Thin Film
Room: 114 - Session TF+PS-ThA

Thin Film Permeation Barriers and Membranes
Moderator: Mariadriana Creatore, Eindhoven University of Technology, Netherlands

2:20pm **TF+PS-ThA1 Synthesis, Characterisation and Engineering of Moisture Barrier Films Deposited in a Roll-to-Roll High Current Dielectric Barrier Discharge**, ***Hindrik de Vries***, FOM institute DIFFER, Netherlands **INVITED**

Atmospheric pressure plasma enhanced chemical vapor deposition (AP-PECVD) is a new and rapidly evolving technology having clear benefits in terms of equipment costs, footprint size and possibilities for in-line processing. The excellent scalability of the dielectric barrier discharge combined with the possibility to generate non-thermal plasma in low-cost helium free gas mixtures, are essential requirements for large scale processing of functional films on web-rolled substrates.

In this work a cylindrical drum shaped DBD reactor configuration was implemented to facilitate roll-to-roll processing. We performed a systematic study of the discharge physics investigated by fast ICCD camera and voltage-current waveforms and we comprehensively analyzed the silica-like films deposited under barrier deposition conditions using AFM, XPS, SE and FTIR.

The time evolution of the atmospheric discharge was studied in 2 orthogonal directions of the cylindrical electrode geometry showing a glow-like discharge character. Detailed AFM morphology study and surface statistical analysis of the silica growth dynamics was carried out. The microstructure of the silica layers was studied using polarized ATR-FTIR and linked to the water vapor transmission rate (WVTR). The remarkable power law scaling between WVTR and film thickness was tentatively explained by the percolating nature of the moisture transport through the films. Based on this hypothesis, different approaches were investigated towards (bi-)layer architectures using AP-PECVD as well as other deposition techniques. Such a bi-layer architecture typically consists of a first porous silica layers that is subsequently covered by a dense silica capping layer.

In this contribution we will focus on the processing of silica bi-layers synthesized in different deposition regimes. The process conditions of the layers will be discussed in the frame of different scaling parameters like the energy spent per precursor molecule and the local deposition rate. Gas permeation properties were characterized by Technolox Deltaperm and calcium test. It was shown that AP-PECVD grown silica thin films of less than 30 nm deposited on a porous silica layer can yield excellent overall moisture barrier values (WVTR) typically ~$6*10^{-4}$ g/m^2 day at 40ºC, 90%RH accelerated ageing conditions.

3:00pm **TF+PS-ThA3 Investigation on Nano-Porosity in Moisture Permeation Barrier Layers by Electrochemical Impedance Spectroscopy**, ***Alberto Perrotta***, Eindhoven University of Technology, Netherlands, *S.J. Garcia Espallargas*, Delft University of Technology, Netherlands, *J.J. Michels*, Max Planck Institute for Polymer Research, Germany, *M. Creatore*, Eindhoven University of Technology, Netherlands

High-tech devices relying on organic semiconductors require device encapsulation against moisture and oxygen permeation, which would otherwise negatively affect the device opto-electrical performance.

The water permeation in inorganic moisture barriers has been shown to occur through macro-scale defects/pinholes (ranging from tens of nms to several µms) and nano-pores, down to sizes approaching the water kinetic diameter (0.27 nm). Both permeation paths can be identified by the calcium test, which allows discerning between the effective water vapor transmission rate (WVTR) and the intrinsic WVTR, the latter solely attributed to the permeation through the nano-porosity characterizing the bulk of the barrier layer. Recently [1], we have shown that ellipsometric porosimetry (EP) is a valid method to classify and quantify the nano-porosity content of inorganic barriers and a correlation has been found between their relative pore content and intrinsic WVTR values [1]. However, no information can be retrieved on the macro-scale defects nor on the kinetics of water permeation through the barrier, both essential elements in assessing the quality of the barrier layer.

In this study, electrochemical impedance spectroscopy (EIS) is demonstrated as a sensitive method to obtain quantitative information on both nano-porosity and macro-scale defects, complementing the barrier property characterization obtained by means of EP and calcium test.

EIS analysis is carried out on thin SiO_2 barrier layers deposited by plasma enhanced-CVD. The layer capacitance has been determined by modelling the impedance data with the proper equivalent circuit and the change of the capacitance upon water permeation has been followed. The Brasher-Kingsbury equation has been successfully applied and water uptake in the range of 0.8-4% have been found, in agreement with the nano-porosity content inferred by EP. A good linear correlation between the nano-porosity and the values of the electrical components used in the fitting procedure of the EIS data has been obtained, suggesting the direct calculation of open nano-porosity from an EIS fit. Furthermore, the kinetics of water permeation can be followed by EIS: the water diffusivity for the SiO_2 layers has been determined and found in agreement with literature values. Moreover, differently from ellipsometry-based techniques, EIS data are shown to be sensitive to the presence of local macro-defects, inferring its possible use for the prediction of the barrier performance with the calcium test.

[1] A. Perrotta *et al.*, Microporous Mesoporous Mat., 188 (2014) 163-171

4:00pm **TF+PS-ThA6 Thin-film Dielectrics for Chronic Nonhermetic Encapsulation of Electrically Active Neural Implants**, ***Stuart Cogan***, The University of Texas at Dallas **INVITED**

The needs of emerging clinical applications of neural stimulation and recording in the treatment of many diseases and disorders are driving a reduction in the size of implanted devices and the development of strategies to manage the large number of electrical interconnects between implanted electrodes and control electronics. The requirements for large numbers of electrodes, exceeding many hundreds for vision prostheses, and the ability to interface with nerves that may be as small as 100 microns in diameter, precludes the use of conventional packaging with hermetically sealed metal or ceramic cans. One of the few practical alternatives to hermetically sealed enclosures is the use of thin-film dielectrics, possibly combined with polymer over-layers. Besides the need for these thin-film coatings to provide effective passivation against corrosion, they also serve a multifunctional role providing adhesion between polymer and metal layers in flexible devices, providing a biocompatible interface to neural tissue and in some devices, providing a surface for functionalization with bioactive molecules. Conventional passivation materials such as silicon dioxide and silicon nitride are prone to corrosion *in vivo* and recent experience with polymer encapsulation such as Parylene-C suggests that this otherwise excellent barrier layer may fail after chronic implantation for more than about one year. The implanted electronics on these devices operates typically at 3 V or higher and neural stimulation involves pulsatile currents that may also induce unexpected failures at interfaces. In this context, other thin-film materials such as amorphous silicon carbide (a-SiC), ultra-nanocrystalline diamond (UNCD), and atomic-layer-deposition (ALD) Al_2O_3 are being investigated as alternative passivation materials that can provide chronic protection of active implants. A discussion of the physical and chemical requirements for these materials and results reported to date is presented. Emphasis is placed on understanding the constraints of the application including processing compatibility with temperature-sensitive substrates, the need for conformal coatings, and appropriate test methodologies to validate predictions of chronic *in vivo* lifetimes. Early results are promising with some combinations of thin-film and polymer encapsulation exhibiting excellent stability and biocompatibility. Of particular interest, are the relative roles and importance of interfacial properties and bulk barrier properties in achieve long-term chronic passivation of implanted active devices.

4:40pm **TF+PS-ThA8 Atmospheric Pressure Roll-to-Roll Plasma Enhanced CVD of High Quality Silica-like Bi-layer Moisture Barrier Films: The Influence of Input Energy**, ***Fiona Elam***, FUJIFILM Manufacturing Europe B.V., Netherlands, *A. Meshkova, S.A. Starostin*, DIFFER, Netherlands, *J.B. Bouwstra*, FUJIFILM Manufacturing Europe B.V., Netherlands, *M.C.M. van de Sanden, H.W. de Vries*, DIFFER, Netherlands

Atmospheric Pressure-Plasma Enhanced Chemical Vapour Deposition (AP-PECVD) is a new enabling technology that can be easily integrated into many existing manufacturing systems to facilitate the mass production of functional films. To date, roll-to-roll AP-PECVD has been successfully used to produce ultra-smooth, dense, 100 nm single layer silica-like thin films that demonstrate good water vapour barrier performance, therefore showing particular promise as a technique in the field of protective layer synthesis for flexible organic solar cells. However, this technology is only viable for moisture barrier production if high quality films can be manufactured at high throughput and at low cost. The generation of bi-layer silica-like thin films comprising a ‘dense layer’ synthesised using very low precursor gas flows deposited on top of a ‘porous layer’ synthesised at a

high deposition rate, could provide one potential solution to this scientific challenge.

A glow-like AP dielectric barrier discharge in a roll-to-roll set-up was used to deposit a series of ~90 nm bi-layer silica-like thin films composed of a ~60 nm 'porous layer' and ~30 nm 'dense layer' onto a polyethylene 2,6 naphthalate substrate by means of AP-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 'porous layer' were kept constant, while the conditions for the synthesis of the 'dense layer' were varied in order to study the effect of increased input energy per precursor gas molecule (~6 – 70 keV/TEOS molecule) on the chemical composition and porosity of the 'dense layer' and hence, the influence of this 30 nm layer on the moisture barrier performance of the overall film.

Each film was characterised in terms of its water vapour transmission rate, its chemical composition (*s*-, *p*- and *un*-polarised Attenuated Total Reflectance-Fourier Transform Infrared spectroscopy and X-ray Photoelectron Spectroscopy) and its morphology (Atomic Force Microscopy) as a function of the input energy per precursor gas molecule during the 'dense layer' deposition. The analysis provided valuable information concerning the structure of the silica network within each 'dense layer', and hence the influence of input energy per precursor gas molecule on the ultimate film quality.

The ~90 nm bi-layer silica-like thin films were seen to exhibit water vapour transmission rates of at least 6.2×10^{-4} g m^{-2} day^{-1} (at 40ºC, 90% RH), illustrating that it is possible to produce exceptionally high quality moisture barrier films using the presented bi-layer approach in a roll-to-roll AP-PECVD set-up.

5:00pm **TF+PS-ThA9 Use of Aluminum Oxide as a Permeation Barrier for Producing Thin Films on Aluminum Substrates**, ***James Provo***, Consultant, J. L. Provo Consulting

Aluminum has desirable thermal properties (i.e. conductivity, diffusivity and specific heat), electrical and optical properties of resistivity and reflectivity, and the characteristic of being non-magnetic and having a low atomic weight (26.98 g-atoms), but because of its low melting point (660°C) and ability as a reactive metal to alloy with most metals, it has been ignored as a substrate for use in processing thin films. The author, proposed a simple solution to this problem, by putting a permeation barrier of (Al_2O_3) onto the surface of Al substrates, by using a standard oxidation process of the surface (i.e., anodization), before additional film deposition of reactive metals at temperatures up to 500°C for 1 hour, without the formation of alloys or inter-metallic compounds that would affect the properties of the Al substrates. The chromic acid anodization used (MIL-A-8625) produced a film barrier of ~ 10k Å of alumina. The fact that refractory Al_2O_3 can inhibit the reaction of metals with Al at temperatures below 500°C suggests that Al is a satisfactory substrate if properly oxidized prior to film deposition. To prove this concept, thin film samples of Cr, Mo, Er, Sc, Ti, and Zr were prepared on anodized Al substrates and studied by Auger/ argon sputter surface analysis to determine any film substrate interactions. In addition, a thin film of (ErD_2) on an anodized aluminum substrate was studied with and without the alumina permeation barrier. Films for study were prepared on 1.27 cm O.D. high purity Al substrates with ~ 5k Å of the metals studied after anodization. Substrates were weighed, cleaned, and vacuum fired at 500°C prior to use. The aluminum substrates were deposited with the metals studied, using standard electron beam evaporation techniques, and after film deposition the erbium film was hydride with D_2 gas using a standard air-exposure hydriding technique. All processing was conducted in an all metal ion pumped high vacuum system. Results showed that e-beam deposition of all films studied onto Al substrates could be successfully performed, if a permeation barrier of Al_2O_3 from (5-10)k Å was made prior to thin film deposition up to temperatures of 500°C for 1 hour. Dihydrides, can also be successfully produced with full gas/metal atomic ratios of ~ 2.0 as evidenced by the (ErD_2) thin films produced. Thus the use of a simple permeation barrier of Al_2O_3 on Al substrates prior to additional metal film deposition, was proven to be a successful method of producing both thin metal and hydride films of various types for many applications without the formation of alloys or inter-metallic compounds that would affect substrate properties.

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