Monday Afternoon, November 15, 2004

Advanced Surface Engineering
Room 303D - Session SE-MoA

Structure Control of Hard Coatings in Sputtering Processes

Moderator: A.A. Voevodin, Air Force Research Laboratory

2:00pm **SE-MoA1 Control of Nanostructure Evolution in Metastable Transition Metal Nitride Layers using High-Flux, Low-Energy Ion Irradiation during Growth***, **I. Petrov,*** University of Illinois **INVITED**

We use high-flux, low-energy ion irradiation during low-temperature growth to control the kinetic pathways of phase separation in metastable transition-metal nitride layers in order to produce novel nanostructures composed of self-organized nanolamellae in δ-TaN@sub x@ or nanocolumns in Ti@sub 1-x@Ce@sub x@N. Coherent δ-TaN(111)/γ-Ta@sub 2@N(0002) nanolamellae form spontaneously in reactively-sputter-deposited TaN@sub x@ layers when using ion energy E@sub i@ ~ 50 - 65 eV with an ion-to-metal flux ratio J@sub i@/J@sub Me@ ~ 11; at lower E@sub i@ the films are phase-pure metastable δ-TaN @sub x@. The nanolayers are coherent platelets of alternating metastable cubic δ - TaN@sub x@ and thermodynamically-stable hexagonal γ-Ta@sub 2@N phases which are lattice-matched along their hexagonal closed-packed δ-TaN(111) and γ-Ta@sub 2@N(0002) planes. The formation of γ-Ta@sub 2@N nanolamellae is attributed to ion-irradiation-induced ordering of N vacancies within the (111) N planes of δ-TaN that causes hexagonal stacking of the closed-packed Ta planes. The nanolamellar TaN layers exhibit superhardness values (H = 40-45 GPa). During reactive sputter-deposition of metastable Ti@sub 1-x@Ce@sub x@N alloys, we observe nanophase films with x>0.1. Under conditions of low ion-irradiation, i.e. grounded or floating substrates, the nanostructure consists of equiaxed grains which forms due to continuous renucleation induced by CeN segregation. This is analogous to the nanostructure to the one observed in crystalline/amorphous nanocomposites, e.g. TiN/Si@sub 3@N@sub 4@. In contradistinction, a novel nanocolumnar structure forms when the alloys are grown under intense ion-irradiation with J@sub i@/J@sub Me@ ~ 15 and Ei = 45 eV. The intense ion mixing in the near surface area allows sufficient adatom mobility to form local TiN- and CeN-rich areas that propagate along the growth direction.

2:40pm **SE-MoA3 Investigation of the Solubility in (M@sub x@M'@sub 2-x@)AlC (M and M' = Ti, V, Cr) as well as the Cr-Al-C System***, **J.M. Schneider**, D. Music, Z. Sun, R. Mertens,* RWTH Aachen, Germany*; R. Ahuja,* Uppsala University, Sweden

We have performed theoretical studies of the solubility within (M@sub x@M'@sub 2-x@)AlC, where M and M' = Ti, V, Cr by means of ab initio total energy calculations. The theoretical values of equilibrium volume and the optimized c/a ratios are in good agreement with those of experiments (within ~ ± 4% and ~ ± 1.3%, respectively). Furthermore, we show that if x is increased from 0 to 2 the bulk modulus can be increased by as much as 36%. Based on the total density of states analysis as well as the energy of formation, we suggest that the investigated systems show solubility except for the (Cr,Ti)@sub 2@AlC system. In addition to these data we have studied the effect of the chemical composition on the structure in the system Cr-Al-C by combinatorial thin film synthesis. By changing the Cr/C ratio from 1.72 to 3.48 and the Cr/Al ratio from 1.42 to 4.18 the formation of Cr@sub 2@AlC, Cr@sub 2@Al and Cr@sub 23@C@sub 6@ phases was observed. Furthermore, based on X-ray diffraction a single phase Cr@sub 2@AlC composition region is identified (Cr/C ratio between 1.72 and 1.925, Cr/Al ratio between 1.42 and 2.03) in the Cr-Al-C phase diagram. Throughout the studied composition range the lattice parameters of Cr@sub 2@AlC were independent of the chemical composition : a = 2.865 Å ± 0.2%, c = 12.80 Å ± 0.6%. Furthermore, we find that a deviation from the stoichiometric composition of up to 6.3 at % for Al still results the formation of a Cr@sub 2@AlC single phase field. Possible pathways to accommodate the observed deviation from stoichiometry are discussed.

3:00pm **SE-MoA4 Growth and Characterization of New Epitaxial MAX-Phase Thin Films from the Ti@sub n+1@(Si, Ge)C@sub n@ Systems by Magnetron Sputtering***, **H. Högberg**, J. Emmerlich,* Linköping University, Sweden*; J.-P. Palmquist,* Kanthal AB, Sweden*; P. Eklund,* Linköping University, Sweden*; O. Wilhelmssson,* Uppsala University, Sweden*; L. Hultman,* Linköping University, Sweden*; U. Jansson,* Uppsala University, Sweden

This is a presentation of the state-of-the-art for the materials research on M@sub n+1@AX@sub n@ (n=1 to 3) phase thin films. The MAX-phases are a family of ductile inherently nanolaminated ternary nitrides and carbides with a high potential for industrial applications due to their unique combination of metallic and ceramic properties, as recently reported for the archetype Ti3SiC2. These properties stem from a highly anisotropic hexagonal crystal structure, where early transition metal (M) atoms and C or N (X) atoms form edge-sharing octrahedral MX blocks that are interleaved by layers of group 13-15 elements (A). Using DC magnetron sputtering with elemental sources we deposited epitaxial MAX-phase films from the Ti-Si-C and Ti-Ge-C systems on Al2O3(0001) or MgO(111) substrates at temperatures of 900 oC or 1000 oC, which is 500 oC lower than for conventional bulk processes. Besides demonstrating single-crystal growth of the known phases Ti3SiC2, Ti3GeC2, and Ti2GeC we have discovered two phases Ti4SiC3 and Ti4GeC3 as well as four intergrown structures of stoichiometries Ti5A2C3 and Ti7A2C5. The general trend from synthesis and characterization is that both MAX-phase systems show similarities with respect to phase distribution, mechanical, and electrical properties, reflecting the close chemical relationship between Si and Ge. However, XRD shows that the Ti-Ge-C MAX-phases are restricted to a more narrow deposition window and require slightly higher temperatures due to a more limited diffusivity of the larger Ge atoms. From the nanoindentation analysis we see the characteristic large plastic deformation with extensive pile up for both systems, but measure a slightly lower Youngs modulus of 300 GPa for the Ti-Ge-C films compared to the 320 GPa obtained from Ti3SiC2 films. The four-point probe measurements show a lower conductivity for the Ti3GeC2 films compared to their Si-counterparts with resistivity values of 50 and 25 @micro@@ohm@cm, respectively.

3:20pm **SE-MoA5 Epitaxial Growth of B1-NaCl-Structure HfN@sub x@ Layers on MgO(001) by Ultrahigh Vacuum Magnetron Sputter Deposition***, **H.-S. Seo**, T.-Y. Lee, J.G. Wen,* University of Illinois*; D. Gall,* Rensselaer Polytechnic Institute*; I. Petrov, J.E. Greene,* University of Illinois

Group IVB metal nitrides are used in hard coating, wear-resistant, and diffusion barrier applications due to their excellent mechanical, electrical, and electrochemical properties. In the Hf-N system, unlike Ti-N where TiN is the terminal phase, several conflicting claims concerning the existence of N-rich phases have appeared in the literature. Here, we report the results of a systematic investigation of the properties of epitaxial HfN@sub x@ layers grown at 650°C on MgO(001) by ultrahigh vacuum reactive magnetron sputter deposition in mixed N@sub 2@/Ar discharges. X-ray diffraction and transmission electron microscopy analyses show that HfN@sub x@ with 0.8 @<=@ x @<=@ 1.38 grows epitaxially with a cube-on-cube orientational relationship to the substrate. HfN@sub x@ layers with x @<=@ 1.2 are single crystalline while films with x @>=@ 1.24 consist of a mixture of NaCl-structure HfN@sub x@(001) and a N-rich phase with large interplanar spacing (d = 2.7-3.0 Å). The relaxed bulk lattice parameter of HfN@sub x@(001) decreases only slightly with N/Hf ratio from 4.543 Å with x = 0.8 to 4.504 Å with x = 1.38. The room-temperature resistivity @rho@ of HfN@sub x@ varies from 14.2 µ@ohm@-cm for x = 1.0 to 2710 µ@ohm@-cm for x = 1.5, while the hardness H and elastic modulus E values of HfN@sub x@(001) with 0.8 @<=@ x @<=@ 1.5 are 28±4 GPa and 400±60 GPa, respectively. HfN@sub x@(001) layers with 0.8 @<=@ x @<=@ 1.32 are metallic with positive temperature coefficients of resistivity (TCR) between 10 and 300 K and temperature-independent carrier concentrations. They are also superconducting with the highest critical temperature, 9.18 K, obtained for layers with x = 1.0. At higher N/Hf ratios (x @>=@ 1.38), the layers exhibit significant changes in their electronic structure leading to a dramatic increase in @rho@ with a negative TCR, no superconducting transition above 2 K, and a decrease in H and E.

3:40pm **SE-MoA6 Surface Morphological Evolution of Epitaxial CrN(001) Layers***, J.R. Lynch, J. D'Arcy-Gall, S.V. Kesapragada,* ***D. Gall,*** Rensselaer Polytechnic Institute

CrN layers, 7 to 300 nm thick, were grown on MgO(001) at 600-800 @degree@C by ultra-high-vacuum magnetron sputter deposition in pure N@sub 2@ discharges at 20 mTorr. Microstructural and surface morphological evolution were found to depend strongly on the growth temperature T@sub s@. Layers grown at 600 @degree@C nucleate as single crystals with a cube-on-cube epitaxial relationship with the substrate. However, above a critical thickness of ~50 nm, misoriented CrN grains nucleate and develop into cone-shaped grains that protrude out of the epitaxial matrix to form triangular faceted surface mounds. These mounds lead to a dramatic increase in the root-mean-square surface roughness, from 3 to 19 nm, for a 300-nm-thick layer. CrN grown at T@sub s@ = 700 and 800 @degree@C are complete single crystals. Their surfaces exhibit dendritic mounds with fingers extending along orthogonal directions. In addition, the T@sub s@ = 700 @degree@C layer also shows square shaped "super"-mounds which protrude out of the underlying matrix and are attributed to a growth instability related to atomic shadowing effects which were purposely enhanced by non-normal deposition. For all layers, the surface roughness follows a power law with t. The exponent @beta@ is 1@+-@0.2 for the matrix-part of the surfaces, that is, the surfaces excluding the triangular and square shaped mounds for the T@sub s@ = 600 and 700 @degree@C layers, respectively. In contrast, @beta@ increases to 1.8@+-@0.3 when including the protruding grains. The two distinct @beta@-values are related to two roughening mechanisms: kinetic roughening, which is associated with an adatom motion towards ascending step edges due to a kinetic barrier for diffusion over descending steps, and atomic shadowing roughening, which is due to an increased local growth rate of surface protrusions caused by a higher capture rate of the incoming deposition flux.

4:00pm **SE-MoA7 Stress Reduction in Sputter Deposited Tungsten Films Using Nanostructured Compliant Layers by High Working-Gas Pressures***,* ***T. Karabacak****, J.J. Senkevich, G.-C. Wang, T.-M. Lu,* Rensselaer Polytechnic Institute

We present a new strategy of stress reduction in sputter deposited films by a nano-compliant layer at the substrate using physically self-assembled nanostructures obtained at high working-gas pressures prior to the deposition of a continuous film. This technique is all in-situ, and the nanostructures are made of the same material as the deposited thin film and requires no lithography process. This nanostructured layer has a lower material density and can act as a compliant layer to reduce the stress of the subsequently deposited continuous film grown under low gas pressure. By using this approach we were able to reduce stress values significantly in sputter deposited tungsten films and the strategy of alternating high and low Ar gas pressures leads to the growth of much thicker films without delamination.

4:20pm **SE-MoA8 High Powered Pulsed Magnetron Sputtering of Metallic Films in Ar, Ne, and He Plasmas***, S.L. Rohde, J. Li,* ***D.M. Mihut****,* University of Nebraska-Lincoln

High Powered Pulsed Magnetron Sputtering (alternatively, HIPIMS) can yield peak plasma densities >10@super 13@ cm@super -3@, three orders of magnitude higher than conventional sputtering, and also results in a higher fraction of ionized sputtered material. For sputtering of Ti almost 100% ionization has been observed, while for Cu around 70% of the metal was ionized, as compared with 5 to 10% for conventional magnetron sputtering. In the present study, the ionization efficiency of HPPMS has been investigated as a function of working gas using Ar, Ne, and He to sputter a variety of metallic targets (Cr, Al, Ti, and Cu). Successful deposition was achieved using all three working gases, and it was determined that the percentage of ionized metal reaching the substrate surface in each case varies with gas pressure, pulse energy, target metal, and gas species. Even using He as the working gas, it was possible to generate a highly ionized Al-flux - a very unexpected result. Additionally, there are preliminary indications that this highly ionized flux may be utilized in interface engineering during etch and pre-deposition stages. Selected films were studied both in-situ and ex-situ using spectroscopic ellipsometry (SE) to determine their optical properties and provide correlation between the optical properties and chemical/structural changes in the films, and thus providing a valuable resource for future work. In addition, some of these films were characterized post-deposition using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), atomic force microscopy (AFM), and nanoindentation. XPS, AES, and SE were used in tandem to reveal the crystal structure of the films observed under specific growth conditions.

4:40pm **SE-MoA9 The Dominance of Oxygen in Two-Gas Reactive Sputtering of Oxynitride Films***,* ***W.D. Sproul****, D.C. Carter, D.J. Christie,* Advanced Energy Industries, Inc.

Reactive sputtering with two reactive gases and one target material presents special problems. Both reactive gases affect the state of the target surface and the plasma conditions, which means that both affect common feedback control signals such as the cathode voltage and optical emission signals. Modeling has shown that the way to control the two-gas reactive sputtering process is to produce individual control signals for each gas and to control the partial pressure of each reactive gas. Experiments have confirmed the model. When oxygen and nitrogen are the two reactive gases, oxygen usually dominates the reaction. A small change in the amount of oxygen results in large changes in the properties of the films, whereas it usually takes a large change in the nitrogen partial pressure to change the film properties. These results were found during two-gas reactive sputtering of the oxynitrides of aluminum, silicon, and titanium where a differentially pumped mass spectrometer was used to produce individual partial pressure feedback signals for the oxygen and nitrogen. For these three oxynitride systems, oxygen strongly dominated the reaction. Very slight changes in the oxygen to nitrogen partial pressure ratios result in large changes in rate and optical properties for these oxynitrides. The dominance of oxygen is particularly acute when flow control is used for the oxygen and the nitrogen is in partial pressure control. In this situation, it is possible for the oxygen to trap the target in a poisoned state that cannot be reversed until both gases are removed. To avoid this problem, partial pressure control should be used to control both reactive gases. Experimental results showing the dominance of oxygen over nitrogen for the two-gas reactive sputtering of AlOxNy, SiOxNy, and TiOxNy will be shown and discussed.

5:00pm **SE-MoA10 Ion Assisted Deposition of Zirconium Nitride using Balanced and Unbalanced Magnetron Sputtering***,* ***S. Guruvenket****,* Indian Institute of Science, India, India

Zirconium nitride thin films were deposited on Si (111) substrates by balanced and unbalanced magnetron sputtering. The change in the preferred orientation of the deposited films was studied as a function of substrate bias voltage. ZrN films deposited by magnetron sputtering with out any bias voltage showed a preferred orientation of (111) where as, those deposited at higher bias voltages (above â?"60Volt) showed (200) as the preferred orientation. ZrN films deposited by unbalanced magnetron also showed a similar kind of transformation in the preferred orientation but the bias voltage required in this case was about -40V. Better quality films have been obtained with a resistivity value of 50 @micro ohm cm 1@ in unbalanced magnetron sputtering, where as, a resistivity of 63@micro ohm cm 2@ was obtained in case of magnetron sputtered ZrN thin films. The change in the surface roughness as the function of the bias voltage was also studied. @FootnoteText@ 1. @micro ohm cm 1@ 2. @micro ohm cm 2@.

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