Tuesday Afternoon, October 30, 2001

Surface Engineering
Room 132 - Session SE-TuA

Hard and Superhard Coatings
Moderator: I. Petrov, University of Illinois, Urbana

2:00pm **SE-TuA1 Microstructure and Mechanical Properties of Zr-Si-N Films Prepared by r.f.- Reactive Sputtering**, ***M. Nose***, Northwestern University, Japan; *W.A. Chiou,* University of California at Irvine; *M. Zhou,* Osaka University, Japan; *T. Mae,* Toyama National College of Technology, Japan; *M. Meshii,* Northwestern University

ZrN and ZrSiN films were prepared in an r.f. sputtering apparatus which has a pair of targets facing each other (referred to as the Facing Target -type r.f. Sputtering). Films were deposited on silicon wafer without bias application nor substrate heating in order to examine only the effect of silicon addition to transition metal nitride films. The transmission electron microscopy studies were carried out in addition to XRD. For the high resolution TEM observation, the field emission type transmission electron microscope (FE-TEM) was used, which provides a point-to-point resolution of 0.1nm. The samples were observed both parallel and perpendicular to the film surface, which were in-plane and cross-sectional view, respectively. In order to investigate the relationship between mechanical properties and microstructure of films, the hardness was measured by a nano-indentation system at room temperature. The load was selected to produce an impression depth below 60nm (not more than 5% of film thickness) so that the influence from the substrate can be neglected. The contents of zirconium, nitrogen and silicon of the films were determined by ZAF method with EPMA. A study of their microstructure and mechanical properties has provided as follows: (1) The hardness and Young's modulus increase with small Si additions reaching maximum values of 35GPa (at 3%Si) and 370GPa (at 5% Si), respectively; (2) The hardest films containing 3%Si did not consist of nano-crystals but clear columnar crystals in the range of 10 to 25nm; (3) The increment of hardness with small amount of Si atoms can be attributed to the solution hardening by Si to ZrN lattice; (4) In the case of ZrSiN films deposited by r.f. sputtering without bias application nor substrate heating, the available result did not ensure the presence of ZrN nano-crystals embedded in Si@sub 3@N@sub 4@ matrix.

2:20pm **SE-TuA2 Characterization of CrBN Films Deposited by Ion Beam Assisted Deposition**, *S.L. Rohde,* ***S.M. Aouadi***, *D.M. Shultze, T.Z. Gorishnyy,* University of Nebraska - Lincoln; *N. Finnegan,* University of Illinois at Urbana-Champaign

This paper reports on the first attempt to grow and analyze CrBN nanocrystalline materials using physical vapor deposition processes. Coatings were deposited at low temperatures (<200 Â°C) on silicon substrates using ion beam assisted deposition (IBAD). These coatings were characterized post-deposition using X-ray diffraction (XRD), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), infrared spectroscopic ellipsometry (IR-SE), and visible-light spectroscopic ellipsometry (VIS-SE). The primary phases in the films were identified using XRD. The surface morphology and nanocrystalline nature of the coatings (grain size of 5 - 7 nm) were deduced using AFM. The mechanical properties (wear rate, hardness, elastic modulii) of the coatings were evaluated using a nanohardness test. The chemical composition and phase composition of the samples were determined from XPS and AES measurements and were subsequently deduced from the analysis of the VIS-SE data. The film compositions deduced from both techniques correlated well. Additionally, XPS, AES, and IR-SE were used to reveal the crystal structure of the BN phase in these ternary compounds.

3:00pm **SE-TuA4 Thin Film Growth by Physical Vapor Deposition in the Presence of Residual Gas**, ***J.M. Schneider***, Linkoping University, Sweden **INVITED**

Vacuum based techniques are characterized by the presence of residual gas. Depending on the affinity of the residual gas to the growing film material, chemical reactions may be possible. Residual gas based impurity incorporation during thin film growth has been reported previously.@footnote 1,@@footnote 2@ Here, the state of the art in residual gas - growing film interactions is reviewed. Sources for residual gas incorporation as well as incorporation mechanisms are described. Furthermore the effect of impurity incorporation on the film structure and film properties are discussed. @FootnoteText@ @footnote 1@ J.M.Schneider et al, Appl.Phys.Lett. 74, 200 (1999). @footnote 2@ J.M.Schneider et al, Appl.Phys.Lett. 75, 3476 (1999).

3:40pm **SE-TuA6 Boron and Boron-Based Coatings as Produced by Vacuum Arc Technology**, ***C.C. Klepper***, HY-Tech Research Corporation; *J.M. Williams,* Oak Ridge National Laboratory; *R.C. Hazelton, E.J. Yadlowsky, E.P. Carlson, M.D. Keitz,* HY-Tech Research Corporation

In principle, boron as a material has many excellent surface properties, including corrosion resistance, very high hardness, refractory properties, and a strong tendency to bond with most substrates. However, the potential technological benefits of the material have not been realizable because of difficulty in synthesis of coatings. Boron is difficult to evaporate, does not sputter well and cannot be thermally sprayed. In the present program, a robust system, based on the vacuum (cathodic) arc technology, for generation and delivery of boron plasmas to substrates has been developed. The system produces a fully-ionized boron plasma, which allows use of substrate bias to control the energetics of deposition. Films and coatings have been produced on 1100 Al, CP-Ti, Ti-6Al-4V, 316 SS, hard chrome plate, 52100 steel and other materials. Analyses have been performed by Rutherford backscattering spectrometry. Properties are being evaluated by nanoindentation hardness and other techniques. First results are that the coatings are smooth, highly adherent, and pore free. A number of applications are contemplated. @FootnoteText@ @footnote 1@ Research sponsored in part by the National Science Foundation under contract # DMI-0078385 with HY-Tech Research Corporation. Research at Oak Ridge National Laboratory is sponsored by the U. S. Department of Energy under contract # DE-AC05-00OR22725 with UT-Battelle, LLC.

4:00pm **SE-TuA7 Ion-bombardment Induced Phase Transformation of Cubic Boron Nitride Studied by Reflection Electron Energy Loss Spectroscopy**, ***Y.Y. Hui***, *K.W. Wong,* Chinese University of Hong Kong, P.R. China; *W.M. Lau,* Chinese University of Hong Kong, P.R. China, People's Republic of China

The phase transformation of cubic boron nitride (c-BN) in the near surface region of a c-BN (111) facet induced by low energy argon ion bombardment has been investigated by reflection electron energy loss spectroscopy (REELS), with the objective of tracking possible growth mechanisms of c-BN in ion assisted vapor deposition. By removing Tougaard background of the REELS spectra, we can quantitatively measure the percentage of different BN phases on c-BN surface after ion bombardment. In addition, varying the energy of the incident electron beam from 250 eV to 650 eV allowed the adjustment of sampling depth of a c-BN surface from 14 Å to 27 Å. It was found that with an ion energy of 500 eV at a fluence of 5 x 10@super 16@ ions/cm@super 2@, 76 % of c-BN was found transformed to h-BN and a-BN in a top surface layer of 8 Å. Lowering down the argon bombardment energy to 200 eV reduced the defective layer thickness to 5 Å. A damage saturation was observed at a fluence of 6 x 10@super 16@ ions/cm@super 2@, at which about 10% of c-BN was transformed into non-cubic phases. Through further investigations on the damage saturation at other ion energies, the effects of ion beam bombardment on a c-BN surface was comprehensively studied. The present work gives, for the first time, a quantitative explanation of the difficulty in growing pure c-BN films with ion assisted deposition and the presence of an upper-bound in ion energy above which h-BN and a-BN are generated.

4:20pm **SE-TuA8 Cubic Boron Nitride Thin Films Deposited on Steel Substrates With Different Interlayers**, *M. Ye,* ***M.P. Delplancke-Ogletree***, Universite Libre de Bruxelles, Belgium

Cubic boron nitride thin films were deposited on steel substrates using electron cyclotron resonance plasma enhanced chemical vapor deposition. Different interlayers, such as BCN, TiBN, Ti, TiN, and hexagonal boron nitride, were investigated regarding to the promotion of cubic boron nitride growth and the improvement of the film mechanical properties. A systematic optimization procedure for the cubic boron nitride formation was carried out regarding the deposition conditions, including the gas composition, substrate temperature, bias voltage. The films were characterized using Fourier transform infrared spectroscopy, transmission electron microscopy, x-ray photoelectron spectroscopy, and atomic force microscopy. It was found that among the different interlayers, hexagonal boron nitride gives the best results.

4:40pm **SE-TuA9 Industrial Laser-Arc Coater for the Deposition of Superhard Amorphous Carbon Films (Diamor)**, ***T. Schuelke***, *H.J. Scheibe, P. Siemroth, B. Schultrich,* Fraunhofer Institute for Materials and Beam Technology

Thin amorphous carbon films (Diamor), deposited through laser-assisted cathodic arc evaporation (LaserArco process), have shown unique properties of great relevance to engineered surfaces for wear and corrosion protection. The high-modulus (> 600 GPa) coatings are superhard

(80GPa) with a low coefficient of friction (0.1 dry against steel). The vast variety of potential applications includes cutting and forming tools as well as components in rolling or sliding contact situations. The LaserArco plasma source and the Diamor deposition process have proven to be consistently reliable on the laboratory scale. Extended application development yielded to an increasing demand for the Diamor coating. Subsequently, the further development aimed at scaling up the technology to industrial dimensions. This development included the design of a flexible and compact plasma source module, which was then integrated into a high volume production coater. The paper discusses the equipment design and capabilities, integration and process transfer issues, and first deposition results obtained in an industrial environment.

5:00pm **SE-TuA10 Deposition of Diamondlike Carbon by Magnetic Pole Enhanced Inductively Coupled Plasma**, *T. Meziani, P. Colpo, G. Ceccone, P. Leray, P.N. Gibson, D. Summa,* ***F. Rossi,*** Joint Research Center, Italy*; P. Ranson,* GREMI, CNRS-Universite d'Orleans, France

The ICP sources are particularly interesting for the deposition of amorphous carbon since they offer the possibility to control independently the ion energy from the ion flux bombarding the substrate, in contrast to capacitively coupled discharge. Diamondlike carbon coatings (a-C:H) were deposited with a novel inductively coupled plasma source (the Magnetic Pole Enhanced ICP or MaPE-ICP) designed and characterized in our laboratory. The MaPE-ICP uses a magnetic pole to concentrate the magnetic flux on the load (i.e. plasma) and shows very interesting features like high plasma density, good plasma uniformity and wide pressure range. Diamondlike carbon coatings were deposited with this source from CH4 and C2H2 precursors. The plasma was studied by Langmuir probe measurements, optical emission spectroscopy and microwave interferometry. Mass spectrometry including ion detection and ion energy distribution measurements have been carried out at the substrate holder surface in order to investigate directly the impinging species on the growing film. The plasma diagnostics and films characterization including FTIR spectroscopy, Raman spectroscopy, and X-ray reflectivity (XRR) were undertaken for various processing parameters. The results were related to the coating properties like hardness and intrinsic stress.

Author Index

Bold page numbers indicate presenter