Plasma and Vapor Deposition Processes
Room Town & Country A - Session PP4-1-WeM

Deposition Technologies for Carbon-based Coatings I

Moderators: Ivan Kolev, IHI Hauzer Techno Coating B.V., Netherlands, **Biplab Paul**, PLATIT AG, Switzerland

8:00am **PP4-1-WeM-1 Molecular Dynamics Study of Interfacial Phenomena in Diamond-Like Carbon Films***, **Kwang-Ryeol Lee (krlee@kist.re.kr)**,* Korea Institute of Science and Technology (KIST), Republic of Korea*; X. Li,* Chinese University of Mining and Technology, China **INVITED**

Due to the experimental limitations in precisely characterizing the complicated evolution of a-C film deposition and their physical and chemical properties, molecular dynamics simulation has been widely employed for atomistic understanding of the structural evolution and investigating structure-property relationship. Especially, much attention has been drawn to reactive molecular dynamics simulation technology that can include the chemical reaction during the atomic scale structure evolution. We compared various reactive force field (ReaxFF) models in terms of the structural properties of the simulated a-C films prepared by atom-by-atom deposition approach. By linking the structural properties of the film with the difference in the parameter sets of the ReaxFF models, we reveal that the carbon triple bond stabilization energy in the ReaxFF model, v_{trip}, significantly affects the growth dynamics and structural evolution of the simulate a-C films. Tribological behavior of amorphous carbon surface was extensively investigated in atomic or molecular scale by the reactive molecular dynamics simulation. Simulational study of friction in hydrogenated surface of a-C revealed that hydrogenating the a-C surface only improved the friction property drastically while not deteriorating the intrinsic properties of a-C films. The analysis of interfacial structure demonstrated that being different with a-C:H cases, the competitive relationship between the stress state of H atoms and interfacial passivation caused by H and C-C structural transformation accounted for the evolution of friction coefficient with surface H content. This disclosed the friction mechanism of a-C with surface hydrogenated modification and provides an approach to functionalize the carbon-based films with combined tribological and mechanical properties for specific applications. The reactive molecular dynamics simulation resulted in fundamental understanding of low-friction mechanism. We comparatively investigated the friction property and structural information of contacting interface under different passivated or graphitized states. For the passivation mechanism, the low friction behavior attributes to the reduction of both the real contact area and shearing strength of graphitized sliding interface due to the passivation of a-C dangling bonds. However, the graphitization mechanism strongly depends on the size and layer number of graphitized structure, causing the transition of sliding interface from a-C/a-C, a-C/G to G/G, which is followed by the low-friction mechanism evolved from passivation synergistic effect between graphitization and passivation to graphitization mechanism.

8:40am **PP4-1-WeM-3 Study of ta-C Thick Film Deposition Using FCVA-Based Hybrid Coating System***, **Jongkuk Kim (kjongk@kims.re.kr)**, J. Kim, J. Jang, Y. Jang,* Korea Institute of Materials Science, Republic of Korea

Tetrahedral amorphous carbon (ta-C) coating film has a high sp^3 content and excellent wear resistance and heat resistance even without hydrogen, so it is used in various industrial fields such as cutting tools, automobiles and molds.

In the vacuum arc process using a carbon target, coating is difficult for a long time due to the unstable movement of the arc spot inside the carbon target, resulting in poor thickness and an enlarged coating area. In addition, the Ta-C coating film deposited by this method has high internal stress, making it difficult to increase its thickness.

We controlled the electric and magnetic fields to stabilize the arc spot movement of the carbon cathode for a long period of time, allowing the carbon arc target to be used stably for up to 24 hours at a discharge current of 160 A.

The designed hybrid coating system consists of 1) anode-layer ion source (ALIS) for the etching processes, 2) an unbalanced magnetron sputter (UBM) for the interlayer deposition, 3) a filtered cathodic vacuum arc (FCVA) source for the ta-C film deposition, and 4) pulsed bias power.

To apply the designed hybrid coating process, a system consisting of a single ALIS, two UBMs, and eight FCVAs with a maximum deposition area of 900 mm in diameter and 500 mm in height was built to deposit a 7 µm coating film on a piston ring used in an automobile engine.

We have also built a smaller machine with similar capabilities that can deposit rainbow coatings (up to 0.7 um) and black coatings (0.7-3 um) on non-ferrous cutting tools for a variety of applications, depending on their thickness.

9:00am **PP4-1-WeM-4 Diamond-Like Films of Tetrahedral Amorphous Carbon Deposited by Anodic Arc Evaporation of Graphite***, **Bert Scheffel (bert.scheffel@fep.fraunhofer.de)**, O. Zywitzki,* Fraunhofer FEP, Germany

A physical vapor deposition process using anodic arc evaporation in combination with a hollow cathode arc discharge was applied to the evaporation of graphite for deposition of hydrogen-free carbon layers. The diamond-like carbon (DLC) films deposited on 100Cr6 steel substrates were investigated by nanoindentation, Raman spectrometry, FE-SEM, AFM and spectroscopic ellipsometry. The relationships between the process parameters and the coating properties are discussed. Coatings deposited without bias voltage at substrate temperatures < 200°C are very hard (61-75 GPa) with also very high Young's modulus (588-685 GPa). The evaluation of the Raman spectra indicated a high proportion of tetrahedral sp3 bonds in the range of 70-88 %. The coatings proved to be completely droplet-free and have a very low surface roughness as confirmed by FE-SEM and AFM. The deposition rates in the range of 4-18 nm/s are exceptionally high for such ta-C coatings, which is a good prerequisite for industrial applications.

9:20am **PP4-1-WeM-5 Constitution and Properties of TiC1-x:H/a-C:H Nanocomposite Thin Films Prepared by HiPIMS Processes at Low and Elevated Temperature***, **Sven Ulrich (sven.ulrich@kit.edu)**, C. Poltorak,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany*; H. Sternschulte, J. Grau,* Technical University of Applied Sciences Augsburg, Germany*; J. Julin, T. Sajavaara,* RADIATE, University of Jyväskylä, Finland*; A. Bergmaier,* University of the Bundeswehr Munich, Germany*; K. Seemann, M. Dürrschnabel, M. Stüber,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany

Carbon-based nanocomposites with tunable multifunctional properties are suitable candidates for diverse fields of applications like tribology or biological, medical and energy technologies. Reactive HiPIMS is selected as a coating process with a Ti-target, an average target power of 5 kW, 50 µs pulse length, 550 µs cycle duration, working gas pressure of 0.3 Pa, 300 sccm Ar working gas flow and up to 40 sccm CH_4 reactive gas flow as well as 200°C and 400°C substrate temperatures. HiPIMS show a high ion fraction of the film-forming particles and the deposited energy by ion bombardment during film growth can be adjusted precisely. The constitution and microstructure war determined by a combination of several analytical techniques: EPMA, ERDA, Raman spectroscopy, XRD, TEM and HRTEM. It is shown that by varying the methane reactive gas flow, the following structures can be adjusted: Ti, TiC_{1-x}:H and TiC:H single layer coatings as well as TiC:H/a-C:H nanocomposites. A clear correlation is identified between the constitution and microstructure with the mechanical properties.

9:40am **PP4-1-WeM-6 Effect of Deposition Temperature and Nitrogen Concentration on Highly Conductive a-C:H:N Films Obtained by Means of DC PACVD***, **Manuel Schachinger (manuel.schachinger@fh-wels.at)**,* University of Applied Sciences Upper Austria*; F. Delfin,* University of Applied Sciences Upper Austria, Argentina*; C. Forsich, D. Heim,* University of Applied Sciences Upper Austria*; B. Rübig, T. Müller, C. Dipolt,* Rubig GmbH & Co KG, Austria

a-C:H films are known for their distinct properties such as excellent wear resistance, chemical inertness and a low coefficient of friction. However, these films are typically highly electrically insulating materials. In view of the constantly increasing demands on technical components, it is critical to further expand the areas of application of a-C:H coatings by combining their desired and well-established material properties with low electrical resistivity. One way to decrease the specific electrical resistance of DLC films substantially is via the utilization of high-temperature DC PACVD. For further optimization of the electrical properties, nitrogen doping may be applied. In this work, a-C:H:N films were deposited at 450°C and 550 °C via DC PACVD on steel and titanium substrates, employing C_2H_2 and an additional N_2 flow. This resulted in an N_2 concentration of 0-63 vol. -% in the gas mixture. Subsequently, film characterization was carried out via nanoindentation, density measurement, calotest, the van der Pauw method, GDOES and Raman spectroscopy. Nanoindentation showed that hardness was increased at higher deposition temperatures and continued to increase with nitrogen gas concentrations up to a certain point. Thereafter, at trend inversion was observed. Density was higher for 550°C deposition compared to the 450°C process and increased for both temperatures with higher N_2 gas concentrations up to 31 vol. -%. Thereafter, a trend reversal was observed, pointing towards an increased fraction of terminating structures such as C-H or CN triple bonds and a lower fraction of C-C sp^3 bonding in the material. Coating thickness decreased from 40 µm to 14 µm at 450°C and from 32 µm to 12 µm at 550°C with increasing nitrogen flow following an exponential function. Specific resistivity reached an average minimum of 1688 µΩ cm at 31 vol. -% N_2 for 550°C, which approximates the conductivity of compressed graphite powders. In addition, it decreased by several decades at 450°C, reaching an average minimum of 45 000 µΩ cm. GDOES analysis showed that nitrogen concentrations in the films were markedly low ranging from 0,08 to 1,3 at. -% on average. Raman analysis indicates that nitrogen incorporation induces disordering effects in the film structure, combined with a rise in the number and size of aromatic clusters. In summary, the addition of nitrogen as a process gas successfully enhanced the properties of the film, resulting in materials that exhibited higher hardness than martensitic steels with an electrical resistivity equivalent to that of compressed graphite powders.

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