Surface Engineering
Room 201 - Session SE-TuA

Surface Engineering: Surface Preparation to Postcoating Surface Finishing

Moderator: Y.-W. Chung, Northwestern University

2:00pm **SE-TuA1 Surface Engineering by Plasma Immersion Ion Processing**, ***M.A. Nastasi,*** Los Alamos National Laboratory **INVITED**

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

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

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

3:00pm **SE-TuA4 Enhanced Passivity of Austenitic AISI 304 Stainless Steel by Low-Temperature Ion Nitriding**, ***S. Rudenja,*** Tallinn Technical University, Estonia; *I. Odnevall Wallinder, C. Leygraf,* Royal Institute of Technology, Sweden; *P. Kulu, V. Mikli,* Tallinn Technical University, Estonia

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

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

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

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

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

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

During the fabrication of integrated circuits with tungsten plugs, the tungsten surface undergoes chemical mechanical planarization (CMP). It is important to characterize the effects of any pre- or post-processing cleaning steps on the tungsten surface. To investigate this, we have examined tungsten films prepared by chemical vapor deposition (CVD) to carefully characterize how they respond to common cleaning and etching procedures. Topography changes were examined by atomic force microscopy and surface chemistry was characterized by X-ray photoelectron spectroscopy (XPS). Cleaning and etching procedures investigated in this study include solutions of KNO@sub 3@ and H@sub 2@O@sub 2@, KOH, a buffered solution of KIO@sub 3@ and NaOH as well as the RCA SC-1 clean. The relative ability of these cleaning treatments to remove residual hydrocarbons from the W surface has been evaluated. In addition, the influence of these treatments on the native tungsten oxide layer has been measured as well. The XPS results show a general increase in the oxidation state in W for most solutions, specifically entailing an increase in W@super 6+@ and a corresponding decrease in W@super 4+@. These results are relevant to both material removal during the CMP process and the effectiveness of cleaning procedures. A correlation of the results shows that weakly oxidizing solutions are not as effective in removing organic contaminants as strongly oxidizing solutions.

4:20pm **SE-TuA8 Reactions of Fluorocarbon Polyatomic Ions with Polymer Surfaces***, **M.B.J. Wijesundara**, L. Hanley,* University of Illinois at Chicago

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

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

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

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

Films formed from plasma polymerization of carbon containing, silane-based monomers have shown great promise as intermediate adhesion and anti-corrosion promoters on a number of substrates. Incorporation of oxygen in the deposition process has been shown to modify the surface energy of deposited films, yielding a fully variable range of surface wettability from hydrophobic to hydrophilic. A photoemission investigation of films formed with several monomers and various plasma ignition techniques was carried out. It yields insight regarding the chemical changes at the interface with oxidized surfaces, the surface structure of post-deposition plasma treated films, and the mechanism responsible for elemental bonding changes between types of deposition. Aging of a D.C. trimethylsilane plasma polymer was observed to primarily involve the oxidation of Si sites with a loss of carbon bound to silicon sites, which is correlated to spectroscopic ellipsometry data indicating the tendency for a more silica type index of refraction as the film ages. The aging/oxidation study then further correlates to the observed effects of the incorporation of oxygen with the monomer during deposition. Partial support for this project was provided by DARPA under U.S. Air Force contract # AF F33615-96-C-5055.

Author Index

Bold page numbers indicate presenter