Monday Afternoon, October 25, 1999

Thin Films Division Room 620 - Session TF+VM-MoA

Advances in Hard and Superhard Coatings II Moderator: B. Holloway, College of William & Mary

2:00pm TF+VM-MoA1 Characterization of PVD TiN/CN@subx@ and TiN/Si@sub3@N@sub4@ Multilayer Coatings, Y.H. Chen, Y.W. Chung, Northwestern University

TiN coatings are commonly used in various tribological applications for their wear resistance and inertness to steels. However, TiN coatings predominantly grow with a columnar grain structure. The columnar grain boundaries become the usual sites for crack initiation, resulting in earlier failure of TiN coatings (especially thick coatings). In our research, TiN/a-CN@subx@ and TiN/a-Si@sub3@N@sub4@ nanolayered superlattice coatings are developed to suppress the columnar structure. We used a-CN@subx@ and a-Si@sub3@N@sub4@ primarily to periodically interrupt and renucleate the growth of TiN. In addition, the amorphous layers may serve to suppress the transmission of dislocations from one TiN layer to another, thereby enhancing the hardness of the coating. Both coatings have been demonstrated to achieve hardness in the 50 GPa range, consistent with recent reports for high hardness of TiN/a-Si@sub3@N@sub4@ nanocomposites. The correlation between microstructure and mechanical properties of these coatings will be presented.

2:20pm TF+VM-MoA2 Effects of Interface Mixing on Adhesion of Amorphous Carbon Films Synthesized by Variable-Energy Direct Carbon Ion Beam Deposition, *M.H. Sohn, S. Kim,* SKION Corporation

Using a variable-energy direct carbon ion beam deposition technique, thin amorphous carbon films were grown on silicon substrate. Interface modification was performed using C@super -@ energies in the range of 300-500 eV prior to the growth of the film to enhance adhesion of the film. By lowering the energy of the C@super -@ beam to 150 eV, amorphous carbon film was continuously grown after the interface modification. Highresolution electron microscopy illustrated that the silicon surface was severely damaged by 500 eV C@super -@ beam and the thickness of damage layer was about 15 nm. Carbon composition profile in silicon investigated by electron energy loss spectroscopy showed that 500 eV C@super -@ beam implanted carbon into silicon up to 30 nm in depth and carbon was mixed with silicon at this implanted region. Silicon L-edge study at the C/Si mixed region found C-Si bonding formation only at the surface of silicon over 2-3 nm-thick layers. The damage layer or C/Si mixing was not observed at 300 eV C@super -@ beam modification. Wear testing found that strong adhesion occurred in samples modified at 500 eV, which indicated complete mixing at the interface. At 300 eV, modified samples exhibited delamination failure, which indicated inferior adhesion of the films.

2:40pm TF+VM-MoA3 Synthesis of Diamondlike Carbon Films with Superlow Friction and Wear Properties, *A. Erdemir, O.L. Eryilmaz, G. Fenske,* Argonne National Laboratory

In this study, we introduce a new diamond-like carbon (DLC) film providing friction coefficients of 0.001 and wear rates of 10-9 to 10-10 mm3/N.m in inert gas environments (e.g., dry nitrogen and argon). The film was grown on steel and sapphire substrates in a plasma enhanced chemical vapor deposition system using a hydrogen-rich plasma. Employing a combination of transmission electron microscopy, electron diffraction, Raman spectroscopy, and electron energy loss spectroscopy, we explored the structural chemistry of the resultant DLC films and correlated these findings with their friction and wear mechanisms. The results of tribological tests under a 10 N load (creating an initial peak Hertz pressure of 1 GPa on steel test pairs) and at 0.2 to 0.5 m/s sliding velocities indicated that a close correlation exists between the friction and wear coefficients of DLC films and the source gas chemistry. Specifically, films grown in source gases with higher hydrogen-to-carbon ratios had the lowest friction coefficients and the highest wear resistance. The lowest friction coefficient (i.e., 0.001 on a sapphire substrate) was achieved with a film derived from a gas mixture consisting of 25% methane and 75% hydrogen. The wear-debris particles found in and around the wear scars and tracks were analyzed by Raman spectroscopy and FTIR to elucidate the wear mechanism of DLC films. @FootnoteText@ *Work supported by the U.S. Department of Energy under contract W-31-109-Eng-38.

3:00pm TF+VM-MoA4 Optical Characteristics of Carbon Nitride: Relationship with Mechanical Behavior and Possible Fullerene-like Microstructure, V. Hajek, D. Poitras, D. Dalacu, Ecole Polytechnique, Canada; A. Bergeron, Optical Coating Laboratory Inc.; L. Martinu, Ecole Polytechnique, Canada; K. Rusnak, J. Vlcek, University of West Bohemia, Czech Republic

Crystalline @beta@-C@sub 3@N@sub 4@ was predicted to exhibit extreme properties, such as hardness, comparable to that of diamond. Although the synthesis of the crystalline metastable phase has not been fully confirmed yet, already prepared "amorphous" CNx films possess very attractive characteristics. In our earlier studies we have shown that these films possess high hardness (up to 30 GPa), high elastic recovery (up to 85 %), and interesting tribological behavior. Such films prepared at temperatures above 200 °C, using magnetron sputtering, are predicted in recent literature to possess a fullerene-like microstructure. In our recent work we suggested to extend this model to account for hydrogen incorporation: Excessive amount (> 1 at. %) of hydrogen in the films is believed to inhibit crosslinking between graphite-like planes containing carbon and nitrogen, and thus to hamper formation of the fullerene-like microstructure. In the present work we focus on the optical properties of CN@sub x@ films studied by spectroscopic ellipsometry and spectrophotometry. Different dispersion relations such as Sellmeier, Cauchy and Drude-Lorenz oscillator were used to determine optical constants n and k. The optical behavior is related to the film microstructure and the film fabrication conditions. CN@sub x@ layers were deposited on Si substrates by reactive DC magnetron sputtering of graphite target in nitrogen plasma at a substrate temperature of 600 °C and at a substrate bias ranging from -300 to -700 V. Films were found substoichiometric in nitrogen (from 12 to 24 at. %), and a concentration of hydrogen between 1 and 5 at. % was revealed by elastic recoil detection (ERD) analysis. Increased hydrogen content was accompanied by lower hardness, elastic recovery and adhesion, by higher electrical resistivity (from 20 to 970 @ohm@cm), by formation of C-H and N-H bonds (FTIR), and by higher optical transparency in the VIS and IR regions. The latter characteristics are related to the variation of optical bandgap which increases with hydrogen incorporation.

3:20pm TF+VM-MoA5 Preparation and Properties Enhancement of Silicon Carbonitride Films Using Reactive Magnetron Sputtering, X.-M. He, K.C. Walter, M. Nastasi, Los Alamos National Laboratory

Silicon carbonitride (Si(C,N)) films were synthesized on Si (100) and metal substrates by reactive d.c. magnetron sputtering with Ar as the sputtering gas and N@sub 2@ as the reactive gas. The composition and properties of the films were studied with respect to the influences of the bias voltage applied to substrates, the deposition temperature, and the gas flow ratio of N@sub 2@ to Ar (or F@sub N2@/F@sub Ar@). The Si(C,N) mechanical properties, hardness, fracture, and tribological properties, were observed to be highly depended on the processing conditions such as substrate temperature, the arrival ratios of ion to deposition atom, J@sub i@/J@sub a@, the negative bias voltage and F@sub N2@/F@sub Ar@. Under optimum conditions amorphous coatings with high wear resistance and harnesses as high as 40 GPa were prepared. The role of synthesis parameters on the structure, compositions, and mechanical properties will be discussed in detail.

4:00pm TF+VM-MoA7 Bonding Structure and Optical Properties of Sidoped Diamond-like Films Synthesized by Plasma Immersion Ion Processing, X.-M. He, K.C. Walter, M. Nastasi, Los Alamos National Laboratory

Silicon-doped diamond-like carbon (DLC) films were prepared on Si(100), glass, and PMMA (polymethyl methacrylate) substrates at room temperature by using C@sub 2@H@sub 2@-SiH@sub 4@-Ar plasma immersion ion processing (PIIP) and their compositions were modified by changing deposition parameters of the gas composition and the negative bias voltages applied on the substrates. The influence of the Si dopant on the bonding structure and the properties of the DLC films were investigated by using ion beam analysis techniques, Raman shift, infrared spectroscopy, and by analyzing the measured density and hardness. The electrical and optical properties of Si-doped DLC films have been evaluated by the study of the electrical resistivity, the refractive index, the absorption coefficient, and the optical gap energy for the films. It was found that the variation of Si dopant was highly correlated with the changes of chemical bonding structure and properties. The careful control of gas flow ratio of C@sub 2@H@sub 2@ : SiH@sub 4@ : Ar in low pressure PIIP was needed for the growth of DLC films with optimal combinations of increased sp3

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bonding structure, high hardness and density, and improved optical properties. The resultant Si-doped DLC films with a Si content up to 28 at % exhibited a higher optical transmittance in the visible light range. The tribological tests of Si-doped DLC films were carried out using a pin-on-disk tribometer in ambient air at about 15% relative humidity. The results shown that Si-doped DLC films exhibited a low friction coefficient of 0.03-0.08 and an enhanced wear resistance despite of deposition of the films on Si (100), glass, or PMMA substrates. The effects of ion impingement during PIIP deposition on the formation of Si-incorporated DLC films were discussed.

4:20pm TF+VM-MoA8 Surface Acoustic Wave Propagation Properties of Nitrogenated Diamond-like Carbon Films, J.Y. Kim, H.J. Chung, H.J. Kim, Seoul National University, Korea; H.M. Cho, H.K. Yang, J.C. Park, Korea Electronics Technology Institute

Surface acoustic wave (SAW) devices have become more important as mobile telecommunication systems need high-frequency, low-loss, and down-sized components. Higher-frequency SAW devices can be more easily realized by developing new high-SAW-velocity materials. The ZnO/diamond/Si multilayer structure is one of the most promising material components for GHz-band SAW filters because of its high SAW velocity above 10,000 m/sec. Recently, DLC films are also considered to have a potential for this application, since their physical properties, such as hardness and elastic modulus, are comparable with those of diamond. However, the residual stress during deposition is an obstacle to this application, because the film having high residual stress could not sustain during the full fabrication process of SAW devices. Recently, there have been many reports of the nitrogenated DLC films, which is mainly driven by the possibility of realizing the superhard @beta@-C@sub3@N@sub4@ phase. Some researchers reported the residual stress reduction by nitrogen incorporation without any other significant change in film mechanical properties. In this study, nitrogenated (a-C:N) films were deposited by reactive sputtering method. The a-C:N film properties were investigated using Raman spectroscopy, FT-IR, AES, and x-ray reflectivity (GIXR). To investigate the SAW propagation characteristics of the a-C:N films, SAW filters were fabricated using interdigital transducer electrodes between the ZnO layer and a-C:N/Si(100), which were used to excite surface acoustic waves. SAW velocities were calculated from the frequency-response measurements of SAW filters. A generalized SAW mode with velocities between 5,000 m/s and 7,000 m/s were observed as well as a high velocity Pseudo-SAW mode with 14,000 m/s. We also calculated the film elastic constants from SAW propagation velocities in the layered structure.

4:40pm TF+VM-MoA9 High Deposition Rate Diamondlike Carbon Films Deposited using Permanenet Magnet Electron Cyclotron Resonance Plasmas, C. Doughty, J.B. Bailey, ASTeX PlasmaQuest

We report deposition of hard diamondlike carbon films at deposition rates exceeding 500 nm/min using permanent magnet ECR plasma CVD. These films are characterized by high hardness ~10-20 GPA and stresses ~300-500 MPa. The deposition rates obtained exceed typical values for plasma CVD deposition by a factor of 10-50 and enable a range of novel applications including economically attractive deposition of >10-um-thick films. These films have electrical resistivities ~10^12 ohm cm at 1 MV/cm, and optical bandgaps ~2 eV. Index of refraction can be controlled over the range 1.7 - 2.2 by manipulation of the deposition parameters. Film hardness has been measured by nanoindentation and will be reported as a function of deposition parameters. Adhesion promoting processes have been developed and films exceeding 5 um thickness have been deposited on silicon, glass and stainless steel substrates without delamination failures. Thin films (

5:00pm **TF+VM-MoA10 Polymerization in Remote Hydrocarbon Deposition Plasmas**, *A. de Graaf, M.F.A.M. van Hest,* **M.C.M. van de** *Sanden, K.G.Y. Letourneur, D.C. Schram,* Eindhoven University of Technology, The Netherlands

The chemistry of expanding argon plasmas into which either methane (CH@sub 4@) or acetylene (C@sub 2@H@sub 2@) is injected for fast deposition of a-C:H, DLC and diamond films was studied by means of mass spectrometry, Fourier transform infrared absorption and in situ ellipsometry. The measurements reveal that the plasma chemistry of the expanding Ar/C@sub 2@H@sub 2@ and Ar/CH@sub 4@ plasmas is dominated by argon ion induced dissociation of the precursor gas. For acetylene injection the ion-induced dissociation is very efficient leading to complete depletion under certain conditions. For methane injection however, even under conditions of highest reactivity 100% dissociation of the precursor gas can not be reached. In an Ar/CH@sub 4@ plasma under

certain conditions up to 40% of the injected precursor flow is transformed into C@sub m@H@sub n@ (m>1) polymers. In an Ar/C@sub 2@H@sub 2@ plasma the polymerization is much less (maximum 4%) and preferentially C@sub 2m@H@sub n@ polymers are formed. This suggests that in an Ar/C@sub 2@H@sub 2@ plasma the C@sub 2@H radicals are the main building blocks in the polymerization process and that they are probably also the dominant radicals in the deposition process. In the case of acetylene injection the deposition rate as measured in situ by ellipsometry is proportional to the depletion of the precursor gas. For methane injection however this proportonality does not hold even when the polymerization is taken into account. The difference in the polymerization rate and the dependence of the deposition rate on the gas depletion for the two plasmas is attributed to the different loss probabilities of the radicals formed in the dissociation. It is suggested that the large amount of C@sub 2@H@sub 2@ formed in the Ar/CH@sub 4@ plasma may lead to formation of radicals which, due to their relatively high loss probability, may become the dominant growth precursors.

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