

## 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 ( $U_{\text{sub s}}@-1200$  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 20 $\mu$ m 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  $H_p$  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  $L_{\text{sub c}}@ > 50$  N 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 SiO<sub>2</sub> 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  $\mu$ m-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)

# Tuesday Morning, October 30, 2001

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 root 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.

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