Tuesday Morning, November 5, 2002

Thin Films
Room: C-101 - Session TF-TuM

Mechanical Properties of Thin Films
Moderator: L. Hultman, Linkoping University, Sweden

8:20am **TF-TuM1 Mechanical Properties of TiN and $Ti_{1-x}Si_xN_y$ Coatings using Surface Acoustic Wave Techniques**, ***D.C. Hurley***, National Institute of Standards and Technology, *A.J. Richards*, CSIRO, Australia, *V.K. Tewary*, National Institute of Standards and Technology, *A. Bendavid, P.J. Martin*, CSIRO, Australia

Surface acoustic wave (SAW) spectroscopy is a nondestructive, noncontacting technique to determine thin-film mechanical behavior. In some cases, it may be more suitable than other, more conventional methods. The approach involves optical generation and detection of SAWs over a bandwidth of several hundred megahertz. Measurements of the SAW displacement versus propagation distance allow the frequency dependence of the phase velocity (dispersion relation) to be determined. Quantitative values for properties like Young's modulus E and film thickness d are obtained by comparing the dispersion data to analytical models. Our model allows analysis for anisotropic film properties and uses an elastodynamic Green's function method. We illustrate our techniques with results on TiN and $Ti_{1-x}Si_xN_y$ coatings for enhanced wear resistance. In TiN films prepared with filtered-arc physical vapor deposition techniques, E increased from 368 to 453 GPa with increasing d and decreasing compressive residual stress. SAW results were in good agreement with those from two destructive methods: instrumented indentation techniques (IIT) for E and scanning electron microscopy for d. $Ti_{1-x}Si_xN_y$ films with a nanocomposite structure were prepared by concurrent reactive deposition of Ti by a cathodic arc source and Si by a magnetron sputter source. Values greater than 40 GPa for the microhardness H were measured by IIT. SAW and IIT values for E were in good agreement and ranged from 325 to 417 GPa. Both H and E were observed to depend on the magnetron power or atomic per cent of Si in the films. From these results the ratio H/E, an indicator of wear resistance, was found to be relatively high.

8:40am **TF-TuM2 Mechanical Testing of Thin Films: Experiments and Analysis**, ***O. Kraft***, Forschungszentrum Karlsruhe, Germany, *R. Schwaiger*, Massachusetts Institute of Technology **INVITED**

Several specialized testing techniques have been developed to study the mechanical behavior of thin films, including thermal cycling experiments, micro-tensile testing, bulge testing, nanoindentation, and microbeam deflection. They are specifically aimed at determining material properties such as Young's modulus, yield strength, strain hardening rate, ultimate tensile or fracture strength of thin film materials. For these techniques, however, the required sample geometry, loading and straining conditions can be quite different, and as a result, comparisons between the different techniques are not straightforward. This is illustrated in this paper by studying the deformation behavior of sputter-deposited Cu films with thicknesses between 200 and 1500 nm by considering results from several techniques. In particular, nanoindentation and microbeam deflection experiments on identical samples will be compared which were both analyzed by using finite element modeling. The main difference between the two techniques is that the plastic strain is less than 1 % during a bending experiment while it is about 8 % during indentation. It will be shown that it is not possible to describe the stress-strain behavior of the films over this wide range of plastic strains by the use of a simple bi-linear material law. Nevertheless, both techniques show that during deformation of thin metal films strong strain hardening effects are present.

9:20am **TF-TuM4 Copper Gallium Thin Film as the Stress-release Coating for Optical Fiber Metallization**, ***M.X. Ouyang***, *L.D. Kinney*, Corning Inc.

It is well known that the strength of optical fiber can be degraded dramatically during fiber stripping and UV irradiation.[1] The existence of defects which has been created both on the surface and inside optical fibers during the fiber fabrication process is the reason for their mechanical degradation.[2] Flaws on the surface of glass fibers have a significant effect on the fiber strength. However, little is reported on optical fiber mechanical strength change due to fiber surface treatment and metallization. The report discusses mechanical properties of metallized optical fibers (strength, adhesion, stress, solderability) and the impact on optical properties such as PMD spectra. The fiber strength of polymer removed optical fibers with different surface and coatings is studied. Using a thin Cu:Ga film (80 nm)[3] to replace Cr or Cr2O3 film as the adhesion enhancement layer between Pt film (1 µm) and single mode fiber (SMF), the average fiber pulling strength increased 5-6 times. Polarization mode dispersion (PMD) spectra shows that only 0.1 nm blue shift is observed comparing with 0.3-0.4 nm shifting using Cr or Cr2O3 as under layer or only Pt film without underlayer. Cu:Ga film has excellent wetting properties to Pb:Sn (1:1) solder. Cu:Ga films on glass and Si substrates are solderable.

[1]Varelas, D., et al: "UV-induced mechanical degradation of optical fibers", Electron. Lett., 1997, 33, (9).pp.804-806

[2]R. Olshansky and D.R. Maurer: "Tensile strength and fatigue of optical fibers": J. Appl. Phys, 1976, 47, (10), pp4497-4499

[3]Mike X. Ouyang, et al: US patent : US6347175 B1

10:00am **TF-TuM6 Role of Interface Free Energy in Hardness Enhancement in PTFE/Al, PTFE/Cu, and PTFE/Ti Nanomultilayered Thin Films**, ***E. Kusano***, *N. Kikuchi, I. Yoshimura, A. Kinbara, H. Nanto*, Kanazawa Institute of Technology, Japan

In nanostructured materials, interface or surface affects their mechanical properties strongly. In this study internal stress and hardness in polytetrafluoroethylene (PTFE)/Al, PTFE/Cu, and PTFE/Ti nanomultilayered thin films have been investigated as a function of modulation period, i.e., the number of interfaces in the films. PTFE, which has a low surface energy of 17 mJ/m^2 was used to introduce a large interface energy in thin films. The designed value of interface energy accumulated in thin films is up to 80 J/m^2. PTFE thin film was deposited by rf magnetron sputtering using the target of a PTFE sheet. Al, Cu, and Ti were deposited by dc magnetron sputtering. Multilayers were fabricated sequentially without breaking vacuum on aluminosilicate glass. The total thickness of films was about 200 nm for all samples. Modulation period was changed from 10 nm to 200 nm. Internal stress in metal layers was evaluated from strain obtained by X-ray diffraction measurements. Hardness was measured by nanoindentation. The surface energy of a monolithic PTFE film deposited by sputtering was about 18 mJ/m^2. The compressive internal stress evaluated by XRD increases with decreasing the modulation period. Hardness enhancements were also investigated for films with a short modulation period. Further it was shown that the hardness has a linear relationship to internal stress. A large compressive stress introduced in thin films increases the energy needed to drive cracks made by a nanoindentation deep into the film, resulting in the increase in hardness. The results emphasize an important role of interfaces in mechanical properties of nanomultilayered thin films.

10:20am **TF-TuM7 Pulsed Laser Ablated MoS_2-Al Films Characterized for Friction and Wear in Humid Conditions**, ***J.J. Nainaparampil***, AFRL/MLBT, *A.R. Phani, J.E. Kraznowski*, University of New Hampshire, *J.S. Zabinski*, AFRL/MLBT

Molybdenum disulphide films are well known solid lubes in dry environmental conditions. However, even a slightest increase in humidity can adversely affect the performance of these films. Different authors tried various additives to strengthen the system and to change microstructure in such a way that wear life could be increased even in dry conditions compared to pure MoS_2 films.[1,2,3] Some of those work addressed the problem of humidity by adding metals and oxides of metals. However, the complete explanation of the phenomenon has not been discovered and an approach that focuses on both tribochemical reactions and microstructure is required. The work reported here deals with addition of Al metal as an additive to resist the degradation of MoS_2 coatings in humid conditions. Since aluminum shows very high affinity for (OH) radicals to form $Al(OH)_3$, it is suggested that aluminum likely reacts with H_2O in humid conditions. $Al(OH)_3$ is relatively soft and may enhance lubrication and reduce friction and wear. The microstructure of Al-containing films and their mechanical properties may also contribute to tribological performance. Films for this study were prepared by pulsed laser ablation of MoS_2 targets along with magnetron sputtering of aluminum to form aluminum alloyed MoS_2 films. Data from pin on disc tribotests showed long wear life and a friction coefficient between 0.1 and 0.2 even at high relative humidity (i.e., 50%). The microstructure and stoichiometry of these films are under further study to control mechanical properties such as hardness, adhesion and toughness. Micro-Raman and high-resolution SEM pictures of wear tracks will be presented.

[1]Stupp B. C. Thin Solid Films, 84, 1981, 257

[2]J. S. Zabinski, M. S. Donley, and S. D. Walck, Tribol. Trans. 38(4) 1995, 894

[3]E. Pfluger, J. D. Holbery, A. Savan, Y. Gerbig, Q. Luo, D. B. Lewis, W. D. Munz, Proceedings of II World Tribology Congress, Vienna, 2001, 313.

10:40am **TF-TuM8 Thin Films of TiSiC MAX Phase - Growth, Characterisation and Properties**, ***J. Emmerlich***, Linköping University Sweden, *J.-P. Palmquist*, Uppsala University, Sweden, *T. Seppänen*, *J. Molina*, Linköping University, Sweden, *U. Jansson*, Uppsala University, Sweden, *J. Birch*, Linköping University, Sweden, *P. Isberg*, ABB Group Service Center AB, Sweden, *L. Hultman*, LinköpingUniversity, Sweden

Ti_3SiC_2 a so-called MAX-Phase (M: early transition metal; A: element of A-group III, IV (V); X: C or N) with a chemical composition of $M_{n+1}AX_n$ belongs to a new class of ternary carbides. The unique compilation of properties like high electrical and thermal conductivity, ductility, low friction additional to high oxidation and thermal shock resistance make for highly interesting materials. The Ti_3SiC_2 is readily machinable as well as damage tolerant. Polycrystalline Ti_3SiC_2 in bulk form has been investigated and well-characterised since late 1960s. Single crystal Ti_3SiC_2 thin films were recently reported by Palmquist et al. Magnetron sputtering was employed as deposition technique using either Ti and Si targets with a C_{60} evaporation source or deposition from a stoichiometric Ti_3SiC_2 target. This presentation describes a third and new method of employing three single-element-targets: Ti, Si and C. We could establish epitaxial and single-crystalline growth of Ti_3SiC_2 above 700°C. Best results were achieved with -30 V bias and using TiC as nucleation layer. Two epitaxial orientations were deposited on MgO: Ti_3SiC_2(0001)//TiC(111)//MgO(111) and Ti_3SiC_2(104)//TIC(100)//MgO(100). Deviations in Si content led to a mixture of Ti_3SiC_2 and the new Ti_4SiC_3 MAX-phase. Friction measurements carried out with a Hysitron system gave values of µ lower than 0.1. The E-modulus was 325GPa. A conductivity of $4x10^6$ $(\Omega m)^{-1}$ was reported. Nano indentations and nano-tribology experiments in situ AFM and ex situ TEM were made to investigate the deformation behaviour and revealed delaminations, pile-up and kink formation around the indent.

11:00am **TF-TuM9 Carbon Incorporation in Boron Suboxide Thin Films**, ***D. Music***, *V.M. Kugler*, *Zs. Czigány*, *A. Flink*, *O. Werner*, Linköping University, Sweden, *J.M. Schneider*, RWTH-Aachen, Germany, *L. Hultman*, *U. Helmersson*, Linköping University, Sweden

Boron suboxide thin films, with controlled carbon incorporation, were grown by RF dual magnetron sputtering of boron powder and sintered carbon targets in an argon-oxygen atmosphere. Film composition, structure, mechanical, and electrical properties were evaluated by x-ray photoelectron spectroscopy, x-ray diffraction, transmission electron microscopy (TEM), nanoindentation, and high-frequency capacitance-voltage measurements, respectively. B-O-C films (O/B=0.02, carbon concentration <2.0 at.%), albeit x-ray amorphous, showed an increase in density from 2.0 to 2.4 g/cm^3 as the carbon concentration was increased and the film with the highest density had nanocrystalline inclusions, as observed by TEM. All measured material properties were found to depend strongly on film density. The elastic modulus increased from 188 to 281 GPa with increasing film density, while the relative dielectric constant decreased from 19.2 to 0.9. Hence, B-O-C films show a potential for protective coatings and even for application in electronic devices.

11:20am **TF-TuM10 Synthesis and Characterization of Nanolayered TiB_2/TiC Coatings for Possible Elevated Temperature Applications**, ***K.W. Lee***, *Y.-W. Chung*, *L. Keer*, *E. Ehmann*, Northwestern University

Multilayered coatings composed of 3 nm TiB_2 and various individual layer thicknesses of TiC were synthesized using non-reactive dual-cathode magnetron sputtering techniques with substrate rotation on silicon (001), M2 steel and WC cutting inserts. The two coating materials were chosen for their high hardnesses, melting temperatures, and immiscibility. The goal of the research is to synthesize hard and chemically stable coatings that provide wear protection at high contact pressures and temperatures. Under appropriate deposition conditions, we obtained coatings with TiB_2(001) preferred orientation. Room-temperature hardness of these coatings approaches 60 GPa, far exceeding the rule-of-mixture value. High-resolution transmission electron microscopy and low-angle x-ray diffraction studies confirmed that the layer structure of these coatings was preserved after one-hour annealing in argon at 1000C. Scanning electron microscopy shows that coatings were rapidly oxidized at 800C in 25% oxygen/argon environment. Wear and durability tests on coated M2 steels and C6 WC cutting inserts demonstrated the improved room temperature tribological performance of these coatings under unlubricated conditions compared with standard coatings such as TiN. Actual dry machining on coated C3 WC cutting inserts was performed. Scanning electron microscopy and white-light interferometry were used to evaluate durability of these coatings before and after machining. These results will be presented and discussed in terms of the coating's potential in dry machining and high-temperature tribological applications.

11:40am **TF-TuM11 Fluorinated Amorphous Carbon Thin Films: Analysis of the Role of the Plasma Excitation Mode on the Structural and Mechanical Properties**, *L. Valentini*, *M.C. Bellachioma*, University of Perugia, Italy, *S.I.-U. Ahmed*, *G. Bregliozzi*, *Y. Gerbig*, CSEM Centre Suisse d'Electronique et de Microtechnique, *H. Haefke*, CSEM Centre Suisse d'Electronique et de Microtechnique, Italy, ***J.M. Kenny***, University of Perugia, Italy

Fluorinated amorphous carbon (a-C:H:F) thin films were grown using a 13.56MHz radio frequency pulsed plasma source by varying the on-time plasma excitation from 1ms to 0.1s. The effect of the plasma excitation mode on the mechanical and tribological properties of the films was investigated by depth sensing indentation and microfriction tests using a reciprocating microtribometer. Nanoindentation measurements showed increased elasticity of the film, as well as increased hardness upon reduction of the plasma excitation time while a decrease of the friction force was also detected. The structural arrangement of the films investigated by means of thermal induced gas effusion shows that for a plasma excitation time of 1ms the material is relatively compact and the effusion of hydrogen related species (hydrogen molecules and hydrocarbons) dominate. For the highest on-time plasma excitation (0.1s) a strong change in the effusion characteristics indicates that an interconnected network of voids is present. Strong effusion of CF4 related species is found to be consistent with a surface desorption process and can only be observed when the void network dimensions are large enough, i. e., for films deposited with the highest on-time excitation. Raman spectroscopy is successfully applied to corroborate the effusion results indicating a structural transition from diamond-like to polymer-like film with increasing the plasma excitation time.

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