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

Advances in Hard and Superhard Coatings I

Moderator: F. Sequeda, Universidad del Valle, Columbia

8:20am **TF+VM-MoM1 Advances in Hard and Superhard Coatings for Tribological Applications**, ***A. Matthews,*** *A. Leyland,* University of Hull, UK **INVITED**

Over the past twenty years there has been considerable progress both in the development of advanced coating processes and in the scientific understanding of tribological mechanisms. Typically these developments have occurred completely separately, to the extent that coatings researchers may seek to develop a new coating with a specific extreme property (such as high hardness) driven primarily by scientific curiosity, rather than a desire to fulfil an identified tribological need. Usually that need will (for example) require an enhanced range of properties (such as hardness, toughness and resistance to environmental degradation). Coatings researchers are now increasingly recognising this need and are fulfilling it through several exciting developments. These include multi-layered and nanocomposite coatings which combine high hardness (H) with a relatively low elastic modulus (E) (to provide increased toughness). These coatings thus minimise the E/H ratio - which is known to be a parameter which is closely related to wear resistance. Other developments involve so-called 'hybrid' or 'duplex' combinations of processes to fulfil specific tribological needs. We are now in sight of achieving functionally-graded coating structures which combine tough and stress-equalised bulk properties, together with the extreme hardness, thermal and chemical properties of the exterior. The paper discusses the developments which have been necessary to achieve this - such as optimisation of compound compositions in the case of nanostructured composites based on nitride, carbide and boride phases. Also in the case of hard oxide ceramics, mention is made of growth modelling studies and plasma process developments to achieve the desired phases.

9:00am **TF+VM-MoM3 Ion-Assisted Filtered Cathodic Arc Deposition (IFCAD) Technology for Production of Superhard Thin-Film Coatings**, ***M.L. Fulton,*** Ion Arc Corporation

A new Ion-Assisted Filtered Cathodic Arc Deposition (IFCAD) system has been developed for low temperature production of superhard thin-film coatings. Only ions within a well defined energy range arrive at the substrate surface depositing thin-films with excellent mechanical and optical properties.@footnote 1@ The new IFCAD system consists of a cylindrical rotary deposition chamber with two (or four) Filtered Cathodic Arc (FCA) sources, each associated with an end-Hall Ion-Assisted-Deposition (IAD) ion gun.@footnote 2@ By coupling IAD with FCA the development of cost effective deposition processes for applying superhard advanced thin-film materials such as: Amorphous Diamond-Like-Carbon (A-DLC); Aluminum Oxide (Al2O3); Aluminum Nitride (AlN); Carbon Nitride (C3N3); Titanium Nitrite (TiN); Titanium Nitride Carbide (TiCN); Titanium Oxide (TiO2: Rutile); and others in multi-layer thin-film structures suitable for tribological and electro-optical applications is now feasible. The IFCAD film properties are superior to other processes at elevated deposition temperatures, for example: the A-DLC thin-films have a micro-hardness in excess of 50 GPa (Diamond = 100 GPa); and the amorphous Al2O3 films have a hardness in excess of 20 GPa (bulk sapphire is 35 GPa). This new IFCAD technology has been included in advanced commercial, military and space development programs, such as: EUV mirrors; plastic and glass lens coatings for optical systems; wear resistant coatings on various metal substrates; and ultra smooth, durable, surface coatings for injection molds. @FootnoteText@ @footnote 1@ P. J. Martin, R. P. Netterfield, A. Bendavid, and T. J. Kinder, "The deposition of thin films by filtered arc evaporation," Surface and Coatings Technology, 54/55 (1992) 136-142. @footnote 2@ M. L. Fulton, "Application of ion-assisted-deposition using a gridless end-Hall ion source for volume manufacturing of thin-film optical filters," in Optical Interference Coatings, Florin Abeles, Editor, Proc. SPIE 2253, (1994) 374-393.

9:20am **TF+VM-MoM4 High Rate Reactive DC Magnetron Sputtering of Al Oxide and W Oxide Thin Films; Large Area Coatings**, ***M.K. Olsson,*** Fraunhofer Institute for Solar Energy Systems, Germany*; K. Macák,* Linköping University, Sweden

Recently we reported stable high-rate deposition of Al oxide with any composition, including stoichiometry, utilizing a conventional reactive DC magnetron sputter system in laboratory scale.@footnote 1,2@ Due to the proper system geometry, including large enough target-to-substrate distance, and/or sufficient process gas pressure, it was possible to keep the target in the metallic mode by taking advantage of the scattering of the sputtered Al atoms through the inert gas. Moreover, the relatively high working pressure caused an increase in the back-deposited Al atoms to the non-eroded areas of the target, thus keeping these areas conducting, thereby avoiding arcing, without requiring the use of any other devices. We have applied this concept to a sputtering system considered for large area thin film production. A construction for increasing the cathode-to-sample length was designed with our technical possibilities in mind. After installation the desired O/Al arrival ratio was obtained and it was possible to produce stoichiometric aluminum oxide with an order-of-magnitude higher deposition rate. Choice of a sufficient pressure was crucial for the long-term stability of the process.@footnote 3@ Once the target is in the metallic state one may increase the growth rate linearly by increasing the target current. However, the experiments and analysis of the deposition process based on MC simulation of sputtered particles transport extended by Rossnagel's model of gas heating@footnote 4@ confirmed that the efficiency of the gas scattering process is for heavy elements partially eliminated at high discharge currents. To deal with this, we applied our concept of proper choice of process conditions for sputtering to less reactive materials with relatively high atom mass. It was possible to improve the sputtering condition for making films of stoichiometric amorphous W oxide at relatively high target current.@footnote 5@ @FootnoteText@ @footnote 1@M. Kharrazi Olsson, K. Macák, U. Helmersson, and B. Hjörvarsson, J. Vac. Sci. Technol. 16, 639 (1998). @footnote 2@K. Macák, T. Nyberg, P. Macák, M. Kharrazi Olsson, U. Helmersson, and S. Berg, J. Vac. Sci. Technol. 16, 1 (1998). @footnote 3@M. Kharrazi Olsson, K. Macák, W. Graf, Submitted. @footnote 4@S.M. Rossnagel, J. Vac. Sci. Technol. 6, 19 (1988). @footnote 5@M. Kharrazi Olsson, K. Macák, Submitted.

9:40am **TF+VM-MoM5 Elastic and Plastic Behaviors of Al/TiN Multilayered Thin Films Evaluated by Nanoindentation**, ***E. Kusano,*** *Y. Sawahira, N. Kikuchi, H. Nanto, A. Kinbara,* Kanazawa Institute of Technology, Japan

Elastic and plastic behaviors of multilayer films of Al (Young's modulus:70GPa) and TiN(Young's modulus:350-400GPa) have been investigated for various layer numbers with different total Al thicknesses in order to reveal the role of hard TiN and soft Al layers on nanomechanical properties in multilayered films. Both Al and TiN layers were deposited by dc magnetron sputtering. Aluminosilicate glass was used as substrate. The number of layers prepared was 4, 20, and 40 for the total Al thickness of 100-500nm. The total thickness of TiN layers was kept at 500nm, including the top layer of 250nm. The microhardness and Young's modulus of the films were evaluated by nanoindentation. The energies consumed for elastic and plastic deformations were calculated from the load-displacement curve obtained by the indentation. The microhardness decreased with increasing the total Al thickness. The hardness enhancement by the multilayer structure was observed for 20- and 40-layer films with Al layer thicknesses of 10 or 5nm (the total thickness of 100nm) and TiN layer thicknesses of 26 and 13nm. The energy dissipated during the indentation also increased with the total Al thickness. The dissipated energy for films with 40 layers of Al/TiN was smaller than that for the films with 4 or 20 layers of Al/TiN for all Al thicknesses. In contrary, the elastic energy was independent both of the total Al thickness and of layer numbers. As a result, the ratio of dissipated energy to the loaded energy during the load/unload of the indentation yielded a minimum at an Al thickness of 100nm for 40-layer films. The ratio at the minimum was about 20% smaller than that of the monolithic TiN film. This means that the 40-layer film with a total Al thickness of 100nm is more elastic than the monolithic TiN. It is concluded that the enhancement in the film microhardness for multilayered films with thin Al layers is related to the decrease in the dissipated energy.

10:00am **TF+VM-MoM6 Gas-phase Chemistry in Up-scaled Plasma Enhanced MOCVD of TiN and Ti(C,N) on Plasma Treated Tool Steel**, ***J.P.A.M Driessen,*** *A.D. Kuypers,* TNO Institute of Applied Physics, The Netherlands*; J. Schoonman,* Delft University of Technology, The Netherlands

In this paper, the deposition of TiN and Ti(C,N) in a relatively large scale reactor vessel is discussed. Tetrakis(dimethylamine)titanium (TDMAT) and tetrakis(diethylamine) titanium (TDEAT) were used for the purpose of depositing TiN and Ti(C,N) at low temperatures. In large scale systems, homogeneous reactions dominate the deposition process resulting in non-

uniform and non-adherent coatings. However, in this study, favourable gas-phase conditions for deposition of Ti(C,N) from in a pulsed DC-plasma have been determined, making use of mass and optical spectroscopy. Decomposition of TDMAT in a pure hydrogen plasma results in the favourable cleavage of dimethylamine from TDMAT but prevents the formation of Ti(C,N) due to the lack of nitrogen and carbon. Addition of N@sub 2@ to the hydrogen plasma results in the formation of NH@sub x@ (1@<=@x@<=@4), opening transamination pathways. Results suggest that transamination plays an important role in the gas-phase of our system. Furthermore, these results were compared with those obtained from using ammonia. However, the depletion of TDMAT by interaction with nitrogen in a H@sub 2@(85%) - N@sub 2@(15%) plasma proceeds in a mechanistic step with a rate constant of k = 4.7 x 10@super -14@ cm@super 3@ mol@super -1@sec@super -1@. Nevertheless, seemingly high quality Ti(C,N) coatings were deposited on blank WN1.2370 tool steel and WN 1.2379 treated in a N@sub 2@/H@sub 2@ plasma. XRD analysis of the plasma treated substrate indicates the presence of CrN, among other species in the top surface layer. These multi-layer coatings, deposited at temperatures between 473 K and 698 K, increased in surface roughness, however, showed good adherence and optimum hardness. Hardness values varied from 1600 Hv to 2000 Hv.

10:20am **TF+VM-MoM7 Effect of Ion-to-neutral Ratio and Ion Energy on Structure and Properties of Boron Nitride Thin Films**, ***M.U. Guruz***, *Y.W. Chung, V.P. Dravid,* Northwestern University

Boron nitride thin films were deposited by dc reactive magnetron sputtering using a B@sub 4@C target in a single cathode chamber. The films were grown on Si (001) wafers, held at ambient temperature. The energy of the ions arriving at the substrate surface was determined by the applied bias. Additionally, an external coil assembly was placed outside the chamber, allowing modification of the magnetic field around the substrate. By varying the field strength, the ion flux on the substrate was enhanced. Thus, the ion-to-neutral ratio and the ion energy were independently controlled during deposition. The effects of these two parameters on the resulting film microstructure were investigated by transmission electron microscopy (TEM), atomic force microscopy (AFM), Fourier transform infrared spectroscopy (FTIR) and nanoindentation. These results and the effects on the formation of cubic boron nitride will be presented.

10:40am **TF+VM-MoM8 Mechanical Properties of Cubic Boron Nitride Thin Films Synthesized by ECR PECVD: Influence of Deposition Conditions**, ***M.P. Delplancke-Ogletree***, *M. Ye,* Université Libre de Bruxelles, Belgium

Cubic boron nitride containing thin films were deposited on (100) Si and steel substrates by electron cyclotron resonance plasma enhanced chemical vapor deposition. The films contain at least 55% of the cubic phase and are 0.5 μm thick. We investigated the dependence of hardness, stress, adherence, friction coefficient and wear resistance as a function of deposition parameters. The studied parameters are substrate bias, gas mixture composition, substrate temperature and processing pressure. These parameters are also correlated to the plasma characteristics measured by Langmuir probe, and mass spectrometer. Nanoindentation, scratch test, cantilever deflection, and ball-on-disk methods were used to evaluate quantitatively the mechanical properties. Films containing 55% of cubic phase are adherent to the two types of substrates, and have stress below 5 GPa.

11:00am **TF+VM-MoM9 Plasma Assisted Physical Vapour Deposition of BN by DC Pulsed Sputtering of a B@sub 4@C Target**, ***L.A. Gea***, *G. Ceccone, F. Rossi,* European Commission Joint Research Centre, Italy

Boron nitride coatings were deposited on Si (100) polished crystals by DC pulsed magnetron sputtering of a B4C target with auxiliary microwave Distributed Electron Cyclotron Resonance (DECR) plasma.The substrates were biased by an independent R.F. source. Characterization of the plasma was undertaken as a function of the total pressure, the nitrogen gas content and the microwave power. The presence of the various species was identified with Optical Emission Spectroscopy.Mass Spectrometry was used to determine the ion energy distribution while the plasma potential and the plasma densities were measured with a single Langmuir probe.The coatings have been characterized by Scanning Electron Microscopy (SEM), Auger Electron Spectroscopy (AES), and Fourier Transformed Infrared Spectrometry (FTIR)

11:20am **TF+VM-MoM10 Field Emission from Flat, Diamond-like Carbon Films Characterized by Scanning Force Microscopy**, *T. Inoue,* Electrotechnical Laboratory, Japan; ***D.F. Ogletree***, *M. Salmeron,* Lawrence Berkeley National Laboratory

Thin films of various diamond-like and carbon based materials on flat cathodes show significant field emission at relatively low voltages, but the exact emission mechanisms are not well understood. Non contact scanning force microscopy with a conductive tip in vacuum, used in the scanning polarization force mode (SPFM) , can detect and characterize emission sites with 100 nm lateral resolution. The SFM tip serves as an anode. It can be scanned over the surface to simultaneously measure local emission currents and local work functions. The tip-sample spacing and the tip bias can be varied to investigate mechanisms. Contact SFM images of emitting regions show local topography, reveal the presence of asperities, and characterize sample conductivity. For one type of CVD cathode material on an Si substrate, the emission sites were found to be (a) ~ 1 micron in diameter (b) not associated with asperities at the cathode-vacuum interface (c) not associated with low work function regions, and (d) semiconducting with a large band-gap. I-Z data indicate that emission takes place within the film, or at the film-substrate interface, rather that at the film-vacuum interface. Single-site emission currents were strongly modulated on a ~ 1 ms time scale, possibly due to charge trapping. Surface potential shifts were correlated with the emission current fluctuations.

11:40am **TF+VM-MoM11 Effect of Nondiamond Carbon on the Electron Transport Path of Field-emitted Electrons from Undoped Polycrystalline Diamond Films**, ***J.Y. Shim***, Yonsei University, Republic of Korea; *K.M. Song,* Konkuk University, Republic of Korea; *H.K. Baik,* Yonsei University, Republic of Korea, KOREA

Diamond has attracted considerable interest recently as a promising field emitter material because of its important properties such as NEA, high thermal conductivity, and low field electron emission. Among the properties, understanding the origin of low field emission is a key factor for the application of diamond to a field emitter. Many investigations have been extensively drawn to clarify the origin of low field emission behavior of diamond. Suggested models explaining the low field emission behaviors up to now are the discontinuous graphitic inclusions in CVD diamond matrix, the defect induced subbands, and the surface emission from metal-diamond-vacuum interface. Besides, there have been several reports on the importance of the electron transport through the substrate/diamond interface. However, the origin of the low field emission behavior is still unclear, and those may be different between diamond crystal and CVD diamond films. It is expected that the field emission mechanism of undoped polycrystalline diamond films can be changed by the structural properties. The present study is mainly focused on the electron transport through the substrate-diamond interface and the diamond layer, and the resulting field emission mechanism of undoped polycrystalline diamond films with different structural properties. In order to examine field emission properties of undoped polycrystalline diamond films, we have prepared the diamond films with different structural properties and/or different substrate-diamond interfaces. It was observed that transport paths of field-emitted electrons could be clearly identified from the spatial distributions of emission sites and the nondiamond carbon content obtained from the diamond films, and the characteristics of the substrate-diamond could modify the field emission properties. From the present study, a possible field emission mechanism for the undoped polycrystalline diamond films is suggested.

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