, and micro-hardness testing. Results will be reported in detail. Field emission tests of the processed large-area electrodes showed that the electrodes were able to quickly achieve a field of 30 MV/m after minimal conditioning, and to hold this field for long periods with a dark current of only 160 pA. The implications for accelerator structures will be described.

9:20am **SE-TuM4 Noncontact Physical Removal of Nano-scale Particles from Surfaces**, ***A.A. Busnaina,*** Northeastern University*; H. Lin,* Clarkson University

There is a need to physically manipulate, control or remove nanoscale particles. The removal of nanoscale particles physically without substrate damage or alteration is needed in nanoscale manufacturing. It is needed to remove existing contaminants from a substrate. Even in the semiconductor industry, such a need is a projected requirement in 2011. However, this need is required toady in nanoscale fabrication. Physical non contact removal using high frequency acoustic streaming had been used to remove submicron particles. However, the removal of 100 nm particles and smaller is becoming a serious challenge. Busnaina et al.@footnote 1@ studied megahertz streaming particle removal and evaluated the effect of acoustic streaming on the cleaning process. High frequency acoustic streaming is a promising technique for nano-scale particles removal. Using DI water, the removal of nano-size particles down to 10 nm can be best accomplished using acoustic streaming with frequency above 1.3 MHz. As the frequency increases, the acoustic boundary layer thickness decreases and the streaming velocity increases thereby increasing the drag force and consequently the removal moment. Softer particles (such as PSL) are more difficult to remove than hard particles (such as silica), because of adhesion-induced deformation, needing a much higher frequency. The experimental results show that a complete removal of silica particles down to 100 nm is achievable. . @FootnoteText@ @footnote 1@Busnaina, A. A. and Gale, G. W, Journal of Particulate Science and Technology, 17(3), 1999.

9:40am **SE-TuM5 Photoresist Removing using Atomic Hydrogen Generated by Heated Catalyzer**, ***A. Izumi***, *H. Matsumura,* Japan Advanced Institute of Science and Technology (JAIST), Japan

It is well known that photoresist films play an important role to define very small pattern, selective etching, ion-implantation process, etc. The residues of photoresist films after these processes should be completely removed. Wet cleaning using a sulfuric acid and a hydrogen peroxide mixture succeeding to O@sub 2@ plasma ashing is used as a conventional removing method of the residues. However, this conventional method is not effective for removing high doped ion-implanted resists. O@sub 2@ ashing plasma induces a lot of problems such as plasma damage to devices and oxidizes semiconductor substrates and/or interlevel dielectric films. In this work, we propose a novel photoresist removing which is using atomic hydrogen. Atomic hydrogen is generated by decomposition of H@sub 2@ on a heated (1700°C) tungsten catalyzer. Therefore, the plasma damage and the oxidation are not matters of concern. Atomic hydrogen was irradiated to the photoresist coated Si(100) which was doped with B (50 kV, 10@super 15@ atoms/cm@super 2@) by ion-implantation. Following results are obtained. 1) X-ray photoelectron spectroscopy measurements reveal that 1 µm-thick photoresist is removed completely by 15 minutes irradiation of atomic hydrogen. 2) The photoresist removing rates increase as hydrogen flow rate increases. 3) The substrate holder temperature around 85 °C shows the highest photoresist removing rate. 4) Quadruple mass spectroscopy measurements detect a lot of kind of hydrocarbon species during the irradiation of atomic hydrogen. The above results show that this technique is effective for photoresist removing for various kinds of photolithography process.

10:00am **SE-TuM6 Low Temperature Remote Plasma Cleaning of the Fluorocarbon and Polymerized Residues formed during Contact Hole Dry Etching**, ***H. Seo***, *H. Soh, Y. Kim, Y.C. Kim, H. Jeon,* Hanyang University, Korea

Reducing contact hole resistance in ultra large scale integration becomes very important as the contact hole size getting small.@footnote 1@ Reactive ion etching (RIE) using fluorocarbon is widely used to open contact holes due to its high anisotropic and selective silicon etching characteristics. However, the RIE process induces fluorocarbon residues and results in high contact resistance and defects at the metal-silicon interface. Furthermore, these residues polymerized after photo resist (PR) ashing process. These polymerized residues were reported to be non-volatile, and chemically and thermally stable.@footnote 2@ Therefore, these polymer residues must be removed prior to metal contact. In this study, we investigated the low temperature oxygen and hydrogen remote plasma cleaning of the polymer residues formed at the contact hole during RIE and PR ashing processes. Samples having shallow trench isolation structure were prepared by RIE using CHF@sub 3@/CF@sub 4@ gas. The efficiency of cleaning was systematically evaluated at various conditions such as plasma power, exposure time, gas flow rate and sample temperature. Polymer residues before and after cleaning were analyzed using in-situ Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS) and atomic force microscope (AFM) systems. Also, the polymer residues were directly observed before and after cleaning using scanning electron microscope (SEM). Carbon and fluorine impurities were significantly reduced below detection limit of AES after remote plasma cleaning. Also, the C-C/C-H and C-F@sub x@ (x=1,2,3) types bonding were not observed by XPS. This paper presents the efficiency of the remote plasma cleaning of the polymerized residues formed during RIE and ashing processes at the contact hole. @FootnoteText@ @footnote 1@K. Sakuma, K. Machida, K. Kamoshida, Y. Sato, K. Imai and E. Arai, J. Vac. Sci. Technol. B 13(3), May/June (1995) @footnote 2@J. Fonash, J. Electrochem. Soc. 137, 3885 (1990)

10:20am **SE-TuM7 Polymer Metallization - Comparing the Effect of Pre- and Post Surface Modification on the Cu/PVC and Cu/PTFE Systems***, **C.C. Perry**, S.R. Carlo,* The Johns Hopkins University*; J. Torres,* The Johns Hopkins University, US*; D.H. Fairbrother,* The Johns Hopkins University

The increasing requirements of fabricated industrial materials have provided the motivation for research in metallized plastics. Pre- and post surface polymer modification treatments are usually employed in industrial processes to improve adhesion at the metal/polymer interface. One factor that is believed to be important in improving metal/polymer adhesion characteristics during surface modification is the formation of metal salts at the metal/polymer interface. We present results on the effect of Ar@super +@ ion and X-ray pre- and post treatment strategies on the Cu/PVC and Cu/PTFE systems with respect to the formation of copper halides. On unmodified PVC, copper reacts to form copper(I) chloride but is unreactive on native PTFE. Post X-ray treatment of metallized PVC and PTFE was found to increase the metal chloride/fluoride content within the metal organic interface due to the production of reactive halogen species (e.g. fluorine radicals). In contrast to Cu/PVC, where copper(I) chloride is formed on both modified and unmodified PVC, the formation of copper (II) fluoride at the Cu/PTFE interface is shown to occur only after post-surface modification by x-rays and Ar@super +@ ions. The extent of copper (II) fluoride production was similar for both Ar@super +@ and X-ray irradiation post-treatment strategies for comparable initial copper coverages, suggesting a common reaction mechanism for the formation of copper (II) fluoride. Results will also be presented showing the effect of co-evaporated titanium on the nature of the Cu/PTFE interface.

10:40am **SE-TuM8 Metallization of PVC - Physical Vapor Deposition and Effect of Ar@super +@/X-ray Pre and Post Treatment***, **S.R. Carlo**, C.C. Perry,* The Johns Hopkins University*; J. Torres,* The Johns Hopkins University, US*; D.H. Fairbrother,* The Johns Hopkins University

Metallization of polymers is important commercially in both the microelectronic and conventional industries, having applications in the processing of thin film-transistors, compact discs and decorative overlayers. The nature of the metal/polymer interface is especially important with respect to adhesion of the polymer to the overlayer and in semiconductor electrode-polymer connections where diffusion of metal from the polymer into the dielectric can cause capacitance problems. Understanding the process of metallization will enable such problems to be addressed. In this study, we present results on the evolution of the metal-poly(vinylchloride) (metal/PVC) interface using X-ray photoelectron spectroscopy (XPS) following physical vapor deposition of Fe, Ti, Ni, Cu and Au. All of the metals reacted, forming a metal chloride with subsequent deposition of a metallic overlayer. The extent of reaction (as measured by the relative amount of metal chloride production) increased in the order Ti > Fe > Cu > Ni > Au. In all cases, the metal chloride was in the lowest oxidation state e.g. FeCl@sub 2@ and AuCl. The effect of sample pre and post-treatment was also investigated. Pre-treatment of PVC by Ar@super +@ ions increased the yield of FeCl@sub 2@ compared to unmodified PVC. There was negligible difference in the Cu/PVC system, while in the Au/PVC system, the yield of metal chloride was lower compared to unmodified PVC. Post-metallization X-ray treatment increased the metal chloride concentration for each metal/PVC system.

11:00am **SE-TuM9 Does Thermal Spike Effect Ion Mixing at Ion Energy Lower than 1.5 keV?***, **M. Menyhard**, G. Zsolt,* Research Institute for Technical Physics and Materials Science, Hungary*; P.J. Chen, C.J. Powell, L. Gal, W.F. Egelhoff,* National Institute of Standards and Technology

Experimentally measured (Auger, XPS) depth profiles cannot be properly evaluated without knowing the ion sputtering induced alteration. The presently used evaluation routines assume that ballistic mixing occur. It was suggested and some experimental evidences have been presented, however, long time ago, that the thermal spikes might be operating even at low ion energies causing enhanced mixing. Systematic studies on the appearance of thermal spikes in case of depth profiling applying low energy (less than 1.5 keV) ions sputtering has been carried out. Periodic double-layer structures (consisting 10 layer pairs) with double-layer thickness of 4 nm were grown by sputter deposition from pair of elements exhibiting high (Pt-Ti) and low solubility (Pt-Co, Ni-Ti, Co-Ti). Auger spectroscopic depth profiling was carried out with parameters of: specimen rotation, grazing angle of incidence, argon ions, energy range 0.3-1.5 keV. The ion mixing in these periodic structures can be measured by the amplitude of oscillation of the depth profile. The amplitude of oscillations in all cases was linearly dependent on the square roote of ion energy. Thus in the energy range studied a single mechanism was responsible for the ion mixing. Since we cannot suppose that at the 0.3 keV irradiation thermal spikes form it seems that the ion mixing in these cases are governed by ballistic mixing. The depth profiles were also simulated by T-DY4 code assuming ballistic mixing. The difference of the simulated and measured depth profiles was explained by interface roughness.

Tuesday Afternoon, October 30, 2001

Surface Engineering
Room 132 - Session SE-TuA
Hard and Superhard Coatings

Moderator: I. Petrov, University of Illinois, Urbana

2:00pm **SE-TuA1 Microstructure and Mechanical Properties of Zr-Si-N Films Prepared by r.f.- Reactive Sputtering***, **M. Nose,*** Northwestern University, Japan*; W.A. Chiou,* University of California at Irvine*; M. Zhou,* Osaka University, Japan*; T. Mae,* Toyama National College of Technology, Japan*; M. Meshii,* Northwestern University

ZrN and ZrSiN films were prepared in an r.f. sputtering apparatus which has a pair of targets facing each other (referred to as the Facing Target -type r.f. Sputtering). Films were deposited on silicon wafer without bias application nor substrate heating in order to examine only the effect of silicon addition to transition metal nitride films. The transmission electron microscopy studies were carried out in addition to XRD. For the high resolution TEM observation, the field emission type transmission electron microscope (FE-TEM) was used, which provides a point-to-point resolution of 0.1nm. The samples were observed both parallel and perpendicular to the film surface, which were in-plane and cross-sectional view, respectively. In order to investigate the relationship between mechanical properties and microstructure of films, the hardness was measured by a nano-indentation system at room temperature. The load was selected to produce an impression depth below 60nm (not more than 5% of film thickness) so that the influence from the substrate can be neglected. The contents of zirconium, nitrogen and silicon of the films were determined by ZAF method with EPMA. A study of their microstructure and mechanical properties has provided as follows: (1) The hardness and Young's modulus increase with small Si additions reaching maximum values of 35GPa (at 3%Si) and 370GPa (at 5% Si), respectively; (2) The hardest films containing 3%Si did not consist of nano-crystals but clear columnar crystals in the range of 10 to 25nm; (3) The increment of hardness with small amount of Si atoms can be attributed to the solution hardening by Si to ZrN lattice; (4) In the case of ZrSiN films deposited by r.f. sputtering without bias application nor substrate heating, the available result did not ensure the presence of ZrN nano-crystals embedded in Si@sub 3@N@sub 4@ matrix.

2:20pm **SE-TuA2 Characterization of CrBN Films Deposited by Ion Beam Assisted Deposition***, S.L. Rohde, **S.M. Aouadi,** D.M. Shultze, T.Z. Gorishnyy,* University of Nebraska - Lincoln*; N. Finnegan,* University of Illinois at Urbana-Champaign

This paper reports on the first attempt to grow and analyze CrBN nanocrystalline materials using physical vapor deposition processes. Coatings were deposited at low temperatures (<200 Â°C) on silicon substrates using ion beam assisted deposition (IBAD). These coatings were characterized post-deposition using X-ray diffraction (XRD), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), infrared spectroscopic ellipsometry (IR-SE), and visible-light spectroscopic ellipsometry (VIS-SE). The primary phases in the films were identified using XRD. The surface morphology and nanocrystalline nature of the coatings (grain size of 5 - 7 nm) were deduced using AFM. The mechanical properties (wear rate, hardness, elastic modulii) of the coatings were evaluated using a nanohardness test. The chemical composition and phase composition of the samples were determined from XPS and AES measurements and were subsequently deduced from the analysis of the VIS-SE data. The film compositions deduced from both techniques correlated well. Additionally, XPS, AES, and IR-SE were used to reveal the crystal structure of the BN phase in these ternary compounds.

3:00pm **SE-TuA4 Thin Film Growth by Physical Vapor Deposition in the Presence of Residual Gas***, **J.M. Schneider,*** Linkoping University, Sweden **INVITED**

Vacuum based techniques are characterized by the presence of residual gas. Depending on the affinity of the residual gas to the growing film material, chemical reactions may be possible. Residual gas based impurity incorporation during thin film growth has been reported previously.@footnote 1,@@footnote 2@ Here, the state of the art in residual gas - growing film interactions is reviewed. Sources for residual gas incorporation as well as incorporation mechanisms are described. Furthermore the effect of impurity incorporation on the film structure and film properties are discussed. @FootnoteText@ @footnote 1@ J.M.Schneider et al, Appl.Phys.Lett. 74, 200 (1999). @footnote 2@ J.M.Schneider et al, Appl.Phys.Lett. 75, 3476 (1999).

3:40pm **SE-TuA6 Boron and Boron-Based Coatings as Produced by Vacuum Arc Technology***, **C.C. Klepper,*** HY-Tech Research Corporation*; J.M. Williams,* Oak Ridge National Laboratory*; R.C. Hazelton, E.J. Yadlowsky, E.P. Carlson, M.D. Keitz,* HY-Tech Research Corporation

In principle, boron as a material has many excellent surface properties, including corrosion resistance, very high hardness, refractory properties, and a strong tendency to bond with most substrates. However, the potential technological benefits of the material have not been realizable because of difficulty in synthesis of coatings. Boron is difficult to evaporate, does not sputter well and cannot be thermally sprayed. In the present program, a robust system, based on the vacuum (cathodic) arc technology, for generation and delivery of boron plasmas to substrates has been developed. The system produces a fully-ionized boron plasma, which allows use of substrate bias to control the energetics of deposition. Films and coatings have been produced on 1100 Al, CP-Ti, Ti-6Al-4V, 316 SS, hard chrome plate, 52100 steel and other materials. Analyses have been performed by Rutherford backscattering spectrometry. Properties are being evaluated by nanoindentation hardness and other techniques. First results are that the coatings are smooth, highly adherent, and pore free. A number of applications are contemplated. @FootnoteText@ @footnote 1@ Research sponsored in part by the National Science Foundation under contract # DMI-0078385 with HY-Tech Research Corporation. Research at Oak Ridge National Laboratory is sponsored by the U. S. Department of Energy under contract # DE-AC05-00OR22725 with UT-Battelle, LLC.

4:00pm **SE-TuA7 Ion-bombardment Induced Phase Transformation of Cubic Boron Nitride Studied by Reflection Electron Energy Loss Spectroscopy***, **Y.Y. Hui,** K.W. Wong,* Chinese University of Hong Kong, P.R. China*; W.M. Lau,* Chinese University of Hong Kong, P.R. China, People's Republic of China

The phase transformation of cubic boron nitride (c-BN) in the near surface region of a c-BN (111) facet induced by low energy argon ion bombardment has been investigated by reflection electron energy loss spectroscopy (REELS), with the objective of tracking possible growth mechanisms of c-BN in ion assisted vapor deposition. By removing Tougaard background of the REELS spectra, we can quantitatively measure the percentage of different BN phases on c-BN surface after ion bombardment. In addition, varying the energy of the incident electron beam from 250 eV to 650 eV allowed the adjustment of sampling depth of a c-BN surface from 14 Å to 27 Å. It was found that with an ion energy of 500 eV at a fluence of 5 x 10@super 16@ ions/cm@super 2@, 76 % of c-BN was found transformed to h-BN and a-BN in a top surface layer of 8 Å. Lowering down the argon bombardment energy to 200 eV reduced the defective layer thickness to 5 Å. A damage saturation was observed at a fluence of 6 x 10@super 16@ ions/cm@super 2@, at which about 10% of c-BN was transformed into non-cubic phases. Through further investigations on the damage saturation at other ion energies, the effects of ion beam bombardment on a c-BN surface was comprehensively studied. The present work gives, for the first time, a quantitative explanation of the difficulty in growing pure c-BN films with ion assisted deposition and the presence of an upper-bound in ion energy above which h-BN and a-BN are generated.

4:20pm **SE-TuA8 Cubic Boron Nitride Thin Films Deposited on Steel Substrates With Different Interlayers***, M. Ye, **M.P. Delplancke-Ogletree,*** Universite Libre de Bruxelles, Belgium

Cubic boron nitride thin films were deposited on steel substrates using electron cyclotron resonance plasma enhanced chemical vapor deposition. Different interlayers, such as BCN, TiBN, Ti, TiN, and hexagonal boron nitride, were investigated regarding to the promotion of cubic boron nitride growth and the improvement of the film mechanical properties. A systematic optimization procedure for the cubic boron nitride formation was carried out regarding the deposition conditions, including the gas composition, substrate temperature, bias voltage. The films were characterized using Fourier transform infrared spectroscopy, transmission electron microscopy, x-ray photoelectron spectroscopy, and atomic force microscopy. It was found that among the different interlayers, hexagonal boron nitride gives the best results.

4:40pm **SE-TuA9 Industrial Laser-Arc Coater for the Deposition of Superhard Amorphous Carbon Films (Diamor)***, **T. Schuelke,** H.J. Scheibe, P. Siemroth, B. Schultrich,* Fraunhofer Institute for Materials and Beam Technology

Thin amorphous carbon films (Diamor), deposited through laser-assisted cathodic arc evaporation (LaserArco process), have shown unique properties of great relevance to engineered surfaces for wear and corrosion protection. The high-modulus (> 600 GPa) coatings are superhard

(80GPa) with a low coefficient of friction (0.1 dry against steel). The vast variety of potential applications includes cutting and forming tools as well as components in rolling or sliding contact situations. The LaserArco plasma source and the Diamor deposition process have proven to be consistently reliable on the laboratory scale. Extended application development yielded to an increasing demand for the Diamor coating. Subsequently, the further development aimed at scaling up the technology to industrial dimensions. This development included the design of a flexible and compact plasma source module, which was then integrated into a high volume production coater. The paper discusses the equipment design and capabilities, integration and process transfer issues, and first deposition results obtained in an industrial environment.

5:00pm **SE-TuA10 Deposition of Diamondlike Carbon by Magnetic Pole Enhanced Inductively Coupled Plasma***, T. Meziani, P. Colpo, G. Ceccone, P. Leray, P.N. Gibson, D. Summa,* ***F. Rossi,*** Joint Research Center, Italy*; P. Ranson,* GREMI, CNRS-Universite d'Orleans, France

The ICP sources are particularly interesting for the deposition of amorphous carbon since they offer the possibility to control independently the ion energy from the ion flux bombarding the substrate, in contrast to capacitively coupled discharge. Diamondlike carbon coatings (a-C:H) were deposited with a novel inductively coupled plasma source (the Magnetic Pole Enhanced ICP or MaPE-ICP) designed and characterized in our laboratory. The MaPE-ICP uses a magnetic pole to concentrate the magnetic flux on the load (i.e. plasma) and shows very interesting features like high plasma density, good plasma uniformity and wide pressure range. Diamondlike carbon coatings were deposited with this source from CH4 and C2H2 precursors. The plasma was studied by Langmuir probe measurements, optical emission spectroscopy and microwave interferometry. Mass spectrometry including ion detection and ion energy distribution measurements have been carried out at the substrate holder surface in order to investigate directly the impinging species on the growing film. The plasma diagnostics and films characterization including FTIR spectroscopy, Raman spectroscopy, and X-ray reflectivity (XRR) were undertaken for various processing parameters. The results were related to the coating properties like hardness and intrinsic stress.

Magnetic Recording Topical Conference
Room 110 - Session MR+MI+AS+SE-WeM

Magnetic Recording: Tribology & Integration

Moderator: Y.T. Hsia, Seagate Technology

8:20am **MR+MI+AS+SE-WeM1 Nanotribology of Simple and Complex Fluids at Aqueous Interfaces@footnote 1@***, **S. Granick**,* University of Illinois, Urbana **INVITED**

Oil and lubrication are so synonymous that it is easy to discount the importance of aqueous-based lubrication -- not least in our own bodies, wich are full of surfaces in sliding contact. This talk will present recent studies of (a) the hydrophobic effect when surfaces are in relative motion, (b) modifying the boundary conditions of fluid flow, from no-slip to slip, and (c) ongoing attempts to watch single molecules under confinement. These issues of water in intimate contact with solid surfaces point the way to possible new strategies for energy-saving during fluid transport and have relevance to filtration, colloidal dynamics, and microfluidic devices.@footnote 2@ @FootnoteText@ @footnote 1@Work performed with Yingxi Zhu, John Jiang Zhao, Ashish Mukhopadhyay, and Hyungjung Lee @footnote 2@Work supported by the National Science Foundation and by the U.S. Dept. of Energy, Division of Materials Sciences under Award Number DEFG9645439 through the Frederick Seitz Materials Research Laboratory at the University of Illinois at Urbana-Champaign.

9:00am **MR+MI+AS+SE-WeM3 The Ever Changing Disk Drive Environment: Can Filter Technology Keep Pace?***, **A.J. Dallas**, J. Joriman, L. Ding, D. Arends, S.B. Miller, III,* Donaldson Co., Inc. **INVITED**

The cleanliness of the internal environment of a disk drive is critical to its reliability, performance, and longevity. As a result, we have seen particulate and chemical filters become commonplace in the design of disk drives of all types and sizes. The incorporation of chemical filters into the disk drive environment has proven to be an effective means of controlling the humidity and contamination level. Generally, silica gel is used to control the humidity level, whereas carbon and chemically-treated activated carbon are used to minimize organic and acid gas contamination levels. As disk drive technology moves into the future, chemical filtration is expected to play an ever-increasing role in the overall drive's performance. How will filter technology change to meet these requirements? This presentation will provide an overview of chemical filtration, filter design, and the current technology. In addition, we intend to focus on: 1) test methods designed to evaluate and identify internal drive contamination; 2) test methods to evaluate materials used in chemical filters; 3) chemical filter performance; 4) extending test methods and chemical filters to low contaminant concentrations; 5) targeting specific chemical species with chemical filters; 6) humidity control; and 7) the future of chemical filtration.

9:40am **MR+MI+AS+SE-WeM5 Effect of Humidity on Lubricated Carbon Overcoats***, **N. Shukla**,* Seagate Technology*; A.J. Gellman,* Carnegie Mellon University*; R. Veerdonk, X. Ma, J. Gui,* Seagate Technology

A quartz crystal microbalance has been used to measure contaminant adsorption on magnetic data storage media under controlled conditions. This apparatus has been developed to make measurements of contaminant adsorption at the level of 0.1 ng/cm2 with a time resolution on the order of seconds. Initially we have measured humidity uptake on amorphous carbon overcoats coated with lubricants. We have been able to estimate the amount of water adsorbed on lubricated carbon overcoats at room temperature and at moderate humidity levels (~ 25% RH). Adsorption and desorption is fast indicating that equilibrium with ambient humidity is reached on timescales of minutes, much faster than the timescales for fluctuations in ambient humidity. We have also studied water adsorption on different types of lubricants deposited at different thicknesses. Interestingly, the amount of water adsorbed on lubricated and unlubricated carbon overcoats is similar suggesting that water adsorption is primarily dependent on the properties of the carbon. We have studied the bonding of water on carbon overcoats and also studied bonding of lubricants on carbon overcoats.

10:00am **MR+MI+AS+SE-WeM6 Tribological Implications of the Confinement in PFPE Boundary Lubricant Films***, **G.W. Tyndall**,* IBM Almaden Research Center **INVITED**

Perfluoropolyether (PFPE) films of nominally 1.0 - 2.5 nm are commonly utilized by the magnetic recording industry to lubricate the head/disk interface in hard-disk drives. In this film thickness regime, the surface of the magnetic recording disk will "energetically confine" the lubricant. This confinement is manifested in physical and mechanical properties of the PFPE lubricant that differ substantially from those of the bulk fluid. In the current talk, the experimental evidence for confinement in the PFPE/carbon system will be reviewed, and the implications to the tribology of the head-disk interface discussed.

10:40am **MR+MI+AS+SE-WeM8 Pushing Perfluoropolyether Molecules Across Surfaces Using Air Shear***, M.A. Scarpulla, **C.M. Mate**,* IBM Almaden Research Center

We have investigated the surface mobility of thin films (<5 nm thick)of linear chain perfluoropolyether polymers on silicon and CN@sub x@ surfaces while subjecting them to air shear stresses. These experiments are elucidating the nature of viscosity in molecularly thin films of lubricants important for magnetic recording. For polymer chains with neutral CF@sub 3@ end groups, we find that the effective viscosity is close to the bulk viscosity even at sub-monolayer coverage. The addition of alcohol end groups to the polymer chains acts to anchor the first layer of molecules to a surface, greatly increasing the effective viscosity relative to the bulk. For the second layer, the alcohol-terminated polymers exhibit effective viscosities near their bulk viscosity, while dewetting is observed in thicker films.

11:00am **MR+MI+AS+SE-WeM9 Kinetics and Energetics of the Desorption of Polyether Lubricants***, **K.R. Paserba**, N. Prashanth, A.J. Gellman,* Carnegie Mellon University

Desorption or evaporation is one of the mechanisms for loss of perfluoropolyalkylether (PFPE) lubricants from the surfaces of data storage media. One approach to minimizing PFPE loss by desorption is the use of lubricants with increasing molecular weight or increasing average chain length. In order to understand the effects of chain length on the lubricant evaporation kinetics we have studied the desorption kinetics of monolayer films of oligomeric ethers with varying chain length adsorbed on the surface of graphite. This study has used monodispersed samples of oligomeric ethyleneglycol dimethylethers, CH3O(CH2CH2O)mCH3, and oligomeric ethyleneglycols, HO(CH2CH2O)mH, as models for the perfluoropolyalkylether lubricants Fomblin Z and Fomblin Zdol. Their adsorption and desorption from the surface of graphite has been measured as a function of chain length, M = 3m+3, or molecular weight by using thermally programmed desorption methods in ultra-high vacuum. The results of these measurements show the surprising result that the desorption energies, @DELTA@E@sub des@, are non-linear in the chain length. What is most interesting is that the desorption energies can be expressed by the power law expression @DELTA@E@sub des@ = a + b M@gamma@ with @gamma@ ~ 0.5. A model has been proposed for the desorption mechanism of such oligomeric lubricants from surfaces which can quantitatively reproduce the dependence of the desorption energies on chain length. The origin of the non-linearity is the conformational isomerism of the oligomers as they desorb from the surface. We will discuss the implications of these results on the desorption of oligomeric PFPE lubricants from the surfaces of magnetic data storage media.

11:20am **MR+MI+AS+SE-WeM10 Ramp Materials Challenges with Load/Unload Technology***, **B. Hiller**,* Maxtor Corporation **INVITED**

Dynamic ramp load/unload technology (or short: ramp load) is replacing contact start/stop technology in hard disk drives. Key reasons are superior shock performance and improved reliability. Ramp load adds a new part to the drive (the ramp) and a new interface (between ramp and suspension lift tab). Proper selection of the ramp material and specification of the ramp/tab interface are key to drive reliability. This talk will address the important issues and will present state-of-the art solutions, as well as an outlook on future developments. As with all in-drive materials, minimal chemical outgassing is required. After that, the most important criteria for the ramp material are low friction and wear, and adequate mechanical stability. Out of a large number of candidate materials, only two materials are primarily used in today's products: Teflon-filled liquid crystal polymer (LCP) and acetal homopolymer (POM). These two materials optimize the materials issues in different ways and have their unique application range. LCP excels at mechanical stability, while POM exhibits superior tribology. Surface roughness affects friction and wear and needs to be controlled for both sliding partners, but control is more crucial for the much harder stainless steel suspension lift tab. Current products employ both spherical and cylindrical lift tab shapes. The relative merits of both approaches will be discussed. Tribological and mechanical properties are so multi-faceted that a large portion of this talk will be devoted to presenting measurement techniques and key results. Other important properties such as electrostatic charging and cost will also be addressed.

Magnetic Recording Topical Conference
Room 110 - Session MR+AS+SE-WeA

Magnetic Recording: Heads & Media

Moderator: D. Weller, Seagate Technology

2:00pm **MR+AS+SE-WeA1 Ultra-Thin Magnetic Media Overcoats through ECR Deposition***, **M.L. Wu**, J. Kiely, Y.T. Hsia, K.J. Howard,* Seagate Research

With increasing demands made on the performance of ultra-thin (<3 nm) overcoats in magnetic recording media, novel deposition approaches are needed to produce films that are mechanically robust and provide corrosion resistance to the underlying media. We have used the ECR (electron cyclotron resonance) approach to create a high-density plasma and have controlled the ion energy via the bias to increase the atomic mobility and density of deposited films. Using this approach, we have deposited a series of a-C:H (N) films with thicknesses as small as 0.8 nm and correlate their corrosion, wear, and nanometer-scale scratch resistance performance with film density measurements. We also present findings that the interaction with the cobalt underlayer changes with the ECR approach. The oxidation state of the cobalt underlayer was investigated by high resolution ESCA and preliminary results showed that the percentage of cobalt oxide was significantly decreased by the ECR approach while the C (1s) spectra showed the formation of cobalt carbide at the interface. We will contrast the behavior of films deposited with this approach with those conventional sputtered a-C:H (N) films, and comment on the extendibility of traditional overcoat designs.

2:40pm **MR+AS+SE-WeA3 Future Directions in Magnetic Storage Technology***, **M.H. Kryder**,* Seagate Research **INVITED**

Magnetic recording technology has advanced in areal density by over 10 million times, since it was first introduced in disk drives in 1957. Recently, the rate of progress in areal density has exceeded 100% per year, far outstripping the pace of Moore's Law for semiconductor technology. Throughout this history there have been a number of innovations that have been made to enable the sustained progress. Today, however, we are approaching areal densities where a change in the form of the recording technology may be required. Longitudinal recording, which has been practiced in disk drives since 1957, is approaching densities at which recordings may become thermally unstable. This is forcing the industry to change the way disk drives are scaled and to consider alternative means of data storage. Technologies such as perpendicular recording, patterned media recording, optically assisted magnetic recording and probe storage are being considered. This talk will describe the methods that are being considered to extend longitudinal recording, the alternative technologies and their prospects for success.

3:20pm **MR+AS+SE-WeA5 Antiferromagnetically-Coupled Magnetic Media Layers for Thermally-Stable High-Density Recording***, **E.E. Fullerton**, D.T. Margulies, M. Schabes,* IBM Almaden Research Center*; M.F. Doerner,* IBM Storage Technology Division **INVITED**

The combination of signal-to-noise requirements, write field limitations, and thermal activation of small particles is thought to limit the potential areal density of longitudinal recording media and is commonly referred to as the 'superparamagnetic limit'. Recording media composed of antiferromagnetically coupled (AFC) magnetic recording layers is a promising approach to extend areal densities of longitudinal media beyond these perceived limits [@footnote 1@,@footnote 2@]. The recording medium is made up of two ferromagnetic recording layer separated by a nonmagnetic layer whose thickness is tuned to couple the layers antiferromagnetically. For such a structure, the effective areal moment density (Mrt) of the composite structure is given by the difference between the ferromagnetic layers allowing the effective magnetic thickness to scale independently of the physical thickness of the media. This allows AFC media to maintain thermal stability even for low Mrt values. Experimental realization of this concept using CoPtCrB alloy layers that demonstrates thermally stable low-Mrt media suitable for high-density recording will be discussed. @FootnoteText@ @footnote 1@ E. E. Fullerton et al, Appl. Phys. Lett. 77, 3806 (2000). @footnote 2@ E. N. Abarra et al, Appl. Phys. Lett. 77, 2581 (2000).

4:00pm **MR+AS+SE-WeA7 Optimization of Media Properties in Magnetic Thin Films***, **E.B. Svedberg**[1], J.M. van de Veerdonk, K.J. Howard,* Seagate Research*; L.D. Madsen,* Carnegie Mellon University

Film depositions by ultra high vacuum magnetron sputtering with controlled gradients across the wafer in terms of composition and thickness have allowed (i) efficient exploration of a large number of variables, and (ii) the interdependencies between parameters to be studied. Output parameters such as coercivity and squareness of magnetic loops for magnetic media were measured and subsequently models were extracted that incorporated both the dependencies and co-dependencies of the input parameters. An added bonus to this approach is the tight control maintained on the "fixed" parameters (e.g. temperature and background pressure) through making many samples in a single deposition. To achieve the gradients, six tilted magnetrons were used to deposit the films. In one experimental setup the effect of underlayers was studied. The samples consisted of a set of layers as follows: Ta, RuxCo1-x, CoCr, CoCrPtB. In this setup, there seems to be an optimum Ru concentration in the range of 80-85% for achieving a maximum squareness, while the coercivity increases monotonically with the Ru concentration, hence, is not possible to maximize both the coercivity and the squareness in the same disc in terms of data. In a second set of samples the effort was focused on the hard magnetic layer and investigating the effect of the additives Ta, Nb, Pt and Ti to the CoCr to promote the desired magnetic properties. From the experiments it seems that the combination of Pt and Ta/Ti additives promotes a different growth mode than Pt or the additives alone. Further, to verify the possibility of structural characterization automation, two CoCr/Pt multilayers consisting of ten bi-layers each were mapped by x-ray diffraction. In the samples, the thickness of each Pt layer was kept constant over the surface of the wafer and the thickness of the CoCr layer was varied along with the total thickness.

4:20pm **MR+AS+SE-WeA8 Magnetic Nanoparticles and Nanoparticle Assemblies***, **S. Sun**,* IBM Research **INVITED**

We present our chemical synthetic approaches to monodisperse magnetic nanoparticles (Co and FePt) and nanoparticle superlattices. Advances of magnetic recording technology have driven the development of new magnetic nanoparticle-based media with uniformity in both particle size and particle magnetics. Self-assembly of magnetic nanoparticles may offer an easy way of fabricating such media. The key step for successful self-assembly approach is to use structurally stabilized magnetic nanoparticles as building blocks to form uniform nanoparticle arrays. We have found that steric repulsion from long chain hydrocarbon surfactants is effective in particle stabilization process. A combination of surfactants such as trialkylphosphine/oleic acid (for Co) and oleic acid/oleyl amine (for FePt) has been successfully employed to control particle growth, stabilize the particles, and protect them from oxidation. The particles can be prepared by metal salt reduction and metal carbonyl decomposition. By varying metal/surfactant or metal/metal ratio, both particle size (2-11nm) and alloy composition can be tuned. These monodisperse magnetic nanoparticles can self-organize into regularly arrayed magnetic superlattices. Microscopic studies of the assemblies have shown that the symmetry of these assemblies is dependent upon many factors including particle's size and shape. Thermal annealing is applied to adjust interparticle spacing of the superlattice assemblies and to control internal particle structure. Magnetic properties of these assemblies can be easily tuned from superparamagnetic to ferromagnetic. These well-controlled magnetic nanoparticle assemblies are of interest for future fabrication of nanoelectronic devices, and will have great potential for ultra-high density magnetic recording.

5:00pm **MR+AS+SE-WeA10 Thermal Stability of Granular Perpendicular Magnetic Islands Patterned using a Focused Ion Beam***, **S. Anders**, C.T. Rettner, M.E. Best, B.D. Terris,* IBM Almaden Research Center

We have studied the thermal stability of patterned magnetic media islands as a function of island size. A focused ion beam (30 keV, Ga+) was used to pattern granular CoCrPt media to produce square arrays of islands of different periods, ranging from 70-750 nm. Islands with periods smaller than 130 nm appear as single magnetic domains in MFM images, while larger islands show multi-domain behavior. The samples were magnetized perpendicularly in a field of 20 kOe (far in excess of the ~3 kOe coercivity) to produce fully magnetized films. This fully magnetized state should have the highest decay rate, since the demagnetization field is maximized. Magnetic force microscopy images taken at various times after the

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[1] **IUVSTA Welch Scholar**

magnetization show that the patterned structures have a considerably slower thermal decay rate than the unpatterned film. Small single-domain islands were seen to have the smallest decay rate of less than 0.25% per decade compared to one order of magnitude higher decay rates for the unpatterned media. This enhanced stability is analyzed in terms of increased demagnetization fields and increased switching volumes introduced by patterning.

Plasma Science
Room 104 - Session PS+MS-ThM
Conductor Etch and Damage

Moderator: A.E. Wendt, University of Wisconsin, Madison

8:20am **PS+MS-ThM1 An Advanced 300 mm Etcher with Tunable Plasma Source for the Etching of <0.15mm Poly-Silicon Gates***, **J. Holland**,* Applied Materials, Inc., US*; M. Jain, M. Shen, N. Gani, A.M. Paterson, V. Todorov, M.S. Barnes, K. Fairbairn,* Applied Materials, Inc.

The current requirements for etch performance for 300mm poly-silicon gate can only be met by providing a wide enough process window that is capable of achieving uniform etching for the variety of steps needed to complete this etch. The final dimensions of the polysilicon gate are functions of the many different etch steps, the ARC/DARC open, the main-etch , soft landing step and over-etch steps. In order to achieve < 10 nm CD range for <0.15 um polysilicon features, all of these steps need to be very uniform and the CD loss (or gain) needs to be very controllable. In this next generation 300 mm etcher, a tunable inductively coupled plasma source combined with advanced gas injection technology allows etch uniformity to be optimized for all of these different steps. Results of tuning for etch uniformity will be shown. CD control of <5 nm with a total range of 10 nm is achieved. The tunable source is also combined with a precise wafer temperature control using a dual-zone electrostatic chuck to ensure CD uniformity can be achieved across the entire diameter of the 300mm wafer. The wide process window of this etcher should be capable of addressing both current and evolving applications which require etching of multiple films with multiple etch steps involving varied process conditions.

8:40am **PS+MS-ThM2 Plasma-Based Copper Etch Process - Additive Gas Effects***, **S. Lee**[1], Y. Kuo,* Texas A&M University

Copper is an ideal multilevel interconnection material for VLSIC and many other microelectronic devices. However, it is difficult to etch copper into fine lines by the conventional plasma etching method under a mild process condition such as at room temperature or without the inclusion of an extra energy source, e.g., UV, IR, or a high-density plasma source. Recently, authors reported a new plasma-based copper etching method that showed a high etch rate at room temperature using a parallel-plate electrode design.@footnote 1,2@ The success of this method relies on a novel plasma-copper reaction. Instead of removing copper compounds during the plasma processing, copper was converted into a solution soluble compound accumulated on the surface. This reaction product was subsequently removed with a HCl solution. The resulting copper pattern has a vertical profile. In this paper, we are going to discuss the additive gas (Ar, N@sub 2@, CF@sub 4@, and O@sub 2@) effects on the Cl@sub 2@ plasma-based copper reaction process. In addition to the reaction rate, the product's morphology, structure, and the undercut of the photoresist pattern have been studied. The added gas can enhance or hinder the reaction rate and the progress in the radial direction through various mechanisms. Experimental results are interpreted by the plasma phase chemistry, ion bombardment phenomena, and the original copper structure. The composition and chemical states of the reaction product are characterized by EDS and XPS. The film's morphology and structure are examined by AFM, SEM, and XRD. This study enhances our understanding of the unique plasma-based copper etching process that is critical to many microelectronic and optoelectronic applications. Authors would like to acknowledge staffs in the CIMS of Texas A&M University for AFM and XPS analyses. @FootnoteText@ @footnote 1@ Y. Kuo and S. Lee, Appl. Phys. Lett. 78, 1002, (2001) @footnote 2@ Y. Kuo and S. Lee, Jpn. J. Appl. Phys. 39, L188, (2000).

9:00am **PS+MS-ThM3 Silicon Gate Etching: Potential Strategies for Future CMOS Devices***, **G. Cunge**, L. Vallier, O. Joubert, J. Foucher, X. Detter,* CNRS/LTM, France **INVITED**

In less than ten years CMOS devices will operate in the sub-50 nm gate length regime. The fabrication of the gate will be the key issue of the device fabrication process since the variation in gate dimension must not exceed the nominal CD targeted by few nm. In this work, some of the most promising gate strategies are investigated 1) resist mask on SiON antireflective layers versus hard mask approaches 2) standard HBr/Cl@sub2@/O@sub2@ chemistries versus CF@sub4@ (or NF@sub3@) added chemistries. The origin of CD deviation are investigated for each single step of the different strategies: correlations between chemistry and plasma operating conditions analysed by mass spectrometry, passivation layer formation on the feature sidewalls analysed by XPS and CD deviation will be established. Our preliminary experiments show that the passivation layers formed on the mask sidewalls induce very severe CD gain during standard gate etch steps. The objective is first to minimize the CD deviation induced by each individual step of the process (by decreasing the passivation layer thickness). Ultimately, the process has to be tuned so that the CD loss or gain of each individual step compensate each other to maintain the CD in the targeted window. In final, by comparing the impact of mask materials as well as the impact of chemistries (standard or clean) on CD control, we may give some interesting conclusions on the most promising strategy. In parallel to this study, we evaluate the current strategies used to obtain gates smaller than the dimension printed by the lithography (resist trimming or "notched gate approach") and try to draw some clear conclusions on the best approach for manufacturing.

9:40am **PS+MS-ThM5 Sidewall Passivation Mechanism of CF@sub4@ Added Polysilicon Gate Etch Process***, **T. Lill**, F. Ameri, S. Deshmukh, D. Podlesnik,* Applied Materials*; L. Vallier, O. Joubert,* CNRS/LTM, France

For the traditional HBr/Cl@sub2@/O@sub2@ gate etch process, anisotropy is achieved by forming silicon, oxygen, and halogen containing compounds on the sidewall of the etching structures. These compounds inhibit the isotropic etch and are removed by from the etch front via ion sputtering and ion assisted desorption. The introduction of fluorine via CF@sub4@ to a typical HBr/Cl@sub2@/O@sub2@ polysilicon etch process suppresses the formation of SiOxBry or SiOxCly via formation of volatile SiF@sub4@. Speculations that carbon based polymers play an important role in the sidewall mechanism for the CF@sub4@ polysilicon gate etch chemistry have recently been confirmed by in-situ XPS studies in the Silicon DPS chamber at CNRS/LETI in Grenoble. In this paper we present more detailed studies of the sidewall composition for different CF@sub4@ and O@sub2@ flows. The results suggest the coexistence of silicon oxyhalogenides and carbon polymers on the sidewall for theHBr/Cl@sub2@/CF@sub4@/O@sub2@ gas mixture. The carbon content in the sidewall passivation layer increases strongly when the oxygen flow is reduced. The XPS results will be correlated with findings on chamber wall condition (oxide or carbon mode), change of the critical dimension for dense and isolated lines during gate etching (critical dimension microloading), and etch rate differences between doped and undoped polysilicon. We will present experimental line width data that corroborate the idea of change in sidewall passivation from compounds that are formed on the etching surface (silicon oxyhalogenides) to compounds formed in the gas phase (carbon polymers) when CF@sub4@ is added to the plasma. Typically, profile and critical dimension microloading are significantly reduced for the CF@sub4@ added chemistry as a result of the change in the sidewall passivation mechanism. The superior etch performance and the increased productivity due to clean chamber walls explain the rapid acceptance of this polysilicon gate etch chemistry in high volume VLSI production.

10:00am **PS+MS-ThM6 Manufacturing Viability of the "Notched Gate" Process for sub 0.1µm Technologies***, **J. Foucher**[2], L. Vallier, G. Cunge, O. Joubert,* CNRS/LTM, France*; T. Lill,* Applied Materials

The development of new integrated circuit generations, at a unique rate in the semiconductor history, imposes the development of new technologies. Recently, Integrated Circuit manufacturers have evaluated new strategies to make gate transistors smaller than the resolution allowed by the lithographic tool available for manufacturing. One of them is to decrease the resist feature dimension before gate etching (resist trimming), the other approach is to design a "notched gate" etch process with a controlled etch rate of silicon in the lateral direction (the bottom of the gate is smaller than its top). We first describe in details the main differences between a notched gate process and a standard gate etch process and introduce the notion of passivation layer engineering. We demonstrate that when the process is accurately tuned, gate dimension of 10 nm can be obtained on a 200 mm diameter wafer. We mainly concentrate on several aspects of the process which determine its industrial viability: - What are the plasma operating conditions and chemistry required to stabilize a "notched gate" process or in other words what are the impact of the wall conditions on notch reproducibility ? - Can we solve the CD control issues of the notched gate process ? We will present experimental data demonstrating clearly that the notch depth rate is strongly dependent on the gate environment. In other words, the lateral etch rate which controls the notch depth is

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[1] **PSTD Coburn-Winters Student Award Finalist**

[2] **PSTD Coburn-Winters Student Award Finalist**

aspect ratio dependent and impacted by the plasma non-uniformity. In conclusion, we clearly demonstrate the strong limitations of the notched gate process for manufacturing.

10:20am **PS+MS-ThM7 Properties of Pulsed ICPs with rf Substrate Biases@footnote 1@***, P. Subramonium,* ***M.J. Kushner,*** University of Illinois

Pulsed inductively coupled plasmas (P-ICPs) are of interest for controlling reactive fluxes to the substrate in microelectronics fabrication. In particular, negative ion fluxes to the wafer can be obtained in electronegative pulsed plasmas. In order to achieve anisotropy of the fluxes, rf substrate biases must also be used with P-ICPs. This is problematic since the increase in plasma potential obtained with an rf bias tends to trap negative ions. A moderately parallel implementation of the 2-dimensional Hybrid Plasma Equipment Model (HPEM) was used to investigate P-ICPs in electronegative gas mixtures having continuous and pulsed rf substrate biases. Electron properties are obtained using a Monte Carlo Simulation. In Cl@sub 2@ at 10 mTorr (PRF=10 kHz, duty cycle 50%), the electron temperature, after falling in the first part of the afterglow, increases in the late afterglow signifying a transition to a capacitive mode. The onset of the increase in T@sub e@ comes earlier with increasing rf bias voltage. The increase can be attributed to progressively larger rates of sheath heating resulting from the decreasing electron density, increasing sheath width and increasing sheath speed. Coincident with the increase in T@sub e@ comes an increase in sheath potential which prevents negative ions from escaping from the plasma. @FootnoteText@ @footnote 1@Work supported by NSF, SRC and Applied Materials.

10:40am **PS+MS-ThM8 Magnetic Field Effects and Electron Shading Damage***,* ***W.W. Dostalik,*** Texas Instruments, Inc.

The use of magnetically enhanced plasma etch systems (MERIE) is widespread in semiconductor manufacturing. A primary concern with such systems is the risk of plasma process induced damage. In this paper, we discuss several of the candidate mechanisms in which magnetic fields may affect plasma damage associated with the electron shading effect (ESE). In particular, we consider for the case of a permanent magnet MERIE reactor the effects of guiding center drifts (e.g., gradient drift and curvature drift) on charged particle fluxes, of magnetic field effects on individual trajectories, and of non-uniformity in a typical magnetic field map. These effects are calculated in a two-step fashion. In the first step, an experimentally measured magnetic field map of a commercial plasma reactor is input into a computer program that calculates the various drift velocities and non-uniformity for typical plasma parameters. In the second step, the results of these calculations are used to affect incoming charged particle fluxes in local scale Monte Carlo simulations including the magnetic field and local topography. Charge accumulation and the resulting Fowler-Nordheim injection current are accounted for in the Monte Carlo simulations.

11:00am **PS+MS-ThM9 Effects of H@sub 2@, D@sub 2@, N@sub 2@ and Ar Plasma on III-V Compound Semiconductor Devices***,* ***B. Luo,*** University of Florida*; K. Ip,* Agere Systems*; F. Ren, K.P. Lee, S.J. Pearton, C.R. Abernathy,* University of Florida*; R.J. Shul,* Sandia National Laboratories*; S.N.G. Chu,* Agere Systems*; C.W. Tu,* University of California, San Diego*; C.S. Wu,* Win Semiconductor*; K.D. Mackenzie,* Unaxis USA Inc.*; C.H. Hsu,* Feng Chia University, Taiwan

The effects of H@sub 2@, D@sub 2@, N@sub 2@ and Ar plasma exposures on the dc and rf characteristics of pseudomorphic AlGaAs/InGaAs high electron mobility transistors (HEMTs), GaAs metal semiconductor field effect transistors (MESFETs), and AlGaAs/GaAs heterojunction bipolar transistors (HBTs) were investigated. The experiments were conducted in a Plasma Therm 790 inductively coupled plasma (ICP) system. The influences of rf chuck power(10-100W), ICP source power(100-800W), chamber pressure(2-10mtorr) and durations(10-240sec) on device performance were studied. To analyze the rf results, a device equivalent circuit model was proposed to realize damage effects on the transistor small-signal elements. Several plasma damage mechanisms were identified for the degradations of device dc and rf characteristics, including creation of surface and bulk deep level recombination centers, preferential loss of As atom from the surface due to energetic ion bombardment and passivation of Si donors by formation of Si-H and Si-D neutral complexes. Auger and atomic force microscopy (AFM) were also used to characterize the atomic ratio and roughness of plasma damaged surface, respectively.

11:40am **PS+MS-ThM11 Plasma Induced Physical Damage and Contamination on the SrBi@sub 2@Ta@sub 2@O@sub 9@ Thin Film after Etching in Cl@sub 2@/CF@sub 4@/Ar Plasma***,* ***D.P. Kim,*** *C.I. Kim,* Chung-Ang University, Korea*; W.J. Lee, B.G. Yu,* ETRI, Korea

SrBi@sub 2@Ta@sub 2@O@sub 9@ (SBT) have been developed as dielectric materials of capacitor. To fabricate high density FRAM, plasma etching is indispensable process for the anisotropic pattern definition because it has good selectivity and excellent process control. However, the detrimental impact of plasma etching process on device characteristics has been existed. As feature size decreases, the plasma induced damages can decrease the performance of device. The plasma induced damages can be broadly classified as residue contamination, plasma-caused species permeation, bonding disruption and current flow damage. Etching mechanism and damages on SBT thin film during etching process have less reported in the literature. SBT thin films were etched in Cl@sub 2@/CF@sub 4@/Ar plasmas with measuring etch rates at different etching parameters such as gas mixing ratio, rf power, dc bias voltage, and chamber pressure. The maximum etch rate was 1060 Å/min in Cl@sub 2@(10)/CF@sub 4@(20)/Ar(80). The small addition of Cl@sub 2@ into CF@sub 4@(20)/Ar(80) plasma will decrease the fluorine radicals and the increase Cl radical. The etch profile of SBT thin films in Cl@sub 2@/ CF@sub 4@/Ar plasma is over 80°. The chemical reactions on the etched surface were investigated with x-ray photoelectron spectroscopy (XPS). Atomic force microscopy (AFM) was used to investigate the surface morphology of SBT thin films exposed in plasma. High-resolution transmission electron microscopy (TEM), secondary ion mass spectrometry (SIMS) and x-ray diffraction (XRD) were evaluated in order to investigate physical damages. Electrical properties were characterized by measuring leakage current and hysteresys loop of Pt/SBT/Pt capacitor. From the results, damages in SBT etching was occurred in the near surface and Ar ion bombardment and nonvolatile etching by products caused to change of crystallinity and surface morphology.

Tribology
Room 132 - Session TR-ThM

Tribological Surface Engineering for Lubrication & Wear Resistance

Moderator: W.-D. Munz, Sheffield Hallam University

8:20am **TR-ThM1 Tribological Surface Engineering for Lubrication and Wear Resistance***,* ***L.E. Seitzman,*** Caterpillar Inc. **INVITED**

Tribological Surface Engineering is the art of modifying a materials surface or near-surface by some means in order to achieve a desired friction or wear response of the material. One method available to surface engineers involves the application of metallurgical coatings, grown by one of several plasma-assisted vapor deposition processes. Such metallurgical coatings, usually only a few micrometers thick, have been used to improve the performance of cutting and forming tools and dies for many years. More recently, these coating have been successfully applied to mechanical components in order to extend life or to increase productivity of machines. The performance of the coatings depends on a number of factors, including chemistry, microstructure, surface texture and, of course, adhesion. We will illustrate some of these dependencies for coatings subjected to sliding. As a general rule, metallurgical coatings that provide the best friction reduction exhibit short wear life, and coatings with long wear life rarely reduce friction. The reason for this dichotomy and how it provides direction for the R&D community will be discussed.

9:00am **TR-ThM3 Optimization of Wear-resistant Coating Architecture using Finite Element Analysis***,* ***T.Z. Gorishnyy,*** *M.S. Aouadi, L. Olson, S.L. Rohde,* University of Nebraska - Lincoln

Chromium nitride based single layer, bilayer and multilayer coatings were deposited by unbalanced reactive magnetron sputtering on A2 steel and aluminium substrates. Their wear rates were measured using pin-on-disk testing under normal loads of 4 N and 10 N for Aluminum and A2 steel substrates respectively. Finite element analysis (FEA) was utilized to investigate stress distributions in film-substrate systems under conditions, which related to those of the actual wear tests. Two-dimensional asymmetrical models were created for every coating-substrate architecture tested. The FEA results were compared with analytical solutions for Hertzian contacts with and without frictional effects. A good fit was observed. Fracture mechanics in conjunction with FEA data was used to interpret differences in wear rates for different samples. The following possible causes of fracture were considered: (1) failure in individual layers; (2) delamination of multilayered films due to high in-plane interfacial stresses; (3) failure due to crack propagation at film-substrate interface and (4) failure as a result of film buckling.

9:20am **TR-ThM4 Solution-Assisted Tribological Modification of Surfaces Using an Atomic Force Microscope***, R. Hariadi, S.C. Langford,* ***J.T. Dickinson,*** Washington State University

When a surface is subjected to tribological loading, bonds experience time dependent distortions and spatial deformations. In the presence of simultaneous chemical stimulation (e.g., from a solution), this can lead to bond breaking, bond formation, and nuclear rearrangement. We present new studies of combining mechanical and chemical stimuli in model tribological and structural systems, particularly under conditions of solution supersaturation. Thermodynamically, the system tends towards deposition or crystal growth; we show that nucleation and growth on the surface can be controlled on the nanometer size scale using simultaneous mechanical stimulation with an AFM tip. New details of this process are presented with strong support of suggested models using analysis of small perturbations in the frictional force. Careful analysis of the"noise" in the cantilever motion during contact scanning shows that on single crystal surfaces we are very sensitive to the presence of sub-critical cluster formation and re-dissolution, we find that the amplitude of the noise increases by factors of 2-4. We take this as indirect evidence for the presence of these precursors to recrystallization. Furthermore, rich noise spectra are observed on crystal surfaces with low symmetry when one changes the scan directionâ€”we observe modulated signals at frequencies corresponding to calculated times between asperity-lattice row encounters. Again, under supersaturation, the noise levels rise in comparison with pure solvent. Finally, we present structures and surface modifications that can be induced by these mechanical/chemical synergisms.

9:40am **TR-ThM5 Low Frictional Force Coating of Boron Nitride - Copper Complex for Ultra High Vacuum by Magnetron Co-sputtering Technique***,* ***M. Goto****, A. Kasahara, M. Tosa, K. Yoshihara,* National Institute for Materials Science, Japan

Boron nitride - copper complex (BN/Cu) coating films were synthesized by a magnetron co-sputter technique. The characteristics of the films such as surface energy, internal stress, surface morphology, elements configuration and adhesion force were measured. Frictional force of the coating films was also measured with a self-made vacuum-friction measuring system from an atmospheric pressure to the pressure of 10-7 Pa. Frictional coefficients of the BN/Cu films as low as 0.1 is achieved in UHV region. It was found that the mixture structure of boron nitride with copper formed under different discharge time was most effective to change the frictional force. This technique is applicable to produce low-frictional force materials for ultra high vacuum system.

10:20am **TR-ThM7 Aging Evaluations of MoS@sub 2@-Containing Lubricants@footnote 1@***,* ***D.E. Peebles****, M.T. Dugger, W.F. McNamara, J.A. Ohlhausen, E.H. Sorroche,* Sandia National Laboratories

Many solid film lubricants and self-lubricating materials utilize MoS@sub 2@ as the active lubricant phase. Oxidation of MoS@sub 2@ produces MoO@sub 3@ and surface sulfate species, which do not possess the same lubrication properties as MoS@sub 2@. However, the rate and mechanism for oxidation of MoS@sub 2@ is a strong function of the surrounding matrix material and the ambient oxidizing species. This work will review aging studies that have been performed for materials containing MoS@sub 2@ particles in polyimide and epoxy resin matrices. This work will illustrate the aging process from the viewpoint of chemical and performance modifications as a function of oxidation in a variety of atmospheric environments. Evaluations of the chemical state of the lubricant material are assessed by detailed surface chemical studies by x-ray photoelectron spectroscopy, while lubricant performance is assessed by pin-on-disk testing. The understanding of lubricant aging mechanisms obtained from these studies is being used to develop age-aware performance models for electromechanical devices. @FootnoteText@ @footnote 1@Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

11:00am **TR-ThM9 Diamond-Like Carbon Nanocontacts***,* ***R.W. Carpick****, J.R. VanLangedon, E.H. Wilson, K. Sridharan,* University of Wisconsin - Madison

Wear-resistant low-friction coatings are of interest for a variety of applications from automotive engines to sub-micron machines. One particularly important coating is diamond-like carbon (DLC), which can possess mechanical properties approaching those of diamond. We have used atomic force microscopy to study the nanotribological properties of DLC as a function of preparation to investigate the mechanisms that underlie ultralow friction and wear. Furthermore, we have fabricated nano-asperities by coating the tips of atomic force microscope cantilevers with DLC. The unique coating process, plasma-source ion deposition, produces a high-quality conformal coating of DLC. By placing this asperity in contact with a DLC-coated substrate, we are able to measure, for the first time, the mechanical and frictional properties of DLC/DLC interfaces at the nano-scale. We will discuss the fundamental relations governing friction for this interface.

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