Tuesday Morning, November 4, 2003

Advanced Surface Engineering
Room 323 - Session SE-TuM
Nanostructured, Nanocomposite, and Functionally Gradient Coatings

Moderator: Y.W. Chung, Northwestern University

8:20am **SE-TuM1 Influence of Sputtering Condition and Target Material on the Microstructure and Properties of Ti-Si-N Coatings Prepared by r.f.-reactive Sputtering***, M. Nose,* Takaoka National College, Japan*; Y. Deguchi,* Toyama University, Japan*; T. Mae,* Toyama National College of Technology, Japan*; E. Honbo,* Toyama Industrial Research Center, Japan*; W.A. Chiou,* University of California, Irvine*; K. Nogi,* Osaka University, Japan

Since Veprek et al. presented a theoretical concept to design super-hard nano-crystalline composite materials on the TM-Si-N (TM = transition metal) systems consisting of nano-crystalline transition metal nitrides embedded in amorphous Si@sub 3@N@sub 4@, many studies on these kinds of films deposited by PVD have been reported. Although most of them used r.f.- or d.c.-reactive sputtering in an Ar/N@sub 2@ gas mixture, the results were not always consistent with each other. This suggests that the structure of films depends sensitively on the deposition conditions. Hence, we decided to examine the effect of sputtering condition and target material on the microstructure and mechanical properties of Ti-Si-N coatings prepared by r.f.-reactive sputtering. We used the composite targets conisting of Ti (99.99%) plate and Si@sub 3@N@sub 4@ chips as well as the target consisting of Ti plate and Si chips. Thin films were synthesized by r.f. sputtering machine in a facing target-type (FTS) on the substrates of high speed steel. During the deposition, the substrate was heated from room temperature up to ~300 °C and a d.c. bias up to -100V was applied. In the case of films deposited from the Ti-Si target without bias application, the hardness of high Si films (containing ~20 at %Si) showed the lower value of 20 GPa. The hardness of the films increased and reached to a maximum value of 40 GPa around at a bias of -30V, but the crystallite size of the film increased to ~30nm. On the other hand, the hardness of the films (containing ~20 at %Si) deposited from the Ti-Si@sub 3@N@sub 4@ target increased with increasing negative bias voltage, being saturated at a level of ~40 GPa over -80V. Although the crystallite size of the films increased gradually with increasing negative bias, it still remains about 7nm at -80V. The characteristics of the latter film could be attributed to the formation of nano-composite structure defined by Veprek et al.

8:40am **SE-TuM2 Growth and Physical Properties of Epitaxial CeN and Nanocrystalline Ti@sub 1-x@Ce@sub x@N Layers***, T.-Y. Lee,* University of Illinois at Urbana-Champaign, United States*; D. Gall,* Rensselaer Polytechnic Institute*; C.-S. Shin,* Hynix Corporation*; N. Hellgren,* Intel Corporation*; J.G. Wen, R.D. Twesten, I. Petrov, J.E. Greene,* University of Illinois at Urbana-Champaign

While NaCl-structure transition-metal nitrides have been widely studied over the past two decades, little is known about the corresponding NaCl-structure rare-earth nitrides. Polycrystalline CeN, for example, has been reported by different groups to be both a wide bandgap semiconductor and a metal. To address this controversy, we have grown epitaxial CeN layers on MgO(001) and measured their physical properties. CeN is metallic with a positive temperature coefficient of resistivity and a temperature-independent carrier concentration of 2.8±0.2x10@super22@cm@super-3@ with a room temperature mobility of 0.31 cm@super2@ V@super-1@-s@super-1@. At temperatures between 2 and 50 K, the resistivity remains constant at 29 µ@ohm@-cm, while at higher temperatures it increases linearly to reach a room-temperature value of 68.5 µ@ohm@-cm. The hardness and elastic modulus of CeN(001) were determined from nanoindentation measurements to be 15.0±0.9 and 330±16 GPa. We further explore the possibility to alter the microstructure evolution in metastable Ti@sub1-x@Ce@subx@N quasi-binary alloys by controlling, using low-energy ion irradiation, the kinetics of phase separation driven by the large lattice mismatch of the two components (a@subCeN@ = 0.504 nm, a@subTiN@ = 0.424 nm). We observed nanophase films with x > 0.1. During reactive sputter-deposition of alloys, we observe nanophase films with x>0.1. Under conditions of low ion-irradiation, the nanostructure consists of equiaxed nanometer-size grains which form due to continuous renucleation induced by CeN segregation, which is analogous to the one observed in the nanocomposites of TiN/Si@sub3@N@sub4@. In contradistinction, a nanocolumnar structure forms when the alloys are grown under intense ion-irradiation with J@subi@/J@subMe@ ~ 15 and E@subi@ = 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.

9:00am **SE-TuM3 Fabrication of Nanostructured Metallic Thin Films by Femtosecond Pulsed Laser Ablation***, **M. Jaime Vasquez**, T. Fiero, G.P. Halada, C.R. Clayton,* State University of New York at Stony Brook

Pulsed laser ablation is a well-known technique used for deposition of a variety of thin films for various applications. A major disadvantage of the use of excimer lasers has been the deposition of irregular melted droplets on the deposited film attributed to heterogeneities of the target, fluctuations in the laser fluence and other difficulties of process control. The extremely short pulse duration of femtosecond lasers results in reduction or complete prevention of lateral thermal damage as well as lower and more precise threshold fluences of ablation. This presentation focuses on both the mechanism of material ablation using femtosecond lasers as well as a number of examples of nanostructured metallic films of significance to analytical surface studies and catalysis. The femtosecond laser deposition process involves a high intensity laser pulse (10@super -15@ s range) that passes through an optical window of a vacuum chamber (10@super -6@ torr) and is focused onto the target, which can be a single metal, a mix of powders or a reactively arc melted coin. The partially ionized ejected material or ablation plume is then allowed to settle and form a thin film on a Si substrate. The plume itself was studied through analysis of the kinetics of ejected material from a Pt target and through charge screening methods to aid in determination of ionic character. In addition to Pt films, a nanostructured Al@sub 2@CuMg intermetallic thin film was formed (to study corrosion issues in Al aerospace alloys). Films were characterized by Secondary Electron Microscopy (SEM), Energy Dispersive Analysis of X-rays (EDAX), X-ray Diffraction (XRD) and Transmission Electron Microscopy (TEM). Thin films were polyscrystalline and of the same composition as targets and chemically homogeneous. Observations of the morphological and structural features of the ablated films indicate that the technique can be used to reliably create nanostructured thin films.

9:20am **SE-TuM4 Self-adaptation Processes in Nanostructured Hard Coatings***, **C. Mitterer**, P.H. Mayrhofer,* University of Leoben, Austria*; E. Badisch, M. Stoiber, G. Gassner,* Materials Center Leoben, Austria **INVITED**

Hard coatings deposited by plasma-assisted vapor deposition are widely applied to reduce tool wear. In the last decade, nanocomposite coatings have attracted increasing interest, due to the possible design of superhard coatings. Recently, it has been shown that nanostructured coatings also allow the realization of self-adaptive properties. This work summarizes recent developments in this field. The unavoidable Cl impurities in TiN coatings deposited by PACVD using TiCl@sub4@ as precursor is known to deteriorate mechanical coating properties when exceeding several at.-%. However, small and tolerable Cl concentrations of about 3 at.-% cause a reduction of the friction coefficient against various steels and alumina from 0.8 to 0.15. This is due to the formation of an interfacial lubricant film on top of the coating caused by Cl-stimulated rutile formation in humid air. These coatings have been shown to improve the lifetime of metal forming tools significantly. Low-friction behavior at elevated temperatures, which is a pre-requisite for dry cutting operations, can be achieved by liquid oxide lubrication. This can be realized by various nitride phases, e.g. VN, WN, Mo@sub2@N or MoN, which form low-melting oxides in the temperature range between 400 and 550°C. Melting of these phases occurs between 650 and 850°C. Using a nanoscaled arrangement of these phases in a hard matrix results in a self-adaptation of the friction coefficient to values of 0.18-0.4 at 700°C. Self-hardening to increase the wear resistance can be observed in metastable (Ti,Al)N coatings due to spinodal decomposition into fcc TiN and AlN domains. These nanoscaled coherent domains introduce additional stresses into the coating resulting in a hardness increase in the temperature range between 600 and 1000°C. These nanoscale design approaches allow the utilization of functional properties facilitating the development of next generations hard coatings.

10:00am **SE-TuM6 Design of Functional Coatings***, **D. Hegemann**,* Swiss Federal Laboratories for Materials Testing and Research EMPA, Switzerland, Germany*; A. Fischer,* Swiss Federal Laboratories for Materials Testing and Research EMPA, Switzerland

Since materials are commonly chosen with respect to their bulk characteristics, availability, mechanical properties, and costs, their surface characteristics often do not meet the demands for special applications. The plasma technology is an appropriate method to tailor surface properties selectively and offers a convenient way to design even functionally gradient surface coatings. Using low pressure plasmas, various materials and geometries can be treated in batch or reel-to-reel reactors. When long-term stable surface properties such as wettability are of great interest, well-adherent, stable coatings can be provided minimizing aging effects. Using low power inputs in the course of chemical vapour deposition (CVD) processes, monomer structures can be retained in the gas phase yielding dense and homogeneous functional gradient films. The evaluation of the deposition rate of these radical-dominated plasmas was proven to be an appropriate way to design functionally gradient coatings, since also hints for the optimum deposition conditions are given. Chemicals containing functional groups such as amino, carboxy or epoxy are used to mediate the adhesion between substrate and coating. Siloxane-based plasma coatings enable the deposition of hydrophobic, polymer-like layers or hydrophilic, quartz-like films. Gradient layers are suitable to enhance the adhesion of the functional coatings e.g. by adaptation of the mechanical properties, when an inorganic coating is deposited on a polymeric substrate or an organic coating on a non-polymeric material. These gradient layers can be designed considering the reaction parameters power per gas flow and plasma potentials, which control deposition rate, chemical composition, and mechanical properties. Finally, an example of a physical vapour deposition (PVD) process is given, in which a nm-thin silver film has been coated continuously onto the surface of multifilament yarns to enhance the dischargement of a textile surface.

10:20am **SE-TuM7 Functional Profile Coatings and Film Stress***, **C. Liu**, R. Conley, A.T. Macrander,* Argonne National Laboratory

In recent years we have developed a profile-coating technique to obtain functional thickness-profiled thin films and multilayers. This technique uses a linear motion of the substrate in a dc magnetron sputter system and a contoured mask to obtain the desired profile perpendicular to the substrate-moving direction. The shape of the contour is determined according to the desired profile and the knowledge of the film-thickness distribution at the substrate level. Applications of this technique include laterally graded multilayers and elliptical x-ray Kirkpatrick-Baez (KB) mirrors. An elliptical shape is essential for aberration-free optics. The use of profile coating to make x-ray-quality elliptical KB mirrors overcomes the obstacle of polishing asymmetrical mirror surfaces and provides the x-ray community with a practical way to obtain monolithic KB mirrors for microfocusing. Previously we have used gold as a coating material and cylindrical Si mirrors as substrates to obtain elliptical KB mirrors. More recently we are using flat Si substrates to fabricate elliptical KB mirrors. Substantially thicker and steeper gradients of Au films are needed to obtain an elliptical profile from a flat substrate. The Au films may relax to droplets when the stress in the film is too large. The challenges and solutions for this problem will be discussed.

10:40am **SE-TuM8 The Effect of Surface Finish on Field Emission in Nitrogen-implanted, Silicon Dioxide-Coated Stainless Steel***, **N.D. Theodore**, D. Manos,* College of William and Mary*; C. Hernandez, T. Wang, H.F. Dylla,* Jefferson Lab*; R. Moore,* University at Albany Institute for Materials

The purpose of this study was to assess the changes in tunneling parameters associated with field emission from processed stainless steel surfaces, as a function of their prior surface finish. According to Fowler-Nordheim theory (FNT), field emission from a material is governed by two parameters, alpha and beta, which relate to the work function of the material and to its surface morphology. Thus surface roughening may lead to large changes in field emission due to geometrical enhancements associated with sharp features. In this paper, six 304 stainless steel disks were hand-polished to different finishes, ranging from 1 micron to 30 microns rms roughness. These disks were then coated with a nitrogen-implanted silicon dioxide layer. @footnote1@ Depth Auger electron spectroscopy revealed that the thickness of the coating is approximately 240 nm. Field emission spectroscopy maps, STM maps, and AFM and DekTek scans were also taken of each sample. Data from these scans as well as the compositional character of the coating will be presented. Results show that despite surface morphology, each sample possessed 1-3 emission sites, producing current of 2nA at each emitter at threshold electric fields above 85 MV/m. The coated samples have comparable field emission I-V curves. An interpretation of these data in terms of a total electron energy FNT model will be discussed.@footnote 1@C. Sinclair, et al. Proccedings of the 2001 Particle Accelerator Conference. Chicago, IL, 2001.

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