Surface Engineering
Room 201 - Session SE-TuM

Interface Engineering and Graded Films: Structure and Characterization

Moderator: I. Petrov, University of Illinois, Urbana

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

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

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

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

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

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

9:40am **SE-TuM5 Interface Engineering and Graded Films: Structure and Characterisation***, S.J. Bull,* University of Newcastle, U.K. **INVITED**

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

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

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

10:40am **SE-TuM8 Optimization of In Situ Substrate Surface Treatment in a Cathodic Arc Plasma: A Plasma Diagnostics and STEM-EDX Study***, C. Schönjahn, A.P. Ehiasarian, W.-D. Münz, D.B. Lewis, R. New,* Sheffield Hallam University, UK*; R.D. Twesten, I. Petrov,* University of Illinois, Urbana

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

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

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

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

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

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