Plasma and Vapor Deposition Processes
Room Golden State Ballroom - Session PP-ThP

Plasma and Vapor Deposition Processes (Symposium PP) Poster Session

PP-ThP-5 Recyclable Thin Coatings Deposited by Means of Plasma-Assisted Techniques on Polymer Foils for Food Packaging Applications, ***Francisco A. Delfin (Francisco.Delfin@fh-wels.at)***, *C. Forsich, M. Schachinger, S. Augl,* University of Applied Sciences Upper Austria*; S. Brühl,* National University of Technology, Regional Faculty of Concepción del Uruguay (UTN – FRCU), Argentina*; C. Burgstaller, D. Heim,* University of Applied Sciences Upper Austria

The prevalent pollutant in our lands and oceans today is plastic litter. Emphasizing waste recycling is crucial to counter this environmentally harmful issue. Nonetheless, the recycling process faces challenges when items such as food packaging consist of multiple layers of diverse polymers co-extruded together to ensure adequate barrier properties. A solution to this problem lies in applying thin coatings using plasma-assisted techniques on single-layer polymer foils, which can provide similar resistance to water and oxygen permeation. Considering the nanometric thickness of these coatings, it is feasible to recycle them without significant problems.

In this study, thin coatings deposited on polymer foils using two plasma-assisted techniques are compared: Plasma-Assisted Chemical Vapor Deposition (PA-CVD), employing a bipolar DC pulsed discharge, and Magnetron Sputtering Physical Vapor Deposition (MS-PVD). Carbon and silicon-based coatings were obtained with PA-CVD using acetylene C_2H_2 and hexamethyldisiloxane (HMDSO) as precursors, respectively. MS-PVD was used to deposit carbon, silicon, and aluminium coatings. Polypropylene (PP), Low Density Polyethylene (LDPE) and Polyethylene Terephthalate (PET) with a thickness of approximately 20 µm were used as substrate. The effect of coating thickness (directly correlated to deposition time) and chemical composition on the barrier properties was examined. Characterization included Fourier Transform Infrared Spectroscopy (FTIR), Raman Spectroscopy, Scanning Electron Microscopy (SEM), Surface Free Energy (SFE), Water Vapor Transmission Rate (WVTR) and Oxygen Transmission Rate (OTR).

The FTIR spectra of the Si-coated films exhibited a characteristic band at around 1075 cm^{-1}, corresponding to the asymmetric stretching vibrations of Si–O–Si. Carbon based coatings displayed a broad band at around 1600 cm^{-1} related to C=C bonding vibrations. Raman spectra of carbon coatings showed the typical D and G bands which are characteristic of amorphous carbon. SFE was about 45 mN/m for carbon- and about 20 mN/m for silicon-based coatings, while that of the untreated polymers is in average 30 mN/m. SEM cross-sections allowed for an estimation of coating thickness between 50 and 150 nm, which is considered to be neglected in conventional recycling processes. Depending on thickness and chemical composition, barrier properties improved by 20 to 50%, with Al-PVD coating showing the best performance with an improvement of up to 10 times.

PP-ThP-6 Design and Manufacturing of Low-Cost Atomic Layer Deposition System to obtain Semiconductor and Dielectric Thin Films, *J. Navarro-Rodríguez, F. Mateos-Anzaldo,* Instituto de Ingeniería-Universidad Autónoma de Baja California, Mexico*;* ***Jesús Román Martínez-Castelo (jesus.roman.martinez.castelo@uabc.edu.mx)***, Facultad de Ingeniería, Mexicali-Universidad Autónoma de Baja California, Mexico*; A. Pérez-Sánchez, J. Ruiz-Ochoa,* Facultad de Ciencias de la Ingeniería y Tecnología, Valle de las Palmas-Universidad Autónoma de Baja California, Mexico*; A. Gaytán-Pérez,* Facultad de Ciencias de la Ingeniería y Tecnología-Valle de las Palmas-Universidad Autónoma de Baja California, Mexico*; H. Tiznado-Vázquez,* Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México*; N. Nedev,* Instituto de Ingeniería-Universidad Autónoma de Baja California, Mexico

This work describes the design and manufacturing of a lab-made ALD system. In the system, the chamber reactor was designed using SolidWorks software and machined with a lathe. The chamber is of aluminum and has an internal diameter of 3.5 inches, with two entries for precursors with a diameter of 1/64 inch, and one exit with a diameter of 1/2 inch. To dose the precursor and the oxidant, two 3-way diaphragm valves were used. This type of valves allow a continuous flow of nitrogen as carrier gas and permit formation of high- and low-pressure zones, which allow a high-speed deposit. To heat the system, a flat circular resistance controlled by a PID was used. The control of all the system is carried out using a graphical interface of LabView.

PP-ThP-7 Neon Addition to the Plasma for Enhanced Ionization in the Deposition of Cr films by HiPIMS-DOMS, ***João Carlos Oliveira (joao.oliveira@dem.uc.pt)***,** University of Coimbra, Portugal*; S. Adebayo,* University of Coimbra, Nigeria*; R. Serra,* University of Coimbra, Portugal

In magnetron sputtering-based deposition processes, particles that arrive at oblique angles relative to the growing film's surface promote the atomic shadowing effect which, ultimately, results in porous and underdense columnar microstructures. Energetic particles bombardment helps to prevent this effect by increasing the ad-atoms mobility, promoting subplantation of the impinging species and/or triggering re-deposition processes. However, bombarding the film's surface with highly energetic particles comes with a heavy cost: the formation of a high density of defects, which disrupts the crystalline structure of the films, and the creation of compressive stresses.

In a previous work, the authors have shown that in Deep Oscillation Magnetron Sputtering (DOMS), a variant of High-Power Impulse Magnetron Sputtering (HiPIMS), the atomic shadowing mechanism is mostly controlled by the ionization degree of the sputtered material[1]. Thus, at high ionization degree, dense and compact films can be deposited without the need of high energy particles bombardment. The most straightforward route to achieve high ionization of the sputtered species in HiPIMS is to increase the peak power. However, this also increases the average energy of the sputtered species and brings about energetic bombardment. Partially replacing Ar by Ne in the process gas promotes an increased mean electron energy which increases plasma ionization, as the ionization energy of Ne (21.56 Ne) is significantly higher than that of Ar (15.75 eV). In this work, partial substitution of Ar by Ne in the DOMS process gas was investigated as a mean to increase the ionization degree of the sputtered species without increasing their average energy.

In this work, Cr thin films were deposited by DOMS in pure Ar and mixed Ar + Ne plasmas up to 60 % Ne. Adding Ne to the plasma resulted in 25 % increase in the ions saturation current density (ISCD) as measured by an electrostatic flat probe placed at the substrate location. All the deposited films have a dense and compact columnar microstructure with an almost complete [110] out of the plane preferential orientation. The lattice parameter of the Cr films increased with increasing Ne content in the plasma while their surface roughness decreased from 6 to 3 nm. The hardness and young's modulus of the Cr films were evaluated by nanoindentation.

PP-ThP-9 Mechanical Properties Thermal Stabilities of Multilayered AlCrBN/AlTiSiN Hard Coatings, ***Chung-En Chang (abcd0214milk@gmail.com)***,** *T. Tsai, H. Feng, M. Yang, Y. Chang,* National Formosa University, Taiwan

AlCrN and AlTiN coatings have been applied widely in cutting tools and mold dies because of good mechanical properties, tribological properties and oxidation resistance as resulting from the incorporation of Al into CrN and TiN. The AlCrN coating possesses good oxidation resistance even at 1000 °C while the AlTiN has high hardness at high temperature. To make further improvement of these two coatings, multilayer coatings with alternate AlTiN and AlCrN layers have been designed. In addition, it is known that adding Si and B to coatings can effectively enhance their mechanical properties. Through combining the characteristics of Si and B, multicomponent and multilayer AlCrBN/AlTiSiN coatings were prepared using an electro-magnetic controlled cathodic arc ion plating method, and their thermal stabilities at high temperature up to 900 °C and 1000 °C were studied to align with the requirements of high-temperature applications. The microstructure of the deposited coatings was characterized by using a field emission scanning electron microscope (FESEM) and a high-resolution transmission electron microscope (HRTEM) equipped with energy-dispersive X-ray spectroscopy (EDS). In this study, multilayered AlCrBN/AlTiSiN coatings were deposited using cathodic arc evaporation with periodic layering structures. Nanoindentation measurements and SEM/TEM observations revealed that when the samples were subjected to vacuum annealing at 900 °C, the addition of Si and B not only suppressed the unfavorable formation of h-Cr_2N and w-AlN phases that would deteriorated mechanical properties, but also resulted in the phenomenon of increased coating hardness due to the formation of nanometer-sized c-TiN and c-AlN after the phase decomposition of the coating. In comparison,

the hardness of AlCrN coatings decreased continuously with increasing temperature due to the absence of inhibiting h-Cr_2N formation. And, strengthening mechanisms from the phase decomposition was not observed in this AlCrN at high temperature. The AlCrBN/AlTiSiN coatings exhibited the capability to maintain or even enhance their mechanical properties at high temperature. In addition to the improved oxidation resistance, secondary hardening mechanism at high temperature could contribute to the successful application of such coatings in high-temperature environments.

PP-ThP-10 CVD Equipment: Yesterday, Today and Tomorrow, ***Anne Zhang (anne.zhang@ihi-bernex.com)***, *H. Strakov,* IHI Bernex AG, Switzerland

Bernex coating systems are used worldwide to produce coatings on metal / ceramic compounds for the purpose of reducing wear and/or friction, providing corrosion and oxidation protection,or obtainingother specific surface characteristics. The CVD coating processes are based on chemical reactions on hot surfaces between reactant gases, which directly yield the solid coating material. One of the advantages of CVD resides in the ability to coat a wide range of materials with complex shapes, even porous and hollow ones, and is also suitable for coating internal surfaces. Applications include industrial components, aerospace, cutting inserts, forming/molding/extrusion tools, etc.

Bernex coating systems cover various CVD technologies, including Chemical vapor aluminizing (CVA), Chemical vapor infiltration (CVI) and CVD with solid metalorganic precursors (MOCVD). These systems are highly modular and provide significant process flexibility. Based on customer requirements, the systems can be pre-configured upon purchase, or extended at any time. This not only includes hardware and software components, but also comprises external units and accessories.

Coatings developed by Bernex will be presented, along with new process modules and general improvements on hardware and software modules. An insight of future developmentswill also be provided.

PP-ThP-12 Synthesis and Characterization TiAlZrTaNbN Coatings Obtained by High-power Impulse Magnetron Sputtering, *I. Gonzalez Avila, J. Gónzalez Lozano, O. Piamba Tulcan,* ***Jhon Jairo Olaya Florez (jjolaya@unal.edu.co)***, Departamento de Ingeniería Mecánica y Mecatrónica, Universidad Nacional de Colombia

TiAlZrTaNbN coatings were obtained by High-Power Impulse Magnetron Sputtering and deposited on superalloys and Ti alloy substrates. The effect of working pressure and bias voltage on hardness, corrosion and wear resistance was investigated and correlated with the microstructure of the samples. The microstructure, morphology and chemical composition of the coatings were analyzed by X-ray diffraction, Scanning Electron Microscopy and Energy Dispersive X-ray spectroscopy. The sample porosity and corrosion resistance were studied by electrochemical methods. The mechanical properties were evaluated by means of nanoindentation, and the tribological properties was studied with pin-on-disk technique. The pulse power and current peak have been affected by working pressure which modified significantly the films properties. The relationship between growth conditions, microstructure, wear and corrosion resistance is presented and discussed in this work. Finally, the effect of substrate-coating system and the deposition parameters are highlighted in order to further enhance HiPIMS coatings properties.

PP-ThP-13 Residual Stress Analysis in 30 µm thick High-Speed PVD Coatings, *K. Bobzin,* surface Engineering Institute - RWTH Aachen University, Germany*; C. Kalscheuer,* ***Max Philip Moebius (moebius@iot.rwth-aachen.de)***, *P. Hassanzadegan Aghdam,* Surface Engineering Institute - RWTH Aachen University, Germany

Several studies focus on the impact of residual stress in coatings, predominantly synthesized by conventional physical vapor deposition (PVD) techniques like Arc PVD and Magnetron Sputtering (MS). High-Speed PVD (HS-PVD) is a PVD variant based on hollow cathode gas flow sputtering. It enables the deposition of thick PVD coatings s >20 µm in contrast to Arc or MS-PVD, where coating thickness is limited due to compressive residual stress. Therefore, the effect of the residual stress on coating and compound properties of several HS-PVD coatings was analyzed for the first time in this study.

The aim is to evaluate the influence of diverse substrate materials, different coating systems, and process parameters on the residual stress state in HS-PVD coatings. Herein different coatings systems like AlCrN and AlCrO, were deposited at different process parameters such as reactive gas flow, deposition time, and bias voltage. The residual stress of oxide coatings with s ≈ 30 µm, deposited on WC-CO and steel X40CrMoV5-1, was analyzed using X-ray diffraction (XRD) and the $\sin^2\psi$ method. For the nitride coatings, in addition to the XRD method, the residual stresses were measured by the focused ion beam-digital image correlation (FIB-DIC) ring-core method to investigate different measuring methods.

With increasing coating thickness, a reduced compressive residual stress is determined by both analysis methods. AlCrN and AlCrO coating systems show higher adhesion strength with increasing thickness. Moreover, AlCrO coatings deposited on WC–Co indicate higher residual stresses than coatings deposited on steel substrate.

Using HS-PVD, the deposition of thicker coatings with simultaneously higher adhesion strength is possible, which is typically a limitation of Arc and MS-PVD. Additionally, lower residual compressive stresses are unexpectedly observed at higher coating thickness. This indicates an outstanding research demand to investigate, how an increased coating thickness in HS-PVD leads to reduced residual stresses.

PP-ThP-14 Corrosion and Tribocorrosion Behavior of DlC/CNx/CrC/Cr Multilayers Deposited by Hipims in Synthetic Seawater, ***Martin Flores (martin.fmartinez@academicos.udg.mx)***, *L. Flores, L. López,* Universidad de Guadalajara, Mexico*; A. González,* Unversidad Autónoma de Tamaulipas, Mexico

Diamond-like carbon (DLC), CNx and CrC coatings have a wide range of potential applications to reduce the sliding friction and improve wear and corrosion resistance of bearings and other components. AISI 4317 steel is used in bearings of crane grabs for the transport of minerals with sulfur and fluor content in port facilities. These steels suffer from tribocorrosion and corrosion promoted by chloride ions at the port and the ions from the minerals. The multilayers were deposited by High Power Impulse Magnetron Sputtering (HIPIMS). The ion etching using Ar ions cleans the substrate and the metal ion etching (Ar^+ and Cr^+) promotes a good adhesion of the film. In this work the metal ion etching was performed with a delay in the synchronized polarization pulse of the substrate with respect to the applied to the Cr target, the ion energy distribution function was studied for each plasma used to deposit the multilayers. This work reports the results of the potentiodynamic polarizations to evaluate the corrosion and the measurements of open circuit potential during the tribocorrosión tests. Synthetic seawater was used as electrolyte. The structure of Cr and CrC layers was studied by XRD. Raman spectroscopy was used to study the sp2 and sp3 bonds of DLC and CNx. The results show an improvement in the corrosion and tribocorrosion resistance of the samples coated with the multilayer.

PP-ThP-15 Stable Hybrid HiPIMS/RF Sputtering Process on a Single Magnetron for arc-free Deposition of Compact Oxide Films, *A. Fromm,* Fraunhofer Institute for Mechanics of Materials IWM, Germany*; C. Adam,* Fraunhofer Institute for Mechanics of Materials IWM, MELEC GmbH, Kiel University, Germany*; F. Meyer,* Fraunhofer Institute for Mechanics of Materials IWM, Germany*;* ***Günter Mark (guenter.mark@melec.de)***, *J. Löffler,* MELEC GmbH, Germany*; M. Thomas, M. Wirth, F. Burmeister,* Fraunhofer Institute for Mechanics of Materials IWM, Germany

Thin, insulating coatings are required for electronics, sensors and medical technology. Most of them are deposited by reactive magnetron sputtering and involve an RF or MF excitation of the plasma (radio/mid frequency). However, this often results in sub-stoichiometric layers with process-induced, but undesired residual porosity. With HiPIMS (high power impulse magnetron sputtering), significant advantages over conventional sputtering processes can be achieved, such as the production of coatings with high adhesion and almost bulk density. However, the deposition rates are lower when compared to an RF or MF process with the same average power. In addition, process stabilization is not trivial due to high peak currents and short pulse durations. Instabilities are induced by arcing between insulating areas on the target, leading to droplet formation, which significantly reduces the achievable film quality [2]. To overcome these difficulties, we have for the first time investigated the combination of an RF and HiPIMS excitation in a single magnetron.

Therefore, a HiPIMS generator from Melec company was combined with a RF-Generator and connected to a single magnetron. To avoid back reflections, a special RF-Filter was used.Al_2O_3 layers were deposited in a hybrid RF/HiPIMS process using a metallic Al target and O_2 as reactive gas, with variations in power and pulse parameters.

A stable reactive hybrid RF/HiPIMS process on a single magnetron, with higher process stability when compared to a simple HiPIMS process, has been demonstrated for the deposition of Al_2O_3 layers. The number of arcing

events could be significantly reduced. A higher deposition rate with higher nano hardness of the deposited coatings could be achieved [5].

A proof of principle for a combination of RF and HiPIMS excitation in one source has been established and opens up a new route for the arc-free deposition of Al_2O_3 and other oxidic layers. Further investigations will include the influence and optimization of pulse parameters as well as the relationship of average HiPIMS and RF power. For a pulsed superposition of RF and HiPIMS, further developments of ultrafast impedance matching techniques are also necessary.

[1] Surf Coat Tech 122.2-3 (1999), p. 290–293.

[2] Surf Coat Tech 257 (2014), p. 308–325

[3] Surf Coat Tech 250 (2014), p. 32–36.

[4] J of Vac Sc & Tech A 30.6 (2012), p. 061504.

[5] C. Adam “Untersuchungen zur plasmagestützten Abscheidung von Al2O3-Schichten im reaktiven hybriden MF/HF-HiPIMS-Sputterprozess”, Thesis Freiburg 2023.

Author Index

Bold page numbers indicate presenter