Wednesday Afternoon, May 22, 2024

Plasma and Vapor Deposition Processes
Room Town & Country A - Session PP4-2-WeA

Deposition Technologies for Carbon-based Coatings II

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

2:00pm **PP4-2-WeA-1 DLC-Coating Against the Backdrop of High Economic Requirements**, ***Jens Emmerlich (jens.emmerlich@de.bosch.com)**, D. Tiedemann,* Robert Bosch Manufacturing Solutions GmbH, Germany*; V. Gupta,* Robert Bosch Manufacturing Solutions GmbH, India*; K. Boebel,* Robert Bosch Manufacturing Solutions GmbH, Germany **INVITED**

In the pursuit of economic viability, this study delves into the strategic utilization of Diamond-Like Carbon (DLC) coatings, emphasizing the distinctive advantages offered by diverse deposition sources. Microwave and cathodic arc deposition, magnetron sputtering as well as High-Power Impulse Magnetron Sputtering (HiPIMS) emerge as pivotal techniques, each contributing unique attributes to the economic landscape. Microwave and cathodic arc deposition showcase efficiency in scalability and uniformity, optimizing the cost-effectiveness of large-scale applications. Sputtering, on the other hand, proves adept at achieving precision and controlled film properties, catering to industries with specific coating requirements. The innovative approach of HiPIMS introduces enhanced adhesion and superior film density, paving the way for extended component lifespan and reduced maintenance costs. Beyond these, the infusion of artificial intelligence (AI) emerges as a pivotal factor in predicting coating parameters and thus orchestrating cost reduction and minimizing scrap rates. By leveraging AI algorithms, the deposition process is optimized with unprecedented precision, ensuring an ideal balance between coating thickness, quality, and resource utilization. This study delves into the economic benefits derived from the application of DLC coatings in combination with AI, shedding light on their potential to enhance durability, reduce maintenance costs, and contribute to overall operational efficiency. As industries strive to navigate the intricacies of a competitive economic environment, the integration of DLC coatings emerges as a strategic imperative for achieving both performance excellence and economic viability.

2:40pm **PP4-2-WeA-3 Comparison of Performance Parameters of Carbon Coatings by Different PVD Methods**, ***Martin Kopte (Kopte.Martin@vonardenne.com)**, J. Walther, B. Gebhardt, H. Proehl,* VON ARDENNE GmbH, Germany

PVD based carbon coatings show superior electrochemical resistance enabling durable coatings for metallic bipolar plates in PEM fuel cells etc. High durability and high conductivity (low interfacial contact resistance – ICR) of bipolar plates are essential, nevertheless only a cost-efficient coating method will have the chance for industrialization. Therefore, we only investigated PVD methods which allow scaling of the bipolar plate coating volume to MW and GW powers per year, which are electron-beam based PVD, as the method for highest productivity and deposition rate, and plasma based PVD which is high power magnetron sputtering and (pulsed) cathodic laser arc in our case. The electrical conductivity or ICR and corrosion performance of all those carbon coatings have been optimized to compete with gold coatings at fuel cell operation voltage. Anyway, the limits of the electrochemical corrosion performance of different carbon coatings at high electrochemical potentials occurring for split seconds on the cathode side of the bipolar plate during start/stop of a fuel cell can be crucial for the overall layer stack performance and durability. Depending on the deposition method and parameters, the properties of the carbon layer stack can highly differ from each other which leads to a different corrosion performance at such a high electrochemical potential.

3:00pm **PP4-2-WeA-4 Carbon-Based Coatings with Tailorable Properties as a Function of sp^3:sp^2 Hybridization**, ***Biplab Paul (b.paul@platit.com)**, G. Wahli, J. Kluson, H. Bolvardi, A. Lümkemann,* PLATIT AG, Switzerland

Carbon-based coatings offer a variety of exceptional properties, including mechanical (hardness, elastic modulus, friction coefficient), physical (optical, electrical), chemical (chemical inertness), and biomedical (biocompatibility) properties. However, to exploit the entire range of functionalities from this class of coatings we need appropriate technologies to make the coatings preferentially engineered. For example, carbon-based coatings can be engineered to be graphite like or diamond like by preferentially tuning the ratio of sp^3/sp^2 hybridization in the coatings. The monolithic tetrahedrally-bonded coatings (ta-C), with 100% sp^3 content, provide the highest hardness, while amorphous carbon (a-C) coatings with $sp^3/sp^2 < 1$ provide softer coatings with low coefficient of friction (COF), useful for many frictionless mechanical applications. PLATIT's advanced coating units, integrating sputtering, arc and PECVD techniques, provides the unique scope to grow a plethora of diamond like coatings (DLC) with varying functionalities, categorized as DLC1 (metal doped a-C:H with sp^2 > 50%, i.e., $sp^3/sp^2 < 1$), DLC2 (Si doped a-C:H), and DLC3 (hydrogen free ta-C with sp^3 > 50%, i.e., $sp^3/sp^2 > 1$). The DLC1 coatings are grown by sputtering from metal targets (e.g. Ti, Cr, etc.) in acetylene atmosphere, offering the scratch proof aesthetic black coatings, useful for decorative and biomedical applications. The DLC2 coatings are grown by PECVD technique, offering the hard coatings (Hardness = 30-35 GPa, Lc2 = 30 N), useful for cutting tools and for various mechanical and electronic components. The DLC2 coatings being grown by PECVD technique, they offer the coating possibilities on difficult parts with complex geometries and miniaturized dimension (e.g., microtools). The DLC3 coatings are done by sputtering from carbon target at low temperature, providing hardness (H) > 40 GPa, and scratch resistance with Lc2 > 30 N, while COF < 0.2. With such high hardness and low COF values the DLC3 coatings offer the best coating solution for machining nonferrous materials. The physical properties of carbon-based coatings can be directly corelated to their color, which is defined by L*a*b* values. Figure 1 shows the L* values of carbon-based coatings as a function of hardness. The high L* values for DLC3 coatings indicate their higher transparency than other DLC coatings. This is attributed to the higher degree of sp^3 hybridization in DLC3 coatings as compared to that of DLC1 and DLC2 coatings.

3:20pm **PP4-2-WeA-5 Atmospheric Pressure Plasma Functionalization of Diamond Particles for Use as Quantum Sensors**, *G. McGuire,* Rivis, Inc., USA*; M. Torelli, **Nickolas Nunn (nnunn@adamasnano.com)**, O. Shenderova,* Adámas Nanotechnologies, Inc., USA **INVITED**

Negatively charged nitrogen vacancy centers (NV^-) in diamond have unique properties making them excellent candidates for nanoscale magnetic and electric field sensors, as quantum bits as well as other applications. As quantum sensors they promise comparable sensitivity at room temperature to commonly used magnetic field sensors that must be cooled to liquid helium temperature, for example. NV centers may occur as neutral NV^0 or negatively charged NV^-, however, it is only NV^- that exhibits this magnetic sensitivity. With growing interest in the use of quantum sensor it is necessary to ensure predictable and reliable performance which requires uniform NV^- formation. However, the stability of NV^- centers is strongly influenced by the surface functionalization of diamond particles. Both nitridation and fluorination have been shown to help stabilize NV^- centers especially for shallow NV centers which provide greater sensitivity. Uniform functionalization of particles in batches is necessary for cost effective production. This has been investigated using an atmospheric pressure plasma system. Results of treatment in fluorine and nitrogen-based plasmas will be reviewed. Fluorescence spectroscopy was used as a means to determine the presence of NV^0 and NV^- following treatment and the impact of the treatment will be discussed.

4:00pm **PP4-2-WeA-7 Quantification of the sp^3 Content in DLC Films Deposited by HiPIMS Using EELS and NEXAFS**, ***João Carlos Oliveira (joao.oliveira@dem.uc.pt)**,* University of Coimbra, Portugal*; A. Vahidi,* University of Coimbra, Pakistan*; R. Serra,* University of Coimbra, Portugal

Diamond-like carbon (DLC) films are a class of amorphous carbon materials with unique properties, including high hardness, low coefficient of friction (CoF), high wear resistance and chemical inertness, biocompatibility, and excellent electrical insulation. Therefore, these films have been commonly used in various industries, such as aerospace, automotive, biomedical, and microelectronics.

The advent of High-Power Impulse Magnetron Sputtering (HiPIMS) in the last two decades opened a new route for magnetron-sputtered coating. In HiPIMS, a large fraction of the sputtered atoms is ionized due to the several orders of magnitude higher plasma densities than in DCMS. Although HiPIMS has been successfully implemented for many metals, it is much less effective for DLC coatings deposition since C has significantly higher ionization energy and lower ionization cross-section than typical metals.

In previous works, the authors have shown that adding Ne to the plasma significantly improves the properties of DLC films deposited by Deep Oscillation Magnetron Sputtering (DOMS), a variant of HiPIMS. Replacing half of the Ar process gas by Ne allowed for the deposition of denser films, with hardness up to 25 GPa, while still retaining a low CoF. Furthermore, the specific wear rate (SWR) of the DLC films decreased by close to 50 %, both in linearand reciprocating slidingagainst steel counterparts, being comparable with state-of-the-art hard DLC deposited by CAD and PLD.

The main objectives of the present work were to quantitively evaluate the sp^3 content in DLC films deposited by DOMS, to identify the relevant film formation mechanisms and to better understand process-properties relationships resulting from the addition of Ne to the plasma. DLC films were deposited by DOMS both in pure Ar and in mixed Ar + Ne plasmas. Quantitative evaluation of the sp^3 content in the films was performed by Electron Energy Loss Spectroscopy (EELS) and Near Edge X-ray Absorption Fine Structure (NEXAFS). Additionally, for comparison purposes, Raman spectroscopy was also used for qualitative assessments of the film's sp^3 content. Although hydrogen was not purposefully incorporated in the DLC films deposited in this work, the hydrogen content was measured by Elastic Recoil Detection Analysis (ERDA) in combination with Rutherford Backscattering Analysis (RBS). T. The surface morphology of the DLC films was characterized by Scanning Electron Microscopy (SEM) while their microstructure was investigated by High-Resolution Transmission Electron Microscopy (HRTEM).

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