Hard Coatings and Vapor Deposition Technologies
Room California - Session B3-2-MoA

Deposition Technologies and Applications for Diamond-like Coatings II
Moderator: Frank Papa, Gencoa

1:40pm **B3-2-MoA-1 Transfer of DLC Coating Processes between Different Coating Machines Assisted by Plasma Simulation***, **Marcus Günther**, O Schmidt, W Dobrygin, G Schütze,* Robert Bosch GmbH, Germany

Hydrogenated amorphous carbon films (a-C:H) as a kind of diamond-like carbon (DLC) coatings combine unique optical, electrical and mechanical properties, resulting in numerous industrialized applications. These plasma coatings are continuously of high interest for research and industry because of the possibility to adjust their layer properties in a wide range by varying the deposition conditions like pressure, temperature or bias voltage. DLC films are widely used in the automotive industry due to their unique tribological properties, e.g. as an enabler for modern fuel injection equipment.

Important goals of a modern flexible industrial production especially for automotive mass production are the realization of good adhesion, functionality of the layer system and the fundamental control of the deposition process regardless of the kind of coating machine and coated component geometry. The combination of plasma simulation, coating experiments and plasma diagnostics enables the monitored deposition of hydrogenated amorphous carbon films and the prediction of the resulting layer properties, e.g. hardness, intrinsic stress or hydrogen content.

The study will present a global model for acetylene and argon plasmas to support the process development for the functional a-C:H-layer and the process transfer between different coating machines for the industrialized deposition to guarantee consistent a-C:H-layer quality. With the presented simulation, it is possible to calculate all partial pressures of reaction products, relevant plasma parameters and particle fluxes. By transferring all relevant machine parameters (e.g. bias voltage, gas flow, …) into only one main virtual parameter, the energy per deposited carbon atom, it is possible to compare and generically predict the coating quality of various coating machines with different chamber sizes and vacuum pumping systems.

2:00pm **B3-2-MoA-2 Stress-Free ta-C Industrially Deposited by PLD for High Performance Stamping Applications: Results and Challenges of 1st Production Year***, **Martin Hess**,* Fritz Stepper GmbH & Co. KG, Deutschland, Germany*; S Weißmantel, R Bertram,* Hochschule Mittweida University of Applied Sciences, Germany

At the 45th ICMCTF conference, we presented PLD as a new system technology for the production of stress-free ta-C coatings which are summarizable by a very high hardness of over 60 GPa while retaining the common layer thicknesses of 3 to 4 µm (which are previously and still used for our PVD tool coatings coated by Sputter- and Arc-PVD). Among other things PLD allowed us to deposit ta-C without changing tool drawings (which are proven over many years) if we mix ta-C- with PVD coatings in our high performance progressive die tools. Moreover we can avoid egg shell effects, which may be a drawback if very hard but relatively thin (ca. 1 µm) coatings are used in highly stressed applications.

PLD ta-C achieves, compared to so far used PVD coatings, almost double hardness in combination with a significantly artifact less surface. As a result the abrasion resistance against some stamping strips and active component lifetime are boosted by a magnitude and more – which saves tool cost and press down time. As presented in 2018 our daily quantities and tool sizes are relatively small, even for compliance with compact PVD systems, we decided to design a PLD system dedicated to our requirements for our final products: Complex modular die tools (with more than 1000 coated active elements) which are able to produce multi-millions of electrical contacts in a 24/7 operation without any maintenance.

In the meantime our PLD coating system has been in operation for more than one year. Driven by demanding applications, such as Si-containing high-strength bronze, stainless steel, the ta-C coatings became smarter (e.g. integrated run-in layer, tailored hardness and Young's modulus, etc.) and more performing. Significant progress was e. g. also made regarding the coating of die cavities.

The purpose of the present contribution is to introduce latest developments of ta-C produced by PLD. For this purpose, relevant mechanical properties as well as new successful applications will be presented.

2:20pm **B3-2-MoA-3 Hollow Cathode Discharges for Rapid DLC***, **Thomas Casserly**, S Gennaro, F Papa, A Tudhope,* Duralar Technologies, USA**INVITED**

The application of Diamond Like Carbon coatings has been limited by the cost and time required to deploy the coating. Hollow cathode discharges are characterized by their high ion densities and hot oscillating electrons capable of multiple ionization events. Through harnessing the power of hollow cathode discharges internal surfaces of conductive hollow articles can be coated rapidly with DLC (and other materials). This internal deposition technology enables numerous applications of DLC for low wear and low friction in engine cylinders, actuators, hydraulic cylinders, and more as well as anti-wear, anti-fouling and anti-corrosion applications in upstream oil and gas and adjacent markets. Deposition rates in excess of 5 µm per minute have been achieved for specific geometries allowing for cost effective deployment of advanced coatings. This high rate hollow cathode deposition technology has been extended to coat external surfaces as well; initially, for shafts, plungers, and other cylindrical objects through the application of annular hollow cathode geometries. Using a similar approach designed for high throughput, the deposition technology has been developed to coat the external and internal surfaces of complex objects with applications in armaments, sporting, and automotive components, as well as functional decorative coatings for consumer products. The high deposition rates and throughput afforded by hollow cathode discharge technology greatly reduces the cost of deploying advanced DLC coatings and enables a diverse set of applications.

3:00pm **B3-2-MoA-5 Hard Cr-doped DLC Coatings Deposited by Low-frequency HiPIMS with Enhanced Tribomechanical Behavior at High Temperature***, **José Antonio Santiago Varela**,* PVT Plasma und Vakuum Technik GmbH, Germany*; I Fernandez,* Nano4Energy SL, Spain*; A Wennberg,* Nano4Energy, Spain*; M Monclus, J Molina Aldareguia,* IMDEA Materials*; V Bellido-Gonzalez,* Gencoa Ltd, UK*; C Rojas, J Sanchez Lopez,* ICMSe CSIC, Spain*; R Gonzalez Arrabal,* Universidad Politécnica de Madrid, Spain*; N Dams, H Gabriel,* PVT Plasma und Vakuum Technik GmbH, Germany

Diamond-like Carbon (DLC) coatings have been recognized as one of the most valuable engineering materials for various industrial applications including manufacturing, transportation, biomedical and microelectronics. Among its many properties, DLC stands out for a good frictional behaviour combined with high surface hardness, offering an elevated protection against abrasive wear. Nevertheless, a factor limiting the widespread application of DLC coatings is their thermal stability. DLC is very temperature-sensitive since its sp^3-sp^2 structure undergoes a graphitization process at high temperatures that deteriorates both hardness and coefficient of friction. In order to overcome this limitation, new ways to modify DLC coatings for acceptable high temperature performance have been explored. In this work, we investigated the deposition of hard DLC coatings doped with Cr using HiPIMS technique at industrial scale. Extraordinary highly ionized plasma discharges were obtained during chromium and carbon codeposition at low HiPIMS frequencies. The high ion energy bombardment at low HiPIMS frequencies allowed doping with Cr the DLC structure while reaching high sp^3 contents. EELS spectroscopy was used to evaluate sp^3 content and Raman was used for sp^2 structural characterization of the films. Enhanced mechanical properties (hardness up to 35 GPa) were observed with nanoindentation for Cr-doped DLC at low frequencies. High temperature nanoindentation tests were also performed from room temperature to 450ºC in order to evaluate the evolution of hardness and Young Modulus with temperature. The results confirm that the mechanical properties at high temperature mainly depend on the sp^3 content. Tribological tests were carried out in air from room temperature to 250ºC. Cr-doped DLC coatings showed lower friction and wear compared to pure DLC. The increased toughness that Cr provides to the carbon matrix together with a high sp^3 bonding structure obtained with low frequency HiPIMS deposition improves the stability of DLC coatings for high temperature applications.

3:40pm **B3-2-MoA-7 Effect of Pulse Shape and Plasma Composition (Ar + Ne) on the Properties of Hard DLC Films Deposited by HiPIMS: Correlation with Substrate Ion Fluxes***, **João Oliveira**, F Ferreira, R Serra,* University of Coimbra, Portugal*; T Kubart,* Uppsala University, Angstrom Laboratory, Sweden*; C Vitelaru,* National Institute for Optoelectronics, Romania*; A Cavaleiro,* University of Coimbra, Portugal

High Power Impulse Magnetron Sputtering (HiPIMS) has been under consideration for hard Diamond Like Carbon (DLC) thin films deposition in recent years. The major driver to use HiPIMS is the possibility of C ions formation in the plasma and their subsequent subplantation upon substrate biasing to promote the formation of sp^3 bonds in a similar way to ARC deposition. However, the low electron impact ionization cross-section of C limits the C^+/C ratio in HiPIMS plasmas to some few percent (~ 5 %). Adding Ne to the discharge gas allows increasing the electron temperature of the plasma and, thus, increasing the C ionization fraction. On the other hand, the use of short pulse on-times (<10 µs) together with high target voltages (>1 kV) has been reported to result in large target current densities.

In this work the effect of adding Ne to a pure Ar discharge and the use of different HiPIMS pulse shapes are investigated. DLC films were deposited by HiPIMS using two different power supplies providing HiPIMS pulses with different temporal duration and peak voltages. The structural and mechanical properties of the DLC films were evaluated by micro-Raman Spectroscopy and Nanoindentation, respectively. The tribological behavior of the DLC films was evaluated by pin-on-disk tests in ambient atmosphere (room temperature and ~ 40% relative humidity). The friction coefficients of the DLC films were obtained by averaging over last 1000 m of the sliding tests. The specific wear rate (k) of the DLC films was calculated from the cross-section profiles of the wear tracks. Additionally, the time-resolved substrate current densities (SCDs) were measured using a flat probe mounted at the substrate position. The measured Ion Saturation Currents (ISCs) were correlated to the structural, mechanical and tribological properties of DLC films.

Adding Ne to the HiPIMS plasma results in a significant increase of both the sp^3 content and the hardness (> 20 GPa) of the DLC films while their fiction coefficient remains within the range typical of DLC films tested under relatively humid conditions (< 0.2). The specific wear rate of the DLC films decreases with Ne addition down to a minimum value of 4 $x10^{-17}$ m^3/Nm.

4:00pm **B3-2-MoA-8 The Comparison of Deposition Processes, Composition and Properties of Hydrogenated W-C:H Coatings Prepared by Different Sputtering Techniques***, **Frantisek Lofaj**, M Kabatova, L Kvetkova,* Institute of Materials Research of SAS, Slovakia*; J Dobrovodsky,* ATRI, Slovakia

The work reviews the processes and subsequent mechanical and tribological properties of hybrid PVD/PECVD sputtering during deposition of hydrogenated W-C:H coatings prepared by High Power Impulse Magnetron Sputtering (HiPIMS) and High Target Utilization Sputtering (HiTUS) as a function of acetylene and hydrogen additions in the Ar atmosphere. The results are compared with those from analogous coatings deposited by conventional direct current magnetron sputtering. TEM observations revealed that a transition from nanocrystalline WC_{1-x} to nanocomposite and amorphous structure occured with the increase of acetylene addition nin all coatings but at different acetylene contents. The concentrations of carbon and hydrogen in the studied coatings measured by Rutherford Backscattering (RBS) and Elastic Recoil Detection Analysis (ERDA) methods depended on the amount of acetylene and hydrogen addition but also on the applied technique. The obtained results were analyzed and the main differences in the possible growth mechanisms between DCMS and HiPIMS were discussed within the von Keudell model for a-C:H growth. The increase of free carbon content in HiTUS W-C:H coatings when C_2H_2 was added resulted to a degradation of indentation hardness and indentation modulus similarly as in DCMS coating. However, almost no degradation was observed in HiPIMS coatings. Low coefficients of friction in HiTUS and DCMS coatings were attributed to the formation of lubricious tribolayer whereas uniform structure was considered to be a property controlling parameter in HiPIMS coatings. The main advantage of HiPIMS compared to HiTUS and DCMS coatings includes lower coefficients of friction at higher hardness values.

4:20pm **B3-2-MoA-9 The Mechanism of Graphite Nucleation in Amorphous Carbon Films Deposited with the Condition of Energetic Bombardment and High Temperature***, **Di Zhang**, P Yi, L Peng, X Lai,* Shanghai Jiaotong University, China

Amorphous carbon (a-C) films exhibit many properties that make them attractive for applications in coating technology. The property of a-C films closely depends on their microscopic structures and a-C films with a graphite-like structure may exhibit high electrical conductivity and excellent corrosion resistance, mainly due to the nucleation of graphite nanocrystals observed in a-C matrix. However, the mechanism of graphite nucleation remains unclear. This work aims to develop a fundamental understanding of the graphite nucleation in a-C films deposited with energetic bombardment and high temperatures. Our experiments revealed that different sizes of graphite nanocrystals were observed in a-C films produced by applying varying deposition bias voltages and temperatures, thus leading to a different durability under the a typical corrosive environment of proton exchange membrane fuel cells. Moreover, we developed an atomistic model to simulate the nucleation of graphite nanocrystals in a-C films using Molecular Dynamics and Monte Carlo methods. Investigations on the structural properties of the atomistic model provide fresh insights into the microscopic structure of graphite-like a-C films.

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