Tuesday Afternoon, November 8, 2016

Advanced Surface Engineering
Room 101C - Session SE+MS+TF-TuA

Innovations in PVD, CVD, Atmospheric Pressure Plasma and Other Surface Technologies

Moderators: Michael Stueber, Karlsruhe Institute of Technology, Germany, Robert Franz, Montanuniversität Leoben, Austria

2:20pm **SE+MS+TF-TuA1 Investigation of Critical Processing Parameters on Laser Surface Processing of Mg-Al-Zn Alloys: Impact on Corrosion Kinetics***, **Michael Melia**, D.C. Florian, J.R. Scully, J.M. Fitz-Gerald,* University of Virginia

Magnesium (Mg) and its alloys have been the topic of intense research over the past 15 years as the automotive and aeronautic industries strive to increase fuel efficiency by reducing the weight of vehicles. However their wide spread implementation is currently limited by poor intrinsic corrosion resistance. Preferential dissolution of the Mg matrix occurs due to the electrochemically noble secondary phases formed during traditional processing routes of Mg alloys. To mitigate the impact secondary phases (e.g. γ-Al_8Mn_5) have on corrosion, pulsed laser surface processing was employed in the ns time regime. Lasers operating in this time regime are capable of melting and solidification rates on the order of 10^9 K/s with the ability to extend the solid solubility limit of the alloying elements. The research herein shows the impact laser processing parameters have on the dissolution of the secondary phases and corrosion resistance in the Mg-Al-Zn alloy, AZ31B.

A KrF excimer laser (λ = 248 nm, pulse duration = 25 ns FWHM) was utilized with a cylindrical focusing lens, a laser spot size of 27 mm x 1.2 mm, and a pulse overlap of 95%. The processing parameters investigated include the laser fluence (0.7, 0.8 and 1.5 J/cm^2), irradiation dosage (pulse per area (PPA) = 20 to 400), and processing pressure (1 to 1280 Torr Ar). The dissolution of the γ-Al_8Mn_5 particles was observed by scanning electron microscopy equipped with a backscatter electron detector. Fiduciary image recognition was utilized to observe the change in γ-Al_8Mn_5 particle size before and after processing. Analysis of the H_2 evolution reaction rate, related to the quantity and density of electrochemically noble secondary phases, was performed by potentiodynamic polarization measurements in 0.6 M NaCl solution.

Results from the fluence study revealed significant dissolution of the γ-Al_8Mn_5 particles when processing was performed above the ablation threshold suggesting that material transport was afforded by a laser induced plasma pressure acting on the irradiated layer, increasing the extent of dissolution. This was also observed by an order of magnitude reduction in H_2 evolution reaction rate. The lowest pressure of Ar investigated, 1 Torr, consistently exhibited the smallest reduction in H_2 evolution reaction rate from the bulk material. All other processing pressures showed an order of magnitude reduction in H_2 evolution reaction rate when a fluence above the ablation threshold was used. The PPA study revealed a plateau in the reduction of the H_2 evolution reaction rate, observed dissolution of γ-Al_8Mn_5 particles, and time to breakdown of the corroding surface after 100 PPA.

2:40pm **SE+MS+TF-TuA2 Engineering a WC/Co Carbide Surface for PVD and CVD coatings***, **Aharon Inspektor**, P.A. Salvador,* Carnegie Mellon University*; D. Banerjee, C. McNerny, M. Rowe, P. Mehrotra,* Kennametal Inc.

The emergence of new coating technologies is driving the development of new cutting tools and improved metal cutting techniques. However, to reach these goals, the coating has to work in concert with the tool substrate material. Hence, building a functional surface that consists of coating and substrate working together, is a key step in the development of new cutting tool. In this paper we will look at the substrate side of the coating - surface interface and discuss how it affects the properties of the subsequent coating. The focus will be on surface engineering of WC/Co carbide surface for Physical Vapor Deposition, PVD, for Chemical Vapor Deposition, CVD, and for CVD diamond coatings. Specifically, Co mobility in the subsurface zone for CVD coatings and surface treatment for PVD coatings. Structure and properties of the resultant surface - coating combination will be presented and discussed.

3:00pm **SE+MS+TF-TuA3 Room-Temperature Ductility in Refractory Transition-Metal Carbides: Potential to Create Ultra-Tough, Flexible Thin Films***, **Suneel Kodambaka**,* University of California at Los Angeles **INVITED**

Transition-metal carbides are high-melting (> 3000 K), extremely hard (10s of GPa), mechanically robust, and chemically resilient compounds capable of operating in extreme environments and are attractive for aerospace and other industries. These hard materials are generally considered to be brittle at low temperatures. Improving their ductility, and hence toughness, is highly desirable but progress thus far has been limited by the lack of a basic understanding of the intrinsic deformation mechanisms in this class of materials. Here, using *in situ* transmission electron microscopy (TEM) coupled with uniaxial compression tests conducted on sub-µm-size pillars, in combination with density functional theory (DFT) calculations, we show that dislocations are mobile at room-temperature and lead to plastic deformation in NaCl-structured group IV and group V transition-metal carbide single crystals, zirconium carbide (ZrC) and tantalum carbide (TaC). We find that the yield strengths of ZrC crystals increase with decreasing size and ZrC(111) is softer than ZrC(100) crystals, an unexpected finding for NaCl-structured compounds. We attribute this anomalous behavior to surprisingly easy dislocation motion and low shear stresses along {001}<1-10> rather than along the commonly assumed {110}<1-10> slip systems. For TaC, in contrast to ZrC, the yield strengths are found to be independent of crystal size and orientation. Our observations suggest that multiple slip systems can be active and operate at room temperature in these hard, refractory ceramics and we expect similar behavior in other transition-metal carbides and nitrides. The insights gained from these studies may help in the development of new material architectures, such as tough and flexible membranes, for new small-scale structural applications.

4:20pm **SE+MS+TF-TuA7 Spray-Coated Carbon-Nanotubes for Crack-Tolerant Metal Matrix Composites as Photovoltaic Gridlines***, **Omar K. Abudayyeh**,* University of New Mexico*; N.D. Gapp, G.K. Bradshaw, D.M. Wilt,* Air Force Research Laboratories*; S.M. Han,* University of New Mexico

Microcracks developing in photovoltaic cells, due to growth defects or due to external mechanical factors, can lead to substantial power loss in solar cells. Microcracks can be critical as they propagate from the semiconductor bulk to the metal gridlines isolating portions of the cell and leading to decreased cell performance. In this work, multiwalled carbon nanotubes are being investigated for reinforcement of metal contacts on photovoltaic solar cells that serve as a secondary conductive network in the presence of cracks. In this effort we have focused on a silver-carbon-nanotube layer-by-layer microstructure. We present the use of a simple, cost-effective, and manufacturable method of depositing carbon nanotubes onto electroplated metal films to create metal matrix composite gridlines for photovoltaic cells. Carbon nanotubes are deposited using a spray coating method to create layer-by-layer microstructure composites. To increase adhesion strength to metal and achieve efficient metal-nanotube stress transfer, carbon nanotubes are chemically functionalized with carboxylic group prior to deposition. Initial strain failure tests show the ability of composite lines to remain electrically connected with fractures up to 28-µm-wide on average, where carbon nanotubes electrically bridge the gap. The metal-carbon-nanotube composites are electrically characterized though current-voltage (*I-V*) sweeps. Our composite lines can carry current densities ranging from 500 to 2500 A/cm^2 in the presence of cracks (5, 10, and 15-µ m-wide). MMC gridlines are successfully integrated on commercial triple-junction solar cells with measured fill factor and efficiency 86% and 26.8% respectively, closely comparing to current triple-junction cells with standard metallization. Dark *I-V* measurements indicate further improvement in the series and shunt resistances of the cells with the optimization of MMC integration process.

4:40pm **SE+MS+TF-TuA8 Atmospheric Pressure Plasma Enhanced CVD of High Quality Silica-Like Bilayer Encapsulation Films***, **Fiona Elam**,* FUJIFILM Manufacturing Europe B.V., Netherlands*; A.S. Meshkova,* DIFFER, Netherlands*; S.A. Starostin, J.B. Bouwstra,* FUJIFILM Manufacturing Europe B.V.*; M.C.M. van de Sanden,* Dutch Institute for Fundamental Energy Research (DIFFER), Netherlands*; H.W. de Vries,* DIFFER, Netherlands

Atmospheric pressure-plasma enhanced chemical vapour deposition (AP-PECVD) is an innovative technology that can be integrated into many existing manufacturing systems to facilitate the mass production of functional films; specifically encapsulation foils. These barrier films are essential to the flexible electronics industry, envisioned to protect devices such as flexible solar cells and organic light emitting diodes against degradation from oxygen and water.

Roll-to-roll AP-PECVD was recently used to produce smooth, 90 nm silica bilayer thin films comprising a 'dense layer' and 'porous layer' that demonstrated exceptionally good encapsulation performance with effective water vapour transmission rates in the region of 6.9×10^{-4} g m^{2} day^{-1} (at 40^{o}C, 90% relative humidity). By using the same material in the multilayer film architecture, and by having AP-PECVD as the deposition method, rendered this investigation highly industrially and commercially relevant to the eventual large scale production of flexible encapsulation foils. It was discovered that increasing the input energy per precursor gas molecule during the deposition of the dense layer, resulted in an improved encapsulation performance. However, the individual role performed by each layer in the overall success of the bilayer films is not yet fully understood, nor is the potential for energy conservation by varying process throughput.

A glow-like AP dielectric barrier discharge in a roll-to-roll set-up was used to deposit silica bilayer thin films onto a polyethylene 2,6 naphthalate substrate by means of PECVD. Tetraethyl orthosilicate (TEOS) was used as the precursor gas, together with a mixture of nitrogen, oxygen and argon. In each case, the deposition conditions for the synthesis of the dense layers were varied in order to study the effect of input energy per TEOS molecule and process throughput on the chemical composition and porosity of the layer. Deposition conditions for the porous layers were kept constant, with process throughput the only exception. Each film was characterised in terms of its water vapour transmission rate, its chemical composition and its morphology as a function of the input energy per TEOS molecule during the dense layer deposition and overall process throughput.

For the first time in AP-PECVD, it was found that the porous layer plays a critical role regarding encapsulation performance and surface smoothening of silica bilayer films. Due to increased throughput, the bilayer architecture also enables a 50% reduction in deposition energy consumption per barrier area, with respect to single layer silica films of equivalent encapsulation performance and thickness.

5:00pm **SE+MS+TF-TuA9 Plasma Polymerization of Organic Coatings at Atmospheric Pressure: Relationship between the Precursor Chemistry, the Plasma Chemistry and the Final Coating Chemistry***, B. Nisol, N. Vandencasteele, J. Hubert, C. De Vos, J. Ghesquière, D. Merche,* ***François Reniers,*** Université Libre de Bruxelles, Belgium

The synthesis of organic coatings using plasma technologies has been developed since many decades. This paper investigates a full series of organic coatings, synthesized in the same dielectric barrier discharge system, in the same operational conditions. The >10 precursors vary from fully saturated molecules, with or without heteroatoms (hexamethylnonane, CxCly, CxFy), to anhydrides, acrylates, with or without double or triple bonds. It is shown that the presence of double bonds not only significantly increase the polymerization rate, but also protect the ester function in acrylates. A combined effect of the plasma power and the presence of double bonds on the C/O ratio is observed for all the relevant precursors used. Correlation between the plasma chemistry and the fragment pattern in the gas phase, as recorded by atmospheric mass spectrometry, with the final chemical composition of the coatings, determined by XPS and FTIR is established. Coatings properties can be easily tuned either by combining precursors, by varying the plasma power or by changing the main plasma gas. By an appropriate combination of the plasma parameters and the precursor, very high deposition rates can be achieved, highly hydrophobic or hydrophilic coatings can be synthesized. These macroscopic results are interpreted in terms of plasma properties, and chemical reactivity.

This work was supported by the Belgian Federal Government (IAP research project P7/34 – Physical Chemistry of Plasma Surface Interactions).

5:20pm **SE+MS+TF-TuA10 Innovations in Atmospheric Pressure Plasma Technologies for Surface Engineering***,* ***David Ruzic,*** *Y.L. Wu, L. Na, S. Hammouti, I.A. Shchelkanov,* University of Illinois at Urbana-Champaign **INVITED**

The growing need for high efficiency-low cost coating tools for large area surfaces drives research efforts for development of innovative techniques. One of the options is an Evaporative Coating at Atmospheric Pressure process (ECAP). The principal of this deposition method is an evaporation of a material, with-in a plasma environment. The appealing advantage of this deposition technique is its atomic nature, and its environmentally safe process as no harmful chemicals compounds are used. With ECAP the evaporated material atoms end up deposited molecule-by-molecule or atom-by-atom as in a Physical Vapor Deposition but without the need for a vacuum chamber. This effect is achieved by using a thermal energy from the microwave plasma, when solid 99.99%+ purity metallic and ceramic target such as Al, Sn, Cr, Au, Ag and $AlCl_3$ could be evaporated and then produce a PVD-like coating on a work piece. The tool is designed to have the evaporated material being submerged into the center of the atmosphere microwave discharge. As the result evaporation occur in a controlled environment where a pure metals can be deposited or their compounds. For example in the aluminum case, a pure alpha phase of Al_2O_3 can be deposited using oxygen from the environment, or if a metallic coating of such a reactive metal as Al, is desired, the deposition can be performed in an pure Ar argon environment with the help of a special gas curtain. The tool provides deposition rate for metals as high as 1-5 um/min with high adhesion. The measured adhesion for copper on steel was at least 250 g/mm^2. The ECAP technology opens broad possibilities for surface processing at atmosphere without environmental impact.

6:00pm **SE+MS+TF-TuA12 Solid-state Dewetting: Control and Applications***,* ***Lukasz Borowik,*** *Y. Almadori, N. Chevalier, J.-C. Barbé,* CEA, LETI, MINATEC Campus, France

The dewetting of ultrathin silicon layers, induced by the thermal budget, is an issue to develop Silicon On Insulator (SOI) and Silicon Germanium On Insulator (SGOI) based technologies. However, dewetting can be controlled to obtain well-arranged agglomerates with similar size or even inhibited. This experimental study aims at demonstrating: the effect of the strain, surface contamination, ion sputtering on the dewetting mechanism, and further applications of dewetting thanks to interfacial reaction between agglomerates and the silicon dioxide. For that purpose, we present the results obtained on: (1) (001) oriented ultrathin (8-22 nm) silicon layers on silicon dioxide, (2) (001) oriented 12 nm silicon-germanium layers on silicon dioxide. In order to understand the dewetting mechanism, samples were heated up to ~800°C under ultra-high vacuum (1×10^{-9} mBar) during tens of minutes. The dewetted samples were characterized by Atomic Force Microscopy (AFM) to put in evidence the influence of the different factors on dewetting mechanism.

In first part of our presentation we will present various methods to control dewetting process by using different parameters such as: strained silicon, [1] surface contamination [2] or argon pre-sputtering. [3] These parameters allow tuning agglomerates size, shape and density. In second part of the talk we will show possible applications of dewetting to form porous silicon dioxide via agglomerates interfacial reaction, and finally how to master stoichiometry of silicon germanium agglomerates. [4] All these methods are promising since permit an easy and fast implementation, it is thus of real interest, since it opens up Si and SiGe agglomerates with tuned Ge concentration to application in innovative technologies.

This work was performed in the frame of the ANR LOTUS project. The measurements were realized on the CEA Minatec Nanocharacterization Platform (PFNC).

References:

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[2] Ł. Borowik et al. Thin solid films 527, 133–136 (2013)

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[4] Y. Almadori et al., 120, 7412–7420 (2016)

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