Tuesday Morning, November 3, 1998

Vacuum Metallurgy Division
Room 328 - Session VM+TF-TuM

Advances in Hard and Superhard Coatings

Moderator: A. Inspektor, Kennemetal, Inc.

8:20am **VM+TF-TuM1 Deposition, Structure, and Properties of Superlattice Thin Films***, **S.A. Barnett**, A. Madan, P. Yashar, I. Kim,* Northwestern University **INVITED**

In this talk, superlattice thin films with nitride/nitride, metal/nitride, and oxide/oxide layers are described. Processing issues for high-rate superlattice deposition using reactive magnetron sputtering are described, including reactive-gas partial pressure control for obtaining stoichiometric layers and use of substrate bias to achieve ion bombardment densification. The stability of the layered structures at elevated temperatures is described; it is found that nanometer thick layers can exhibit excellent stability in cases where the relevant phase diagram shows little miscibility. The key materials criteria for obtaining hardness enhancements are delineated by making comparisons between different superlattice systems. Hardness predictions based on dislocation glide mechanisms are discussed. For cases where both superlattice layers have the same structure, a substantial difference between the layer shear moduli is required to limit dislocation motion and thereby strengthen the material. Superlattices where the layers have different structures, such that there is no common dislocation glide system, can also exhibit large hardness enhancements.

9:00am **VM+TF-TuM3 In-situ and Ex-situ Ellipsometric Analysis of Cr, CrN, Cr@sub 2@N Thin Films***, D.M. Mihut, S.R. Kirkpatrick, **S.L. Rohde**,* University of Nebraska, Lincoln

Chromium nitride thin films have technological applications in the tool and decorative coating industries, as well as providing an "environmentally-friendly" alternative to hard chrome coatings due to their unique combination of properties such as: low cost, high hardness (1600 - 3000 HK), excellent wear, corrosion, and oxidation resistance (up to 800 °C). An array of chromium and chromium nitride film monolithic and multilayered films were deposited in a ultra-high vacuum chamber equipped with an unbalanced magnetron sputtering system that combines the advantages of high-rate magnetron sputtering with high-flux, low energy ion bombardment. Ellipsometric analysis of the films was carried out by modeling layers of both stoichiometric and off-stoichiometry Cr, CrN and Cr@sub2@N thin films deposited on silicon. The ex-situ ellipsometry measurements were compared with X-ray diffraction measurements, and in-situ obtained ellipsometric information. The optical constants for CrN and Cr@sub2@N obtained using optical ellipsometry are given and compared with the optical constants for CrN and Cr@sub2@N found in the literature, and the potential of using ellipsometry in the monitoring and/or control of ionized PVD processes explored.

9:20am **VM+TF-TuM4 AlN/cBN Magnetron Sputtering: Effects on Adhesion and Phase Stabilization***, **W. Otaño**, L.J. Pilione, R. Messier,* Pennsylvania State University*; J.J. Santiago-Avilés,* University of Pennsylvania*; G. Lamaze,* National Institute of Science and Technology

The deposition of cubic boron nitride (cBN) thin films is of interest from a technological and fundamental point of view. It has been well established that the cubic phase stabilization depends on the energetic bombardment of the growing film. As a result of this bombardment the films show high stress levels that eventually produce delamination from the substrate. It is therefore interesting to consider atomic additions and compliant interfaces as alternative pathways to reduce the cBN stress level and/or improve film adhesion. With this purpose cBN thin films were co-deposited with Al reactively sputtered. The effects of the addition of aluminum and/or the use of AlN interlayers in the stabilization and adhesion of cBN films will be presented. The BN films were deposited by rf unbalanced magnetron sputtering and the substrate was biased using a low frequency dc pulsed excitation signal. Films with over 70% of the cubic phase, as measured by FTIR, were deposited at low negative bias voltages. A second dc pulsed power supply was used to reactively sputter the aluminum. AlN was added as an interlayer between the substrate and the BN film as well as co-deposited at different sputtering powers. The films were analyzed by FTIR, RBS and neutron depth profiling. It was found that the addition of Al to the BN films leads to a destabilization of the cubic phase for AlxB1-xN compositions above x=0.04. AlN interlayers deposited at specific pressures were found to prevent the delamination of the cBN films. A 0.7 micron multilayer coating of AlN/cBN was prepared that did not delaminate from the substrate.

9:40am **VM+TF-TuM5 Energetics of Cubic Boron Nitride Deposition***, **R. Clarke**, D. Litvinov,* University of Michigan **INVITED**

As a structural analog of diamond, cubic boron nitride (c-BN)is attracting increasing interest as an ultrahard coating material. An ongoing challenge towards exploiting the favorable properties of c-BN, including its chemical intertness and high thermal conductivity, is its tendency to build up substantial levels of stress at practically useful thicknesses of a few microns. If this stress is not remediated, it can lead to loss of adhesion. In this talk we present recent results demonstrating our approach to characterizing and controlling the intrinsic stress in c-BN coatings. Through an improved understanding of the kinetics of c-BN growth, using dc-biased ECR-assisted sputtering, we have achieved highly adhesive coatings on Silicon with film thicknesses up to 2µm. A novel multibeam optical wafer curvature method allows us to track, in-situ, the stress build-up during growth, and to implement 'reduced-bias' conditions after the initial nucleation and coalescence of c-BN islands. Reducing the kinetic energy of arriving nitrogen ions in this way (to ~ 50eV), leads to fewer defects in the film, reduced levels of stress, and higher growth rates, compared to values obtained at bias conditions necessary to initiate c-BN growth. Work partly supported by ONR grant N00014-94-J-0763, and by k-Space Associates Inc.

10:20am **VM+TF-TuM7 Deposition and Characterization of Ultra Thin CNx Films as a Thin-Film Disk Overcoat***, **X. Chu**, Z.D. Yang, J.F. Ying, S. Wang, B. Zhang,* MMC Technology Inc.

The deposition of CNx films has received great attention recently because of the potential of this material to have mechanical properties similar to diamond. One practical application of magnetron sputtered CNx films is for use as a protective coating for thin film magnetic recording disks. Ever increasing magnetic recording density requires not only a robust head-media interface, but also minimum spacing loss due to fly height, carbon thickness and magnetic layer thickness. A functional overcoat with a thickness of 50 to 100 Å is needed for the next generation recording medium. In this paper, we investigate sputtering process parameter effects on CNx film structure and mechanical properties. Target power, N% in the sputter gas, substrate temperature, and substrate bias were varied and correlated to film properties. XPS and Raman spectrum were used to study the bonding structure of the film. Sputtered CHx and CHNx films with 80 Å thicknesses and ion beam deposited CHx films were also studied for comparison. Nano-scratch wear tests showed that the 80Å film had the best wear property with 10-15% N in the gas. CNx films appear to be more wear resistant than CHx and CHNx films based on the nano-scratch test. Tribology properties of lubricated disks were tested using Contact Start Stop (CSS) testers and CNx carbon wear results can be correlated to the AFM nano-wear test. CHx films also showed good CSS results, suggesting that lubricant - carbon interaction is another important factor in head - media tribology.

10:40am **VM+TF-TuM8 Carbon and Carbon Nitride Films Prepared by Low-Energy, Isotopically-Mass-Separated, Negative C@sub 2@@super -@ and CN@super -@ Ions***, **N.T. Tsubouchi**, A.C. Chayahara, A.K. Kinomura, C.H. Heck, Y.H. Horino,* Osaka National Research Institute, AIST, Japan

Amorphous carbon (a-C) and carbon nitride (a-CN@sub x@) films were prepared by ion beam deposition using isotopically mass-separated, hyperthermal (50-400 eV) negative ion species such as @super 12@C@sub 2@@super -@ and @super 12@C@super 14@N@super -@ under ultra high vacuum (UHV) condition. Variation of optical constants as a function of ion's kinetic energy was investigated in the infrared-visible light region (0.8-1.5 eV). Optical band gaps of the films were estimated from optical constants. For the amorphous carbon films, the gaps were about 1.0-2.3 eV depending on kinetic energy of negative carbon ions. For the CN films, the values which did not almost depend on kinetic energy were about 0.8 eV.

11:00am **VM+TF-TuM9 Investigation on Multilayered Chemical Vapor Deposited Ti/TiN Films***, **J.C. Hu**,* National Tsing Hua Univ., Rep. of China, Republic of China*; T.C. Chang,* National Nano Device Lab, Rep. of China, Republic of China*; L.-J. Chen,* National Tsing Hua Univ., Rep. of China, Republic of China*; Y.L. Yang,* National Nano Device Lab, Rep. of China, Republic of China*; P.T. Liu,* National Chiao Tung Univ., Rep. of China, Republic of China*; S.Y. Chen,* National Tsing Hua Univ., Rep. of China, Republic of China*; C.Y. Chang,* National Chiao Tung Univ., Rep. of China, Taiwan, Republic of China

As the device dimensions scale down to deep submicron level, chemical vapor deposition (CVD) for TiN films provided excellent step coverage and uniformity. Cu is likely to replace Al for interconnect metallization in future integrated circuits. On the other hand, the CVD-TiN films are usually of columnar structure. As a result, the fast diffusion of Al (or Cu) and Si atoms along TiN grain boundaries would degrade the device performance severely. In the present study, a novel multilayered CVD-Ti/TiN structure is formed to alleviate the grain boundary effects. To investigation the barrier property of the multilayered Ti/TiN films, junction leakage current was also measured. All the films were deposited by CVD processed in a MRC multichamber cluster tool, using TiCl@sub 4@, NH@sub 3@ and H@sub 2@ as reactants. The Ti and TiN films were deposited by plasma enhanced CVD and low pressure CVD, respectively. In order to reduce chlorine concentration of the films, NH@sub 3@ plasma post-treatment was applied to multilayered CVD-Ti/TiN films. In addition, electroless deposition of Cu was deposited on the multilayered CVD-Ti/TiN films. Transmission electron microscopy and X-ray diffractometry were utilized to investigate the microstructure and crystal orientation. Auger electron spectrocopy was applied to determine the stoichiometry and uniformity along the depth direction. The morphology was studied by a field emission scanning electron microscopy. Electrical measurement was used by HP-4145. The enhanced multilayered Ti/TiN stack found to be a robust barrier against Al/Si interdiffusion. It also improved the electrical property of the films. The resistivity of the film was found to reduce from 240 to 120 µm@OMEGA@-cm by multilayered Ti/TiN structure with the NH@sub 3@ plasma post-treatment. The leakage current can also be kept low enough for device application. In addition, the thermal stability of electroless Cu/mutilayered (CVD-Ti/TiN)/TiSi@sub 2@/Si structure was improved.

11:20am **VM+TF-TuM10 Chemical Vapor Deposition of Metal (Ti) and Ceramic (TiO@sub 2@, TiN) Thin Films via Gas-Phase Reaction of Titanium Tetrachloride and Sodium Metal Vapor***, **J.H. Hendricks**, M.I. Aquino, J.E. Maslar, M.R. Zachariah,* National Institute of Standards and Technology

A new route for Chemical Vapor Deposition (CVD) of metal and ceramic thin films has been demonstrated. This novel method involves the use of a low pressure coflow diffusion reactor to react sodium vapor with titanium tetrachloride in the presence of a non-reactive gas (Ar) or a reactive gas (N@sub 2@, O@sub 2@). This reaction chemistry is described by the following general equation: (mn)Na + nMX@sub n@ --@super Ar@--> (M)@sub n@ + (nm)NaX. Here, Na is an alkali metal (e.g. Na, K, Cs, or Rb), M is a metal (e.g. Ti, Ta, Pt, W, ...) or non-metal (e.g. B, C, Si, ...), X is a halogen (e.g. F, Cl, Br, or I), Ar is a non-reactive gas (e.g. Ar or He) and m and n are integers. In this reaction, the alkali metal strips halogen from the metal or non-metal halide. The metal or non-metal is then free to form a thin film on a substrate placed in the reaction zone. This chemistry should be generic for the deposition of a wide class of metallic and ceramic thin films, and it is suggested that this technique could be used to grow superhard BN and CN thin films at temperatures which are significantly lower than conventional CVD techniques. Guided by theoretical modeling, reactant concentrations and substrate temperatures were adjusted to prevent salt (NaCl) incorporation into the deposited thin films. Using the described techniques, we have now produced Ti and TiN thin films on Cu substrates at 610 °C, and TiO@sub 2@ thin films on Si substrates at 600 °C. These temperatures are considerably lower than the (1000 to 1200) °C required for conventional CVD of Ti (by decomposition of titanium tetraiodide). The quality and composition of the thin films were analyzed by scanning electron microscopy (SEM), energy dispersive x-ray spectrometry (EDS), x-ray diffraction (XRD), Raman spectroscopy, transmission electron spectrometry (TEM), and selected area electron diffraction (SAED). Future work will focus on the use of this novel technique to grow CN and BN thin films.

11:40am **VM+TF-TuM11 Low Energy Ion Beam Deposition of Oriented Diamond Microcrystallites***, **P.K. Tse**, R.W.M. Kwok, K.M. Lui, W.M. Lau,* The Chinese University of Hong Kong, China

Ion beam deposition provides an additional control of film properties over the chemical vapor deposition (CVD) via the change of ion beam energy. In this study, low energy ion beam deposition of carbon films on silicon in the ion energy range of 200 - 1050 eV was studied. The ion beam was characterized by a Faraday cup equipped with a retarding lens. The films were characterized using X-ray photoelectron spectroscopy, characteristic electron energy loss analysis, and atomic force microscopy. It was found that graphitic films, amorphous carbon films and oriented diamond microcrystallites could be obtained separately at different ion beam energies. Highly oriented diamond microcrystallites were deposited on Si (100) wafer at energy of 200eV and substrate temperature of 420°C. The ion beam deposition will be used as a diamond seeding process which will be followed by a typical hot filament CVD process, for the growth of oriented diamond films on Si (100).

Author Index

Bold page numbers indicate presenter