Tuesday Morning, October 20, 2015

Thin Film
Room: 111 - Session TF+EM+MI+MS-TuM

ALD for Alternative Devices

Moderator: Paul Poodt, Solliance/TNO, Richard Vanfleet, Brigham Young University

8:00am **TF+EM+MI+MS-TuM1 FAST-ALD™ with Close Proximity (CP) Plasma for Low Temperature Applications: Nano-Composite Layer (NCL) Stacks for Flexible Substrates**, ***SangIn Lee***, Veeco **INVITED**

The stress of the film is an important factor in mechanical stability and reliability of the devices, especially flexible electronic applications and microelectro-mechanical systems (MEMS), because it causes mechanical cracks, delamination and degradation in reliability of the device. Moreover, mechanical integrity of nano-scaled devices requires not only the physical properties of the individual films such as thermal expansion coefficient and elastic modulus, but also integral structural properties such as interface adhesion, and therefore residual stress of the film need to be managed.

Veeco's proprietary ALD technology, Fast Array Scanning Technology (FAST-ALD™) with Close-Proximity (CP) Plasma, has unique characteristics that are differentiated from other spatial ALD technologies. CP-plasma in FAST-ALD™ provides very uniform radical streams onto the substrate without plasma-induced damages and substrate heating enabling FAST-ALD™ to provide plasma-ALD films and stable polymeric MLD films from CP Plasma which cannot be obtained from conventional plasma process, for high-quality films at extremely low temperature for use in stress-sensitive device applications such as low-k films on Si wafers or flexible functional films on plastic substrates.

Stresses in inorganic ALD layers can be offset by either carbon-incorporated dielectric (CID) interlayers or polymeric MLD interlayers. The relative percentage of the inorganic ALD film to CID interlayer can be changed to tailor the stress of the stacked film to the device requirements. In this experiment, the combinations of an inorganic dielectric layer (Al_2O_3) with CID interlayers as part of nano-laminates, obviously in the same philosophy with polymeric MLD interlayers, nano-composite layer (NCL) stacks were deposited at 80°C to control the stress of the stacks from tensile to compressive state and vice versa, by changing the thickness and atomic content of Al_2O_3 layer and materials. By changing the ratio of the thickness in NCL stacks, 4:2 stacked film (4 Al_2O_3 layers and 2 CID layers as a sub-stack) and 1:1 stacked film (1 Al_2O_3 layer and 1 CID layer as a sub-stack) with total 30nm thickness show very low tensile stress and compressive stress of +58MPa and -89MPa, respectively, indicating the potential application of these free standing film stacks to nano-scaled devices and/or environmentally sensitive devices. NCL stack shows higher immunity to cracks and competitive barrier properties than that of the single ALD layer. NCL concept approaches can be applied to semiconductor in low-k pore sealing and oxidation barrier in the backend-of-line (BEOL) and cutting-edge devices with flexible substrates.

8:40am **TF+EM+MI+MS-TuM3 Atmospheric Roll-to-Roll Spatial Molecular Layer Deposition for flexible barriers**, ***Fieke van den Bruele***, *F. Grob*, *P. Poodt*, Holst Centre / TNO, Netherlands

Proper encapsulation of devices such as OLEDs and thin-film photovoltaics is critical, as exposure to moisture from the ambient will degrade these devices, reducing their efficiency, lifetime, or even lead to failure altogether. Especially for OLEDs, the barrier requirements are very challenging, with a Water Vapor Transmission Rate < 10^{-6} g/m^2/day. To achieve these very low WVRTs, very high quality barrier layers are required, being pinhole free over the entire device area. Encapsulation of flexible devices is even more challenging as the encapsulation should not affect the device flexibility too much.

The recent development of roll-to-roll and large-area Spatial ALD technology has spurred the interest in ALD for encapsulation and barriers. Thin layers of inorganic material (10-20 nm) made with (spatial) ALD have sufficiently low intrinsic WVTR but often do not meet the requirements for barriers because they are very sensitive to particles and roughness that lead to defects. Thick inorganic films are less sensitive to particles, but suffer from stress and can have a limited flexibility. Various flexible thin film encapsulation techniques have been recently developed, often combining one or more thin inorganic diffusion barrier layers (e.g. SiN_x, Al_2O_3) with an organic layer that acts as stress relief layer but has no additional barrier functionality. One of those proposed interlayers for stress relief and flexibility are organic materials deposited through Molecular Layer Deposition (MLD). A well-studied example are the Alucones, prepared by reacting trimethyl aluminum with an alcohol. There are several reports on the barrier properties of Al_2O_3 – Alucone multilayer stacks, but the results seem to be inconclusive.

Assessing the flexibility these MLD layers are is not straightforward as measuring the mechanical properties of these very thin layers is difficult. We use a simple, qualitative method to test the flexibility of these MLD layers, by combining bending test with a polymer etch test to visualize cracks and other defects in the MLD film caused by bending. Preliminary results show that the flexibility of MLD layers, like their organic counterparts, largely depend on film thickness and can suffer from instability.

The next step in making MLD barriers is upscaling towards large-area and roll-to-roll production. We will present the results of our atmospheric roll-to-roll spatial MLD of alucones on polymer foils. Furthermore, an outlook to full-industrial scale R2R ALD/MLD production of barriers will be discussed.

9:00am **TF+EM+MI+MS-TuM4 Low Temperature, Temporal and Spatial Atomic Layer Deposition of TiO_2 using Titanium Tetra-Isopropoxide as Precursor**, ***Morteza Aghaee***, Eindhoven University of Technology, Netherlands, *P.S. Maydannik*, Lappeenranta University of Technology, Finland, *P. Johansson*, Tampere University of Technology, Finland, *M. Creatore*, Eindhoven University of Technology, Netherlands, *T. Homola*, *D.C. Cameron*, Masaryk University, Czech Republic, *J. Kuusipalo*, Tampere University of Technology, Finland

Spatial atomic layer deposition (S-ALD) is a technique which has been shown to lead to high quality moisture barrier films (e.g. Al_2O_3) in a roll-to-roll process[1]. However, TiO_2 is expected to outperform Al_2O_3 because of its higher stability against long-term degradation than Al_2O_3. For high throughput S-ALD at low temperature, highly reactive precursors with high vapour pressure are necessary. Titanium chloride is typically used but has the disadvantages of residual chlorine incorporation in the film and generation of corrosive by-products. Titanium tetra-isopropoxide (TTIP) is a valid alternative because of its high vapour pressure at room temperature compared to other titanium organometallic compounds[2]. TTIP has not previously been used as a precursor for S-ALD.

In this work, a preliminary investigation has been carried out on the temporal ALD approach consisting of alternating exposure of a polyethylene naphthalate (PEN) substrate to the precursors TTIP and water, ozone or oxygen-fed plasma. The deposition was carried out at a substrate temperature of 80-120ºC. The highest growth rate (0.056 nm/cycle) and refractive index (2.33) values have been obtained by using an O_2- fed plasma. The water vapour transmission rates have been found to be lower than 5×10^{-4} g.m^{-2}.day^{-1} at 38°C, 90% RH conditions for a film thickness of 20 nm. For the water process, WVTR values were found to be in the range of 10^{-3} for a 40 nm film.

Based on these results, a low pressure S-ALD process was developed using a Beneq TFS200R system. Titanium dioxide films were successfully deposited by TTIP and water as S-ALD precursors in the same temperature range as temporal, and their properties were characterised in terms of growth per cycle, refractive index and chemical composition. The growth rate saturated at precursor exposure time of 230 ms at every deposition temperature, which was slightly higher than the growth rate in temporal ALD mode at the same temperature range. Similar properties (refractive index and chemical composition) to temporal ALD have been obtained by adopting S-ALD.

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[1] P. S. Maydannik, T. O. Kääriäinen, K. Lahtinen, D. C. Cameron, M. Soderlund, P. Soininen, P. Johansson, J. Kuusipalo, L. Moro, and X. Zeng, J. Vac. Sci. Technol. A **32**, 051603 (2014).

[2] M. Aghaee, P. S. Maydannik, P. Johansson, J. Kuusipalo, T. Homola, M. Creatore, D. C. Cameron, Submitted to J. Vac. Sci. Technol. (2015)

9:20am **TF+EM+MI+MS-TuM5 Spatial Atomic Layer Deposition into Flexible Porous Substrates**, ***Kashish Sharma***, University of Colorado at Boulder, *D. Routkevitic*, *N. Varaksa*, In Redox, *S.M. George*, University of Colorado at Boulder

Spatial atomic layer deposition (S-ALD) is important for ALD commercialization. S-ALD has been successfully demonstrated on flat substrates. In this work, S-ALD was examined on flexible porous substrates using anodic aluminum oxide (AAO) membranes and Li ion battery electrodes. The AAO membranes were coated with ZnO ALD using diethylzinc and ozone as the reactants. The Li ion battery electrodes were coated with Al O ALD using trimethylaluminum and ozone as the reactants.

These experiments utilized a rotating cylinder reactor for S-ALD that is scalable to roll-to-roll operation [K. Sharma et al., , 01A132 (2015)].

ZnO S-ALD into the pores of AAO membranes depends on gas transport that is determined by the pore diameter, pore aspect ratio and reactant pulse duration. The reactant pulse duration is defined by the substrate speed in S-ALD. Different reaction conditions and AAO membrane characteristics were explored using energy dispersive spectroscopy (EDS) to measure the Zn coverage profiles. Substrate speeds were defined by rotating cylinder rates of 10, 100 and 200 revolutions per minute (RPM). The AAO pore diameters were 50, 100 and 150 nm.

For AAO pore lengths of 10 microns, the EDS analysis revealed that uniform Zn coverage profiles were obtained at 10 RPM. The Zn coverage profiles were less uniform at higher RPM values and smaller pore diameters. These results indicate that S-ALD into porous substrates is feasible. However, the uniformity of the ALD coverage will depend on reaction parameters and the characteristics of the porous substrate. In addition, $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ Li ion battery electrodes on flexible metal foil were coated with Al_2O_3 ALD using the S-ALD reactor at 10-100 RPM. Initial coin-cell testing has demonstrated that enhanced capacity stability of these cathode electrodes is obtained after 2-5 Al_2O_3 ALD cycles.

9:40am **TF+EM+MI+MS-TuM6 Accurate Precursor and Reactant Delivery for Quantitative Atomic Layer Deposition**, ***Masafumi Kitano***, Stanford University, *M. Nagase*, *N. Ikeda*, Fujikin Incorporated, Japan, *P.C. McIntyre*, Stanford University

Atomic layer deposition (ALD) has been widely discussed in the literature from various points of view. Typically, the amount of the precursor and reactant supplied into the ALD chamber is dictated only by controlling valve operation time, and is not quantitatively defined. To achieve a more quantitative ALD process, we have developed new flow rate control system (FCS) which can accurately dose precursor and reactant into an ALD reactor. This FCS consists of an orifice plate, pressure sensor, thermal sensor, and piezo control valve. It can be heated to 250˚C to achieve sufficient vapor pressure for most precursors used in ALD of various inorganic compounds and elements. The FCS controls the flow rate under critical expansion conditions (or choked flow conditions); the flow rate through the orifice is proportional only to the upstream pressure of the orifice.[1,2] The piezo control valve accurately controls the upstream pressure and, thus, the flow rate. This mode of operation makes it possible to control the dosing of precursor and reactant by simply operating an endpoint valve placed close to the ALD reactor, because the upstream pressure is controllable whether the gas flow is running or not.

We have demonstrated an ALD process with trimethylaluminum (TMA) and water vapor (H_2O) reaction for Al_2O_3 deposition using the FCS to accurately control dosing into the ALD reactor. Excellent uniformity and reproducibility of deposition, and high quality dielectric properties of the resulting Al_2O_3 films have been achieved. The critical doses of TMA and H_2O into the chamber have been found to achieve surface saturating ALD of Al_2O_3 on a silicon substrate.

[1] A. Guthrie, R. K. Wakerling, “Vacuum Equipment and Techniques” McGraw-Hill book company, Inc., pp17, (1949)

[2] R. H. Perry, D. Green, “Perry's Chemical Engineers' Handbook, Sixth Edition” McGraw-Hill Co., pp5-14, (1984)

11:00am **TF+EM+MI+MS-TuM10 ALD for Capacitor Technologies**, ***Ramakrishnan Rajagopalan***, *C. Randall*, The Pennsylvania State University **INVITED**

Atomic layer deposition (ALD) is a powerful processing technique that can be used to modify interfacial processes occuring in electrochemical capacitors. Charge storage mechanism in electrochemical capacitors is either due to electrostatic double layer formation or pseudocapacitive faradaic interactions at electrode/electrolyte interfaces. The talk will present an overview of our efforts in developing pseudocapacitive vanadium oxide thin films using ALD approach on high surface area carbon electrodes. The deposition process is dependent upon the carbon properties such as surface functionalization and porosity. We will report our investigation of deposition of ALD films on nanostructured carbon electrodes with controlled porosity in mesopores (<20 nm) to ultramicropore (0.8 nm to 2 nm) ranges. ALD also facilitates the possibility of combining electrochemical effects with dielectric effects. ALD of dielectrics such as Al_2O_3 on electrodes used in aqueous, organic and lithium based electrolytes can mitigate the issues relating to electrochemical stability due to solvent decomposition reactions and leakage performance with limited effect on the ESR performance of the capacitor. There is also possibility of designing novel solid state capacitor structures that synergistically integrates the electrical double layer interactions due to ions with dielectric energy storage.

11:40am **TF+EM+MI+MS-TuM12 Compositionally and Functionally Graded Hybrid Layer for High-Performance Adhesion**, ***Yichuan Ding***, *R.H. Dauskardt*, Stanford University

Reliable bonding of organic/inorganic interfaces continues to be one of the most important challenges in multilayer devices including microelectronic, photovoltaic and display technologies. Hybrid molecular materials which contains both organic and inorganic components has been shown to be well suited for bonding organic/inorganic (metals, metal-oxides, nitrides, …) interface, mitigating moisture degradation and even stress migration. The hybrid films (less than 100nm) made of two primary precursors, an epoxysilane and a zirconium alkoxide, have been deposited via solution based synthesis, with low cost and high throughput. By optimizing sol-gel chemistry and processing conditions, we achieved an impressive tenfold improvement in interfacial adhesion at the epoxy/Si substrate interface, and have proven the suppression of moisture degradation at the interface.

In this work, we emphasized on our newly developed spray deposition technique with more versatility and better suited to large-scale manufacturing. We utilized both bilayer coating and dual-sources spray strategies to create highly compositionally and functionally graded hybrid film compared with films achieved via traditional dip-coating. XPS depth profiling shows highly graded hybrid films with independent compositional control within 80nm can be achieved via spray coating in the dry regime. We took advantage of the compositional control brought by spray coating to unravel the structure-property relationships in the multi-functional hybrid films by varying components/parameters to fine tune the molecular structure of the resulting film and relate that to its properties obtained from our advanced thin-film mechanical testing techniques together with other chemical characterization techniques (XPS, FTIR, NMR and GCMS). The evolution of the hybrid molecular network during film process and how molecular level details of the hybrid film has a large effect on its mechanical properties were better understood.

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