Wednesday Morning, October 22, 2008

Advanced Surface Engineering
Room: 204 - Session SE-WeM

Atmospheric Pressure Treatments and Hard and Nanocomposite Coatings

Moderator: H. Baránková, Uppsala University, Sweden, P.H. Mayrhofer, Montanuniversität Leoben, Austria

8:00am **SE-WeM1 Controlling Plasma Deposition with Liquid Aerosol Precursors**, ***L. O'Neill***, *J.D. Albaugh*, Dow Corning, Ireland **INVITED**

Recent studies have clearly demonstrated that numerous precursors can be used to produce thin film coatings by injecting liquid aerosol droplets into a non-thermal equilibrium atmospheric pressure plasma. The deposition appears to proceed via a controlled free radical polymerisation with controlled precursor fragmentation. It has recently been reported that several different siloxane products and intermediates can be used to prepare thin films by this method and the resultant coatings can be tailored to produce deposits which vary from hydrophobic siloxane to cross-linked silica thin films. Linear, cyclic, dimethyl and Si-H containing siloxanes have been deposited with equally high deposition rates. However, under certain conditions, coatings deposited from linear and dimethyl structures can appear "wet" and have a presumably low cross-link density compared to their cyclic or Si-H counterparts. Therefore, a more detailed study has been undertaken to investigate which factors control deposition rate and cross-link density in liquid aerosol – plasma polymerisation processes. A series of liquids have been nebulised and introduced into a purpose built RF atmospheric pressure plasma jet operating with helium as the main process gas. The resultant coatings have been thoroughly characterised to determine which chemical properties of the precursor directly impact upon the chemistry and morphology of the coatings.

8:40am **SE-WeM3 Deposition of Metallic Nanoparticles using Atmospheric Plasma**, *F. Demoisson,* Universite Libre de Bruxelles, Belgium, *J.J. Pireaux,* Facultés Universitaires Notre Dame de la Paix, Belgium, *H. Terryn,* Vrije Universiteit Brussel, Belgium, ***F. Reniers***, Universite Libre de Bruxelles, Belgium

The deposition of metal nanoparticles on various substrates is of high interest in surface science, as they can induce new chemical properties on surfaces. Applications can be found in catalysis, for gas sensor applications, in environmental science,.... however, the deposition of metal nanoparticles is facing many challenges such as : difficulty to have a strong binding on various surfaces (polymer, carbon, glass,...), technological difficulty of the deposition process, bad dispersion of the particles on the surface, bad particle size distribution,.... Usual processes require today high vacuum evaporation of the metal onto preactivated surfaces, or the use of hazardous organometallic compounds as precursors. In this work we present a new process[1] to deposit, in one step, easily, metal nanoparticles (Au, Rh, Pt) onto various surfaces (HOPG, glass, polymer, metal), using an atmospheric plasma torch (AtomFlo, SurX Technologies). The resulting surfaces are characterized by FEG-SEM and XPS. The results show an excellent particle size distribution, and a very good homogeneity of the particle distribution on the surfaces. Surface coverages in the range of 10-15% were obtained. The adhesion of the particles on the surface was tested using ultrasonication and proved to be very good.

[1]F. Demoisson, JJ Pireaux, F. Reniers, "process to deposit nanoparticles on a substrate" patent pending 08151463.0-1215.

9:00am **SE-WeM4 Design and Applications of the Atmospheric Pressure Hollow Cathodes**, *H. Baránková*, ***L. Bárdos***, Uppsala University, Sweden

The hollow cathode cold atmospheric plasma sources, similarly as hollow cathode plasma sources at the moderate and low pressures, exhibit the Hollow Cathode Effect (HCE). The atmospheric pressure, however, requires reduction of dimensions, so that a typical structure inside the hollow cathode, i.e. the space charge sheath - common negative glow - space charge sheath, is preserved. The experimental results on the hollow cathode generation, using a special construction with a tunable wall separation, are presented. The influence of the gas and the type of generation on the optimum size is investigated. The experimental results are supported by the hollow cathode model. The applications of the hollow cathodes operating at the atmospheric pressure are given.

9:20am **SE-WeM5 Advanced Atmospheric Pressure Microplasma Sources for Surface Treatment**, ***K.-D. Weltmann***, *R. Brandenburg, R. Foest, E. Kindel, M. Stieber, T.V. Woedtke*, Leibniz-Institute for Plasma Science and Technology e.V. (INP Greifswald), Germany **INVITED**

Compact miniaturized atmospheric plasmas exhibit very promising technological potential for surface treatment. Basically, there are two features which make them unique: (I) the tool-like, small size and light weight plasma generation unit allows fast and almost arbitrary 3D movements and (II) the contracted and comparably cold plasmas allow focused small-spot treatments, even of heat sensitive small size objects with temperature loads to the surface between 35°°C and 90°C. Especially in the area of biomedical applications these opportunities triggered significantly increasing research and development of plasma application directly to living objects. But also industrial surface treatment processes such as activation, functionalization, passivation, coating and etching gain importance. Here, an overview of different tailor-made miniaturized atmospheric pressure plasma sources is presented which can be used for specific purposes of surface coating, functionalization and decontamination. Actually, plasma assisted processes for biological decontamination up to the level of sterilization are becoming an alternative to conventional methods especially for heat sensitive materials. However, the realization of industrial plasma-based decontamination or sterilization technology still remains a great challenge. This is due to the fact that antimicrobial treatment processes needs to consider all properties of the product to be treated as well as the requirements of the complete procedure, e.g. a reprocessing of medical instruments. Here the applicability of plasma-based processes for the antimicrobial treatment on selected, heat sensitive products with special geometries is demonstrated. Modular and selective plasma sources, developed at INP are used which match the specific requirements of a variety of complex 3-dimensional structures. Measurements of relevant plasma properties (optical emission in the VIS, UV, and VUV region, along with substrate temperatures) are reported. Following this, a discourse is given about possible treatment processes and the state of the art in the new field of plasma medicine, i.e. about expected benefits of localized plasma treatment of living tissue for healing purposes. In the last part of the presentation the use of different RF-driven plasma atmospheric pressure microplasma-jets for deposition of dense SiO_x films with potential for barrier layers will be described. Measurements of relevant film properties (chemical composition and morphology) are reported and the state of the art of an advanced source tuning regime named “locked mode” is described. This mode leads to improvements of film quality and lateral homogeneity in the deposition spot.

10:40am **SE-WeM9 Stress and Strain in Polycrystalline Thin Films**, ***G.C.A.M. Janssen***, TU Delft, The Netherlands **INVITED**

Polycrystalline thin films on substrates usually are in a “stressed” state. In the presentation the two main methods for stress measurements, wafer curvature and X-ray lattice parameter measurements will be presented. Special attention will be given to the information that can be obtained by applying both techniques. This discussion will be followed by a discussion of recent results on stress in hard polycrystalline films. For Cr and CrN films, it has been shown that the stress is not uniform over the thickness of the film. High tensile stresses are observed near the substrate-film interface. Lower tensile stresses are observed further away from the interface. Moreover, it has been shown that the tensile stress is generated at the grain boundaries. In the case for which the deposition of the film is accompanied by an ion bombardment, a compressive stress is generated. The tensile- and compressive stresses in these films are independent and additive. For TiN films the situation is even more complicated. For TiN higher compressive stresses are observed close to the substrate-film interface. This effect is explained form the observation that for TiN, the evolution of the grain boundary density is accompanied by an evolution of the texture. Various texture components exhibit a different sensitivity to compressive stress generation by ion-peening.

11:20am **SE-WeM11 The Location and Effects of Si in Arc-Evaporated ($Ti_{1-x}Si_x$)N_y Thin Solid Films**, *A. Flink, M. Beckers, B. Alling, J. Bareno,* Linköping University, Sweden, *J. Sjölen,* Seco Tools AB, Sweden, *I. Abrikosov,* ***L. Hultman***, Linköping University, Sweden

Arc-Evaporated ($Ti_{1-x}Si_x$)N_y thin solid films have been studied by analytical electron microscopy, X-ray diffraction, scanning tunneling microscopy, X-ray photoelectron spectroscopy, elastic recoil detection analysis, and nanoindentation. As-deposited films form cubic solid solutions with Si substituting for Ti up to x = 0.09. Si segregation in films with higher Si content, up to x = 0.20, results in a feather-like microstructure consisting of cubic TiN:Si nanocrystallite bundles with low-angle grain boundaries and a

very high dislocation density of 10^{14} cm^{-2} (corresponding to a cold-worked alloy). Correspondingly, N content in the films increases almost linearly with Si content from y = 1.00 for x = 0 to y = 1.13 for x = 0.20. Upon annealing at 1000 °C, films with Si contents between x = 0.04 and 0.20 develop a metastable crystalline SiN_z ($1.0 \leq z \leq 1.33$) tissue phase, which is semicoherent to TiN. These films exhibit retained hardness between 31-42 GPa and are compositionally stable. Thus, superhard TiN-SiN_z nanocomposites without amorphous silicon nitride phase can be produced by arc-evaporation and subsequent annealing. At 1100-1200 °C, the films soften due to amorphization of the SiN_z tissue phase, followed by recrystallization of the TiN grains, and Si and N diffusion out of the film. Ab-initio calculations performed in parallel to these experiments reveal that c-Si_3N_4 can be stabilized with $D0_{22}$ or $L1_2$ ordered Si vacancies in a ZnS-like structure, in agreement with previous experimental results published by us,[1-3] while phonon calculations show that stoichiometric c-SiN is dynamically unstable in the NaCl and ZnS structures.[4,5]

[1]Hans Söderberg, Jon Molina-Aldareguia, Lars Hultman, and Magnus Odén, J. Appl. Phys. 97 (2005) 114327.

[2]Lars Hultman, Javier Bareño, Axel Flink, Hans Söderberg, Karin Larsson, Vania Petrova, Magnus Odén, J. E. Greene, and Ivan Petrov, Phys. Rev. B75 (2007) 155437.

[3]Hans Söderberg, Axel Flink, Jens Birch, Per O.Å. Persson, Manfred Beckers, Lars Hultman, and Magnus Odén, J. Materials Research 22 (2007) 3255.

[4]Axel Flink, PhD Thesis "Growth and Characterization of Ti-Si-N Thin Film" Linköping Studies in Science and Technology, Dissertation No. 1190, Linköping, Sweden (2008). www.ep.liu.se.

[5]B. Alling, E. I. Isaev, A. Flink, L. Hultman, I. A. Abrikosov, submitted.

11:40am **SE-WeM12 Phase Stabilization in CrN by Addition of Si and O**, *L. Castaldi,* EMPA, Switzerland, *D. Kurapov, A. Reiter,* OC Oerlikon Balzers AG, Switzerland, *V. Shklover,* ETH Zurich, Switzerland, ***J. Patscheider***, EMPA, Switzerland

The influences of adding silicon and oxygen during deposition of CrN by reactive cathodic arc evaporation on composition, structure, hardness and thermal stability were investigated. Both Cr-N-X phase ternary systems, where X denotes O or Si, exhibit a strong influence of X on hardness and thermal stability. Addition of these two elements leads to a decrease of the grain size of the cubic Cr-N-X phase, at the composition of optimum performance, down to a third or fourth of that of undoped CrN. XRD investigations suggest at least a partial substitution of N by O accompanied by the formation of an amorphous phase at higher O content, thereby forming a nanocomposite structure. The hardness of Cr-N-O coatings increases with increasing the oxygen content up to a value of 28 GPa, while fully oxidized Cr_2O_3 films showed lower hardness values around 12 GPa. The addition of Si resulted in a maximum hardness of Cr-N-Si of about 25 GPa. Cr-N-X coatings showed both an onset of oxidation which was promoted by about 200°C as compared to that of CrN. The underlying mechanisms, as evidenced by the performed measurements, will be discussed.

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