Thin Film
Room: 104 A - Session TF+VT-WeM

Thin Film Permeation Barriers and Encapsulation
Moderator: L.W. Rieth, University of Utah

8:00am **TF+VT-WeM1 Tuning the Composition and Water Vapor Permeation Properties of the Silica-Like Films Deposited in Atmospheric Pressure High Current Dielectric Barrier Discharge**, ***S.A. Starostin**, H. de Vries,* FUJIFILM Manufacturing Europe B.V, Netherlands*, M. Creatore,* Eindhoven University of Technology, Netherlands*, M.C.M. van de Sanden*, Dutch Institute for Fundamental Energy Research (DIFFER), Netherlands

Atmospheric pressure plasma enhanced thin film deposition is new and rapidly developing technology strongly beneficial regarding equipment costs, footprint size and possibilities of in-line processing. However the main characteristics of the deposition process as well as the properties of synthesized coatings are not known as good as for the traditional low pressure PECVD. Moreover the control over large area plasma at atmospheric pressure imposes serious scientific and engineering challenges. Recently we demonstrated the possibility to produce high quality silica layers using ambient air as a process gas [1] and to synthesize films with ultra-smooth morphology [2].

In this contribution we present study on the thin film properties deposited in high current diffuse dielectric barrier discharge between cylindrical electrode system in industrially relevant roll- to -roll configuration on polymeric PEN and PET webs. As the model case the silica-like films were synthesized from cost efficient gas mixture of N_2/O_2 and TEOS as organosilicon precursor. Film composition and molecular network structure was analyzed by ATR-FTIR and XPS methods. Gas permeation properties were controlled by MOCON and Ca-test.

The energy spent per precursor molecule as well as the substrate temperature were recognized as important parameters influencing thin films composition and gas permeation characteristic. The increased incorporation of nitrogen was detected for good performing gas diffusion barrier layers. An unusual power law dependency of WVTR on the film thickness was found for the 20 nm – 120 nm thick films. It was shown that atmospherically deposited silica like thin films can provide excellent overall WVTR barrier of 7.5 10^{-4} g/m^2 day at 40 ^{o}C and 90% RH which can be extrapolated using experimental activation energy value down to 6 10^{-5} g/m^2 day at standard conditions of 20 ^{o}C /50% RH. The measured intrinsic barrier value at 20 ^{o}C /50% RH was as good as 3 10^{-5} g/m^2 .

[1] S.A. Starostin, P. Antony Premkumar, H. de Vries, R.M.J. Paffen, M.Creatore, and M.C.M. van de Sanden; Appl. Phys. Lett. 96, 061502 (2010)

[2] P. Antony Premkumar, S.A. Starostin, H. de Vries, M. Creatore, P.M. Koenraad, M.C.M. van de Sanden; Plasma Processes and Polymers 10, 313 (2013)

8:20am **TF+VT-WeM2 Measuring the Diffusion Coefficient of Water in High Quality Permeation Barrier Layers**, ***B. Visweswaran,*** Princeton University*, P. Mandlik, J. Silvernail, R. Ma,* Universal Display Corporation*, J.C. Sturm, S. Wagner*, Princeton University

Deposited thin film permeation barriers are of great interest for the protection of flexible organic light-emitting diode (OLED) displays. Water can permeate on three pathways into such barrier coated devices: 1. Diffusion through the bulk of the barrier; 2. Permeation through defects in the barrier; and 3. Permeation along the barrier/substrate interface. During research on new barrier materials, permeation through defects and along interfaces can easily dominate permeation through the bulk of the barrier. This makes evaluation of the inherent permeability of a new barrier material difficult. We present two fast turnaround techniques that measure the diffusion of water in flexible barrier films that have ultra-low permeability: electrical capacitance, and mechanical stress. These techniques are calibrated against the results of secondary ion mass spectrometry (SIMS). Capacitance is measured on layers sandwiched between electrodes on glass substrates. Stress is measured from the curvature of barrier films deposited on silicon wafers. Both the capacitance and the stress technique measure very low diffusion coefficients. All three techniques are applied to one specific type of ultra-low permeability barrier film prepared by the plasma oxidation of hexamethyl disiloxane. Films are exposed to water between 65°C and 200°C, including D_2O and H_2O^{18} for SIMS. From the accelerated diffusion data we extrapolate barrier lifetimes at room temperature. Lifetime is defined as the time required for the permeation of one monolayer of water.

SIMS provides values of H, D, O^{16} and O^{18} concentrations and their depth profiles. We use these to calibrate the concentrations in the capacitance and stress measurements, and to identify the diffusion mechanism. Capacitance is highly sensitive to the in-diffusion of water because of its high dielectric constant (liquid H_2O: 80 vs. SiO_2: 3.9). Mechanical stress also is highly sensitive because the barrier swells as water diffuses in. Each exposure to water produces a change of capacitance and stress from which diffusion coefficients are extracted. We assume that capacitance and stress are linear with water content of the barrier.

For samples exposed to water at 100°C, the diffusion coefficient determined from SIMS is 4.4x10^{-15}cm^2/s, from capacitance 5.6x10^{-15}cm^2/s, and from stress 4.2x10^{-15}cm^2/s. The close agreement suggests that any one of the three techniques will yield reliable results. The activation energy for the diffusion coefficient is 0.7 eV and that for water solubility is -0.2 eV. At 30°C and 100% relative humidity, one monolayer of H_2O will diffuse through a 2.5 micrometer thick barrier layer in 20 years.

8:40am **TF+VT-WeM3 Improving the Reliability of Electronics Using ALD Barrier Films**, ***S. Graham**, H. Kim, A. Sharma, D. Samet, A. Bulusu*, Georgia Institute of Technology **INVITED**

The development of ultra barrier films has been seen as an enabling technology for the packaging and reliability of organic electronic devices. While a number of technologies exists for creating ultra barrier coatings, atomic layer deposition has been viewed as a leading technology for creating single layer and nanolaminate barriers with molecular level control of the film thickness and composition. Such control allows for the creating of barriers with multiple functionality that can be utilized in organic electronics and extended to other electronic platforms. In this talk, we will discuss the development of ALD ultra barrier films based on several oxides that are targeted for packaging organic electronics as well as creating highly stable interfaces for their improved lifetime and stability. Methods to control or enhance the nucleation of these films on polymer and metallic surfaces with the aid of surface functionalization groups will be discussed. The mechanical properties of the ALD films in terms of their onset cracking strain and its impact on the limitations of flexible electronics will be discussed. Finally, the stability of these barrier films when exposed to harsh environmental conditions including damp heat and aqueous solutions will be presented. Stability of the films was determined through a variety of methods including photoluminescence, XPS, UPS, and atomic force microscopy. Films showing superior stability in these environments will be demonstrated through the coating of both organic and inorganic electronics and showing improvements in their stability in harsh environments.

9:20am **TF+VT-WeM5 Long-term Performance of Atomic Layer Deposited Al_2O_3 and Parylene Bi-layer Encapsulation for Utah Electrode Array Based Neural Interfaces**, ***X. Xie**, L.W. Rieth, F. Solzbacher*, University of Utah

Encapsulation of three dimensional neural interfaces with complex geometries and tight gaps between components is one of the greatest challenges to achieve long-term functionality and stability. We present a novel encapsulation scheme that combines atomic layer deposited (ALD) Al_2O_3 and Parylene C for biomedical implantable. Our approach is composed of the highly effective moisture barrier properties of ALD alumina, and Parylene as a barrier to many ions and for preventing contact of alumina with liquid water.

Different configurations of Utah electrode array (UEA) based devices were used to test the encapsulation performance from three different aspects: long-term impedance stability, current drawing level, and long-term wireless signal strength and frequency shift.52 nm of Al_2O_3 was deposited by plasma-assisted (PA) ALD on assembled UEAs at 120 °C. A 6-µm thick Parylene-C layer was deposited by CVD using Gorman process on top of Al_2O_3 and A-174 (Momentive Performance Materials), an organosilane, was used as adhesion promoter.

Hybrid methods were used to de-insulate the tips of the UEAs in order to interact with neurons for recording and stimulation. First, 200 laser pulses with fluence of 1400 mJ/cm^2 were used to remove the Parylene C layer. 3 minutes of oxygen plasma etching was added to remove the carbon residue on the tips from laser de-insulation. Then the alumina layer was removed by dipping the array into buffered oxide etch (BOE) for 10 minutes. Parylene C acted as a mask layer for BOE etching and only alumina in the area where Parylene was removed by laser was etched away. The tip exposure was ~ 35 µm. The devices were then put into saline solution for soak testing.

The median tip impedance of the bi-layer encapsulated wired Utah electrode array increased from 60 kΩ to 160 kΩ during the 960 days of equivalent

soak testing at 37 °C. The loss of tip metal iridium oxide and etching of silicon in PBS solution contributed to the increase of impedance. Also bi-layer coated fully integrated Utah array based wireless neural interfaces had stable power-up frequencies at ~910 MHz and constant RF signal strength of -50 dBm during the 1044 days of equivalent soaking time at 37 °C. Bi-layer coated Utah arrays had steady current drawing of about 3 mA during 228 days of soak testing at 37 °C. The relatively stable tip impedance, constant power-up frequencies and signal strengths, and low current drawing suggested that the alumina and Parylene C bi-layer coating is very suitable for encapsulating chronic implantable devices.

9:40am **TF+VT-WeM6 On the Role of Nanoporosity in Moisture Permeation Barrier Layers***, **A. Perrotta**, G. Aresta, W. Keuning,* Eindhoven University of Technology, Netherlands*, M.C.M. van de Sanden,* Eindhoven University of Technology; DIFFER, Netherlands*, W.M.M. Kessels, M. Creatore*, Eindhoven University of Technology, Netherlands

Although satisfactory results in term of moisture permeation barrier performance have been achieved for the encapsulation of organic electronic devices, a deeper understanding of the relation between barrier properties and permeation pathways is still necessary. This contribution focuses on the role of the residual nanoporosity in the inorganic layer in controlling its barrier performance.

Plasma-assisted atomic layer deposition (PA-ALD) and plasma-enhanced chemical vapor deposition (PECVD) inorganic (i.e. Al_2O_3 and SiO_2) barrier layers have been extensively analyzed by means of IR spectroscopy, spectroscopic ellipsometry, Rutherford backscattering spectroscopy and elastic recoil detection. The calcium test has been performed to determine the intrinsic water vapor transmission rate (WVTR), i.e. by excluding the local white spot development, as well as the effective WVTR values. Ellipsometric porosimetry (EP) has been applied to determine the open porosity and pore size range of the layers. Two different adsorptives have been adopted as probe molecules, i.e. trivinyltrimethylcyclotrisiloxane (d_{V3D3} = 1 nm) and water (d_{H2O} = 0.3 nm). A correlation between the residual nanoporosity and the intrinsic barrier properties of moisture barriers has been found, regardless the chemistry of the layer and deposition technique used. Pores larger than 1 nm with a relative content above 1% have been found responsible for poor barrier layers characterized by a WVTR in the range of 10^{-2}-10^{-3} $gm^{-2}day^{-1}$. Furthermore, the pore size range of [0.3-1] nm and its relative content have been found to drive the transition in WVTR from 10^{-4} to 10^{-5}-10^{-6} $gm^{-2}day^{-1}$, highlighting the role of the residual nanoporosity in controlling the intrinsic barrier properties.

Electrochemical impedance spectroscopy (EIS) has also been adopted as novel technique in the evaluation of the moisture barrier properties. Water diffusion through the barrier has been followed as a function of the variation of the electrochemical properties and related to the layer porosity.

The control at nanoporosity level has also been addressed by coupling a mediocre PECVD SiO_2 barrier layer with an ultra-thin (2 nm) PA-ALD Al_2O_3 layer. The decrease in WVTR by three orders of magnitude in the SiO_2/Al_2O_3 system has been attributed to the filling of the residual nanoporosity in the SiO_2 layer by Al_2O_3. This result is supported by angle-resolved XPS analysis and explained on the basis of the molecular dimension of the Al_2O_3 deposition precursor, i.e. trimethylaluminum (d_{TMA} = 0.65 nm), able to penetrate pores larger than 1 nm.

10:40am **TF+VT-WeM9 Atomic Density and Nano-Porosity Thresholds for Nanoscale Low-k Moisture Diffusion Barrier Materials***, **S.W. King**, E. Mays, J.D. Bielefeld, D. Jacob, B. Colvin, D. Vanleuven, J. Kelly,* Intel Corporation*, M. Liu, D. Dutta, D. Gidley*, University of Michigan

As the semiconductor industry strives to keep pace with Moore 's Law, new materials with extreme properties are increasingly being introduced and tighter control of these material properties is being demanded. Low dielectric constant (i.e. low-k) Cu and moisture diffusion barrier materials are one specific example. Low k diffusion barrier materials are desired to replace the relatively high-k SiN_x:H (k = 7.0) material currently utilized as both a moisture and Cu diffusion barrier layer in order to reduce resistance-capacitance (RC) delays in nano-electronic Cu interconnect structures. Typical methods for producing low-k materials consist of introducing controlled levels of nano-porosity via intentional incorporation terminal organic (CH_x) groups during plasma enhanced chemical vapor deposition (PECVD) of SiO_2 and SiN_x:H network materials. However while lowering k, the introduction of nano-porosity can seriously compromise the performance of such materials as potential moisture and metal diffusion barriers. In this presentation, we will demonstrate that critical thresholds in nano-porosity exist for the diffusion of water and solvents through low-k materials. Specifically, we utilize Fourier Transform Infra-Red (FTIR) spectroscopy, to show that the concentration and size of nano-pores formed in low-k a-SiN(C):H dielectric materials is controlled by the concentration of terminal Si-CH_3 bonding versus Si-N network bonding. We further combine moisture / solvent diffusivity measurement with x-ray reflectivity (XRR) and positron annihilation lifetime spectroscopy (PALS) to demonstrate that low-k a-SiN(C):H dielectrics become poor moisture diffusion barriers at mass densities < 2.0 g/cm^3 and when the pore size approaches that for the molecular diameter of water. Similarly, we show that low-k materials become easily penetrable by solvents and metals when the pore diameter approaches the size of these species. The implications of these critical nano-porosity thresholds on the performance of low-k materials as diffusion barriers and potential limitations on thickness scaling in the presence of defects will also be discussed.

11:20am **TF+VT-WeM11 Low Stress Carbon Films as Gas Barrier Layers***, **J. Rowley**, R.C. Davis, L. Pei, R.R. Vanfleet,* Brigham Young University*, S. Liddiard, M. Harker, J. Abbott*, MOXTEK Incorporated

A low stress, flexible hydrogenated sp2 carbon film(a-C:H) was developed using reactive sputtering of a graphite target in an ethylene/argon gas mixture. This resulted in a corrosion resistant layer. The carbon film was characterized by a series of techniques including Raman, EELS, AFM, XPS, and CHN analysis. An ethylene to argon gas ratio of 0.1 resulted in a film with 83.9% carbon, 5.0% hydrogen and 10.6% oxygen by weight fraction. This corresponds to a mole fraction of hydrogen to carbon of 4:6, a large hydrogen fraction. The films are dominantly sp2 as seen by Raman and EELS. Bulge testing determined a low elastic modulus and strength. The 4:6 a-C:H, 100 micron films showed a stress of 200 MPa(compressive) which is much lower than what has been reported previously for sputtered carbon films.

11:40am **TF+VT-WeM12 The Effective Control of Surface Profile and Arc Discharge during Amorphous Carbon Layer Deposition Process***, **I.-S. Kim**, J. Park, J.H. Lee, M.J. Kim, Y.B. Choi, H.-G. Kim, S.H. Lee, J.W. Hong, J.L. Lee, M.W. Kim, G. Choi, H.-K. Kang, E.S. Jung*, Samsung Electronics Co., LTD., South Korea

Amorphous carbon layer (ACL) has been introduced to the hard mask material for dry etch process under sub 20 nm devices, due to the optical transparency, easy removal and proper mechanical properties. With the shrinkage of device scales, thickness uniformity of hard mask is critically related to the next etch performance, such as etch depth or profile uniformity. Furthermore, in case of thicker ACL deposition for high aspect ratio etch process, the arc discharge is frequently occurred due to the high conductivity of carbon film.

In this study, ACL was deposited by plasma enhanced chemical vapor deposition (PECVD), which consists of capacitive coupled plasma(CCP) at 13.56 MHz, by using the propylene(C_3H_6_Carbon source). The multi-zone gas distributor and partially controlled heater were applied to control the surface profile, resulting in ~1% of thickness uniformity. In addition, the thickness profile was freely controlled from convex surface to concave surface shape, which results in easier and better process integrations for the following etch steps.

During the thick ACL (over 1µm) deposition, the arcing discharge is frequently occurred inside chamber and damaged to the wafers or hardware of equipment. The arc discharge was effectively controlled by introducing various ground paths and modified hardware. As the ground paths were integrated into the chamber, the RMS voltage which is applied to the chamber was decreased while the RMS current was increased. As a result, these tendencies induced to the decrease of impedance in process plasma, avoiding arc discharges. Not only more stable glow discharge is generated, also process efficiency is improved.

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