

## Vacuum Metallurgy Division Room 620 - Session VM-WeM

### Advanced Surface Treatments and Coatings

Moderator: A. Inspektor, Kennametal Inc.

8:20am **VM-WeM1 Microstructural and Surface Morphological Evolution at the Atomic Scale during the Growth of Polycrystalline TiN: a TEM, XRD, HT-STM, and Modeling Study, I. Petrov, S. Kodambaka, P. Desjardins, A. Vailionis, V. Petrova, J.E. Greene, University of Illinois, Urbana; L. Hultman, Linköping University, Sweden; G. Gilmer, Lucent** **INVITED**

TiN is widely used as a diffusion barrier in microelectronics, as a hard wear resistant coating on cutting tools, and as a corrosion and abrasion resistant layer on optical components. Even though its diffusion barrier and elastic properties are known to be extremely anisotropic, little is known regarding the mechanisms and reaction paths leading to the development of preferred orientation in polycrystalline TiN layers deposited by PVD. We have used in-situ temperature-dependent STM measurements during deposition and post-annealing, detailed post-deposition microstructural analyses, and modeling to provide atomic-scale insights into microstructural and surface morphological evolution during TiN film growth. The results show that TiN layers grown at low temperatures ( $T \leq 450^\circ\text{C}$ ,  $T_{\text{sub s}}/T_{\text{sub m}} = 0.20$ ) exhibit competitive texture evolution with a columnar 111 "kinetically-limited" texture eventually becoming dominant. The columns are narrow with inter- and intracolumnar porosity and faceted surfaces. Higher growth temperatures or the use of high incident  $N_{\text{super}} + N_{\text{sub 2}}/Ti$  flux ratios ( $> 5$ ) with low ion energies (20 eV) result in non-competitive growth with the development of a fully dense essentially complete 002 preferred orientation from the initial monolayer. The above microstructural results can be understood qualitatively assuming that the activation energy  $E_{\text{sub s}}$  for surface diffusion and the Ehrlich barrier  $E_{\text{sub b}}$  at descending step edges are larger on 111 surfaces than on 002. Using this, together with the assumption that pseudomorphic forces (i.e., local epitaxy) dominate once island orientation is determined locally, the general features observed in the experiments outlined above can be replicated using kinetic Monte Carlo simulations. The in-situ STM observations of the dynamics of island growth and decay also provide important additional insights into the atomic-scale growth of TiN and related transition-metal nitrides.

9:00am **VM-WeM3 High Refractive Index -Textured Cubic Zirconia Formed in Nanolaminate Coatings Using Titania Interruption Layers, J.D. DeLoach, University of Wisconsin, Milwaukee; C.R. Aita, University of Wisconsin, Milwaukee, US**

Thermodynamic phase evolution of bulk zirconia cooled from the liquidus ( $2680^\circ\text{C}$ ) is as follows: cubic ( $2360^\circ\text{C}$ ) to tetragonal ( $\sim 1075^\circ\text{C}$ ) to monoclinic (STP phase). However, the pseudobinary zirconia-yttria phase diagram shows that the cubic phase is stabilized at room temperature by adding approximately 10 mole % yttria. Therefore, most reports of cubic zirconia formation in coatings of practical thickness involve yttria-doped zirconia. Undoped zirconia single layer film studies report the transformation from cubic to monoclinic zirconia with increasing crystallite size, suggesting that a finite crystal size effect aids in cubic zirconia stabilization. For this reason, zirconia phase control is easier in a multilayer scheme, by the introduction of growth interruption layers. This approach was taken by several investigators who grew cubic zirconia in zirconia/yttria nanolaminates. In these cases, cubic zirconia was formed by heteroepitaxy with either -texture cubic yttria or a -texture interfacial cubic zirconia-yttria alloy. The drawbacks of using yttria for growth interruption layers were: (1) the refractive index of the nanolaminate was considerably lowered by the presence of yttria, and (2) the -texture of cubic zirconia was stabilized by heteroepitaxy, precluding a -texture desirable for certain applications. In this study, a sputter-deposited nanolaminate structure consisting of polycrystalline zirconia-vitreous titania bilayers was used to fabricate high refractive index, undoped cubic zirconia coatings with a strong crystallographic texture. Titania was chosen as the interruption layer material because: (1) its vitreous nature encouraged low surface energy {200} cubic zirconia planes to preferentially orient parallel to the growth interface, resulting in a -texture, and (2) its high refractive index resulted in a nanolaminate with an overall refractive index of 2.23.

9:20am **VM-WeM4 Tribological Performance and Initial Finite Element Modeling of Reactively Sputtered Single and Multi-layer Chromium Nitride Thin Films, S.L. Rohde, D. Mihut, S. Kirkpatrick, University of Nebraska, Lincoln**

This work examines the tribological properties of CrN and Cr@sub 2@N thin films both as single-layers and in a number of different multilayer structures combining CrN, Cr@sub 2@N and Cr. The overall program goal was to test the feasibility of "building-in" load support, by alternating hard/soft film layers to optimize performance on hard materials, such as hardened tool steels, as well on compliant materials like Al-alloys. The first phase of this program centers on the deposition and evaluation of an array of coating structures on various substrates. Thin films were deposited in a mixed Ar-N@sub 2@ discharge, using a single unbalanced magnetron cathode with a Cr-target operating in a metallic-mode. Three differing substrate materials were coated; 52100 bearing steel, A2 tool steel and 2024-alloy aluminum. The adhesion of the thin film/substrate couples was evaluated using scratch adhesion and Rockwell C indentation testing. Scratch adhesion values were found to range from 2 to 8 kg depending on the hardness of the substrate material; with the lowest values occurring on the most compliant substrates (i.e. 2024 Al). The wear behavior was assessed using pin-on-disk and high frequency Cameron-Plint testing. The pin-on-disk tests were performed without additional lubrication at 40 to 50% humidity using alumina and/or tungsten carbide balls as the pin materials. The wear was reduced in most cases, with the multi-layered structures performing best on all substrate materials. The lubricated Cameron-Plint tests run on coated 52100 steel substrates favored the Cr@sub 2@N-based films, although the hardness of these multilayers is frequently lower than the corresponding CrN-based structures. While on the A2 tool steel substrates, the hardest thin film structures yielded the best PoD wear performance, these same films did not perform as well on the more compliant Al-substrates. For the Al-substrates, neither the stiffest nor the most compliant films excelled, instead multi-layer film with alternating hard/soft structures designed to provide a more graded compliance from the substrate up to the rigid top layer yielded the best results. In this case, wear rates were reduced by as much as three orders of magnitudes over uncoated 2024 Al. Finite element modeling studies have been initiated to try to understand the behavior of these multilayered coating/substrate combinations under specific loading conditions. While still in its earliest stages, the ultimate goal of the modeling program will be to facilitate design and optimization of application specific coating structures into the original component design stage. To accomplish this models are being developed for previously tested film structures on various substrates, and these models will then be used to guide the development of second generation coatings, that will be used to verify and improve the efficacy of the models.

9:40am **VM-WeM5 Protective Coatings for Extreme Environments, H.W. Holleck, Forschungszentrum und Universität Karlsruhe, Germany** **INVITED**

Physical Vapor Deposition (PVD) allows multifunctional protective coatings to be achieved for extreme and very complex loading situations. Among various thin-film concepts such as superhard coatings, gradient coatings, composite coatings, superlattice coatings, solid-solution coatings, metastable multifunctional coatings, nanoscale coatings, designed to improve the performance of protective coatings, the nanostructured multilayer films, the nanocrystalline composite films, and the metastable vapor-quenched compound films are able in particular to meet extreme requirements. Knowledge of specific design principles has developed over the past few years, thus adding a scientific design basis to what used to be empirical film development. Properties and functions simultaneously attainable include high levels of hardness, toughness, oxidation and corrosion resistance, abrasion and erosion resistance, as well as low friction and low wear in many applications. Multilayer coatings combining metallic hard materials e.g. TiC and TiN or TiAlN, metallic and covalent hard materials e.g. TiC and C or SiC, as well as combinations of hard and soft materials, e.g. TiN and MoS<sub>2</sub> or C, will be discussed. Functional and structural contributions are responsible for the changes in properties produced by different numbers of single layers. Relations similar to those applying to multilayer coatings can be found for nanocrystalline films, with the grain size being the most important parameter besides phase composition. An almost unlimited source of new multifunctional coatings meeting extreme requirements are vapor-quenched multicomponent films combining materials of different hard material groups in a homogeneous film material optimized with respect to composition and structure. Examples to be discussed are TiC, TiN, TiB<sub>2</sub>, and CrN combined with compounds such as BN, B<sub>4</sub>C, SiC, and AlN. Thermodynamic and kinetic

# Wednesday Morning, October 27, 1999

modeling of the coating system and the deposition process allows the constitution, properties and performance of these coatings to be tailored within broad limits.

**10:20am VM-WeM7 Interface Engineering in a Combined Arc/ UBM Deposition System during Growth of  $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}$  Films on Steel: Effects of Substrate Ion Etching.** *C. Schönjahn, L.A. Donohue, D.B. Lewis, W.-D. Münz*, Sheffield Hallam University, UK; *R.D. Twisten, I. Petrov*, University of Illinois, Urbana

In-situ substrate cleaning by ion etching prior to deposition in PVD processes is a key step in achieving good film adhesion, which is essential for all coating applications. Irradiation with metal or gas ions alters substrate surface chemistry, topography and microstructure thus affecting subsequent film growth. This study compares  $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}$ /steel interfaces formed after Cr- metal ion bombardment at negative substrate biases,  $U_s$ , ranging from 600 to 1200 V during a Cr cathodic arc, stabilized with a 0.06 Pa Ar background pressure. Samples pretreated with a 1200 V Ar glow discharge at a pressure of 0.6 Pa were also investigated. Microstructure and microchemistry of the interfaces was studied by XTEM samples using STEM-EDX analysis. Cr ion etching with  $U_s = 1200$  V resulted in a net removal of over 100 nm of substrate material with the formation, through implantation and radiation-enhanced diffusion, of a Cr-enriched near-surface region extending to a depth of  $\sim 10$  nm. As  $U_s$  was reduced to 600 V, Cr accumulated at the surface as an  $\sim 5$  nm thick layer. Ar was incorporated at the surface to levels of 4 and 5 at % during Cr arc-etching and Ar glow discharge, respectively. Microstructure of  $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}$  overlayers was dramatically affected by pre-treatment procedures. Ar sputter cleaned steel surfaces ( $U_s = 1200$  V) promote nucleation of randomly oriented grains leading to a competitive column growth with small column size and open boundaries. In contrast, Cr irradiation at the same bias voltage results in local epitaxial growth of  $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}$  on steel, which is expected to improve film/substrate adhesion. Coatings deposited after Cr treatment with  $U_s = 600$  V still exhibit small areas of oriented growth but porosity is also present.

**10:40am VM-WeM8 Plasma Treatment of Polycarbonate for Improved Adhesion.** *A. Hofrichter, P. Bulkin, B. Drévilion*, CNRS Ecole Polytechnique, France

The deposition of silicon alloys for protective and optical coatings on polymers is of increasing interest. The understanding of the plasma polymer interaction is of prime importance here. In this work we report a study of the influence of various plasma-treatments on polycarbonate (PC) in order to clarify the adhesion mechanisms of plasma deposited silica films. Treatments and depositions were carried out in a low pressure (1 mTorr range) integrated distributed 2.45 GHz microwave electron cyclotron resonance reactor, which allows the deposition of dense stoichiometric silica at room temperature. The plasma-polymer interaction is studied by in-situ spectroscopic ellipsometry from near UV to infrared and ex situ Raman spectroscopy and atomic force microscopy. The influence of process parameters, such as power and gas composition is studied. To get better insight into the plasma modification mechanisms thin polymer layers, spincoated onto various substrates were used. This allows a precise determination of the absorption properties and the thickness evolution of the plasma modified surface layer by UV-visible ellipsometry. The absorption in the PC layer was found to increase in the UV and is attributed to the different reaction products of photo-Fries rearrangements. Particular attention was taken to evaluate the contribution of the VUV photons. The chain scission and crosslinking of pure and commercial grade polycarbonate is studied by gel permeation chromatography and correlated to the ellipsometric results. Finally we discuss the influence of the treatment on the silica adhesion, evaluated by microscratch test measurements.

**11:00am VM-WeM9 The Effects of Electron Beam Assistance on the Properties of Ion Beam Deposited CN Thin Films,** *Y.H. Kim, D.Y. Lee, I.K. Kim, H.K. Baik*, Yonsei University, Korea

For the direct ion beam deposition process, the kinetic energy of ion beam have been considered as a main factor for the determination of the properties of resulting thin films. But we have investigated the effects of electron beam assistance on the properties of thin film during the ion beam deposition process of CN material. For the verification of the charge-enhanced chemical bonding, the properties of carbon nitride thin films deposited with and without electron beam assistance are compared. For the direct ion beam deposition process, negative carbon ion beam and positive nitrogen ion beam was used simultaneously. Total negative beam

including negative carbon ion and electron can be emitted from the Cs ion bombardment on the graphite target. The filtering of electrons from the total negative beam by the transverse magnetic field is possible and the pure negative carbon ion beam was deposited with positive nitrogen ion beam for the less charge-enhanced chemical bonding process. The properties of DLC and CN thin films were discussed respectively by comparing the thin film growth with and without electron beam assistance. The properties of thin films were characterized by Raman spectroscopy, AES and XPS.

## Author Index

**Bold page numbers indicate presenter**

— A —

Aita, C.R.: VM-WeM3, 1

— B —

Baik, H.K.: VM-WeM9, 2

Bulkin, P.: VM-WeM8, 2

— D —

DeLoach, J.D.: VM-WeM3, **1**

Desjardins, P.: VM-WeM1, 1

Donohue, L.A.: VM-WeM7, 2

Drévilion, B.: VM-WeM8, 2

— G —

Gilmer, G.: VM-WeM1, 1

Greene, J.E.: VM-WeM1, 1

— H —

Hofrichter, A.: VM-WeM8, **2**

Holleck, H.W.: VM-WeM5, **1**

Hultman, L.: VM-WeM1, 1

— K —

Kim, I.K.: VM-WeM9, 2

Kim, Y.H.: VM-WeM9, **2**

Kirkpatrick, S.: VM-WeM4, 1

Kodambaka, S.: VM-WeM1, 1

— L —

Lee, D.Y.: VM-WeM9, 2

Lewis, D.B.: VM-WeM7, 2

— M —

Mihut, D.: VM-WeM4, 1

Münz, W.-D.: VM-WeM7, 2

— P —

Petrov, I.: VM-WeM1, **1**; VM-WeM7, 2

Petrova, V.: VM-WeM1, 1

— R —

Rohde, S.L.: VM-WeM4, **1**

— S —

Schönjahn, C.: VM-WeM7, **2**

— T —

Twesten, R.D.: VM-WeM7, 2

— V —

Vailionis, A.: VM-WeM1, 1