Plasma Science and Technology
Room: 24 - Session PS1-TuA

Plasma Deposition and Plasma Enhanced ALD
Moderator: S. Agarwal, Colorado School of Mines

2:00pm **PS1-TuA1 Looking Down the Rabbit Hole: Impact of Porosity in Plasma-deposited Inorganic Layers on Their Moisture Permeation Barrier Performance**, ***M. Creatore***, Eindhoven University of Technology, The Netherlands **INVITED**

Although very promising results in terms of moisture and oxygen permeation barrier properties have been achieved by organic/ inorganic multi-layers, the impact of the organic interlayer on the global barrier performance is still under discussion. It is generally considered that the organic interlayer acts as smoothening layer for the macro-defects present at the surface or in the barrier layer. It is also hypothesized that the organic interlayer infiltrates into the nano-pores present in the barrier layer, therefore affecting the barrier itself at microstructure level.

In the present work the moisture permeation barrier performance of multi-layers deposited by means of initiated- and plasma enhanced- CVD methods [1] is addressed, with the aim of unraveling the role of the organic interlayer. Calcium test measurements allowed discriminating between the water permeation through the macro-defects/pinholes and the permeation through the matrix porosity. It has been found that the improvement in terms of barrier properties, due to the filling/infiltration of the SiO_2 layer nano-pores by an organosilicon interlayer [2], universally correlates with the residual open micro- (i.e. < 2 nm) porosity in the inorganic (SiO_2 or Al_2O_3) layer, independently of the deposition method (PECVD or plasma-assisted ALD). The residual nano-porosity has been evaluated by means of ellipsometric porosimetry which allows carrying out adsorption/desorption isothermal of a probe molecule in the open porosity. In detail, only for WVTR values of the SiO_2-*like* layer larger than 10^{-3} g m^{-2} day^{-1}, a barrier improvement factor is observed upon deposition of the organic interlayer, although limited to values between 5 and 10. This outcome, in combination with the evaluation of the macro-defect density upon organosilicon layer deposition on the SiO_2 layer, provides the evidence that smoothening plays a major role in the improvement of the barrier performance.

Next to the growth and characterization studies of the organosilicon/SiO_2 multi-layer, the control on the residual open nano-porosity of high growth rate roll-to-roll atmospheric pressure plasma deposited SiO_2 layers is addressed. Upon 2 nm thick Al_2O_3 layer deposition, the water vapor transmission rate of the SiO_2 layer decreases of a factor 10^3, due to the filling of the residual SiO_2 nano-porosity.

[1] G. Aresta, J. Palmans, M.C.M. van de Sanden, M. Creatore, (2012), accepted for publication in J.Vac. Sci. Technol.

[2] G. Aresta, J. Palmans, M.C.M. van de Sanden, M. Creatore, (2012), Microporous and Mesoporous Materials 151, 439.

2:40pm **PS1-TuA3 Dual Etching and Deposition Mechanism of a Microwave Alcohol Plasma on Commercial Polymers for the Enhancement of Adhesion**, ***C.J. Hall***, *P.J. Murphy, H.J. Griesser*, University of South Australia

The use of polymers to replace traditional materials in the automotive, aerospace and other industries is continuing at a high pace. Polymers offer distinct advantages over glass and metals, such as weight, impact strength, and the ability to be formed into complex shapes. To ensure long service life, however, in some applications the polymers must be coated to provide protection from damage due to mechanical abrasion or chemical attack.

One such protective coating currently being developed is a microwave based PECVD coating using tetramethyldisiloxane (TMDSO) and oxygen. This system can be used to deposit an amorphous siloxane coating several microns thick, at industrially relevant speeds. PECVD has high deposition rates with no cure required; it can coat complex parts and has the ability to vertically grade the composition of the coating. These siloxane coatings can provide the polymers with protection from in-service wear and chemical attack. However, traditionally, adhesion of these coatings to many polymers has been marginal.[1]

In this study it has been found that plasma pre-treatments using vapours from the alcohol family are effective at modifying the adhesion of these coatings to five commercial polymers, polycarbonate (PC), polypropylene (PP), polystyrene (PS), poly(methyl methacrylate) (PMMA) and acrylonitrile butadiene styrene (ABS). We have observed that the plasma pre-treatment both etches the polymer and deposits a carbonaceous film some 10 to 20 nm thick. It has also been established that both of these mechanisms are required to improve adhesion. Of further interest is the observation that the pre-treatment time must be tailored depending on the polymer substrate. Optimum adhesion is only achieved after some critical time. For ABS and PS, less than 15 secs is adequate, however for polymers, such as PMMA and PC, treatment times up to 120 and 180 secs are necessary. The duration of pre-treatment appears to be related to the etch rate of the particular polymer. Investigation has revealed that the alcohol plasma creates hydroxyl radicals.[2,3]These radicals are capable of initial hydrogen abstraction from the polymer; however, the subsequent etching proceeds depending on the structure of the polymer. As such there is a need to tailor the pre-treatment time depending on the polymer being treated.

1. B. W. Muir, H. Thissen, G. P. Simon, P. J. Murphy, H. J. Griesser, Thin Solid Films **2006**, 500, 34.

2. C. Hall, P. Murphy, H. Griesser, *Plasma Process. Polym.* **2012**, *Accepted, In Press*, DOI: 10.1002/ppap.201100159.

3. C. Hall, P. Murphy, H. Griesser, *Plasma Process. Polym.* **2012**, *Accepted, In Pres.*

3:00pm **PS1-TuA4 The Roles of Ions and Neutrals in Growth Mechanisms of Plasma Polymer Films**, ***A. Michelmore***, University of South Australia

Plasma polymers have been used since the 1960s and have found a wide range of applications. However the basic processes and mechanisms leading to plasma polymer film growth are poorly understood. Due to this lack of understanding, external parameters such as RF power and monomer flowrate are typically quoted in the literature, which provide no information on processes at the molecular level. Therefore reproducing films with different reactors is usually done by trial-and-error as the critical parameters determining growth processes are largely unknown.

Here we will discuss the roles of ions and neutrals in contributing mass to the film with a view to understanding the molecular processes by which plasma polymer films grow. The pivotal role of monomer chemical structure, specifically sites of unsaturation, in determining which growth mechanisms dominate will also be demonstrated.

4:00pm **PS1-TuA7 Defect Analysis and Mechanical Performance of Optoelectronic Thin Films Deposited on Flexible Substrates**, ***R. Patel***, *C.A. Wolden*, Colorado School of Mines

Plasma deposition enables synthesis of optoelectronic thin films on flexible substrates at low temperature. The ultimate performance of these materials is controlled by defects such as pinholes or cracks. This work focuses on understanding the formation of such defects during both film synthesis as well as during the application of stress. A simple solvent-etch based technique is presented which can be used to visualize and quantify defects in both single and multi-layered films deposited on flexible substrates. This approach allows for quantitative evaluation of crack/defect density evolution. This technique is applied to both sputtered indium tin oxide (ITO) as well as alumina-silicone nanolaminates deposited on flexible polycarbonate films by plasma-enhanced chemical vapor deposition. The use of the nanolaminate architecture is shown to significantly attenuate pinhole density relative to single layers. In the case of sputtered ITO, an optimum thickness is identified that balances electronic performance with mechanical integrity. For both materials their performance under applied stress was examined using an automated bending test setup that explored mechanical failure as a function of applied strain and number bending cycles. The threshold strain for failure under the application of tensile/compressive stress was quantified by bending samples to a given radius of curvature. Below a critical strain these materials demonstrate robust performance during cycling, displaying their strong potential for device applications.

4:20pm **PS1-TuA8 Plasma Polymerization of Ethyl Lactate**, ***S. Ligot***, University of Mons, Belgium, *F. Renaux,* Materia Nova Research Center, Belgium, *L. Denis,* University of Mons, Belgium, *D. Cossement,* Materia Nova Research Center, Belgium, *P. Dubois, R. Snyders*, University of Mons, Belgium

Biodegradable and derived from renewable resources, polylactide (PLA) has gained enormous attention as an alternative to conventional synthetic packaging materials. Nevertheless, PLA presents high water and gas permeability, which leads to a high degradation rate by hydrolysis of the

ester bonds and therefore substantially limits its application for food packaging.

In order to improve the barrier properties of PLA substrate, we propose to cover it with a highly cross-linked PLA-based plasma polymer film (PPF) synthesized by Plasma Enhanced Chemical Vapor Deposition (PECVD). The control of both chemical composition and cross-linking degree would allow to tune the gas permittivity and, as a consequence, the degradation rate of the PLA substrate.

The present work reports on the study of the influences of the experimental parameters (RF power, working pressure and precursor flow rate) on the PPF films properties using a design of experiments tool. The PPF are studied in terms of chemistry and cross-linkage by XPS, FTIR spectroscopy and Tof-SIMS measurements. In addition, *in-situ* IR spectroscopy is used to probe the plasma in order to get a better understanding on the plasma-surface interactions during the growth process. It comes out that, in our conditions, the applied power is the key parameter controlling the PPF properties. By increasing it, the C/O ratio in the coatings increases from 2.5 to 9.3. The decrease of the oxygen content when applied power is increased is correlated with the loss of O-C=O and C-O functions from 15% to 0 % and from 21% to 5 %, respectively. The *in situ* FTIR data support this observation and suggest the formation of alkynes in the plasma.

4:40pm **PS1-TuA9 Functional Carbon Contained Film Formation using Neutral-Beam-Enhanced Chemical-Vapor-Deposition by Microwave Plasma**, ***Y. Kikuchi,*** Tohoku University and Tokyo Electron, Japan*, A. Wada, S. Samukawa*, Tohoku University, Japan

Carbon materials possess various functional properties by forming various structures of carbon atoms. Especially diamond-like carbon (DLC) film is one of the primary materials as alternative of metal electrodes in various devices, in contract a carbon doped silicon oxide (SiCOH) is known as a low-*k* dielectric in ultralarge-scale integration (ULSI) devices . However, it is difficult to precisely control their properties using conventional plasma-enhanced chemical vapor deposition (PECVD). To solve this problem, we have developed a neutral-beam-enhanced chemical vapor deposition (NBECVD) process as an alternative to the conventional PECVD process. NBECVD can almost completely eliminate the irradiation of UV photons and electrons to the substrate surface by a carbon aperture, resulting in a damage-free deposition process. Moreover, the NBECVD can form a film through surface polymerization caused by bombardment of an energy-controlled Ar neutral beam on the surface with absorbed precursors. We previously proposed controlling the molecular-level structures in SiOCH film on 2 inch wafer by using NBECVD process, which can control the film properties (*k*-value and modulus). Since the bombardment energy of the neutral beam can be precisely controlled by Ar plasma above a carbon aperture, selective dissociation of weak chemical bonds in the precursors is possible with applicable plasma source, which enables us to design the film structure by controlling the precursor structure.

In this study, we developed NBECVD equipment for 8 inch wafer selecting microwave plasma source and deposited DLC and SiCOH films. For DLC film, we used toluene as precursors to control sp^2/sp^3 bonds ratio and hydrogen content in the film. DMOTMDS was selected for SiCOH film as reported previously. As the results, we can form high-quality DLC films and high density and low-*k* SiCOH films on 8 inch wafer by controlling the film structure precisely.

5:00pm **PS1-TuA10 Nano-crystalline Silicon Deposition using a Layer-by-layer Technique**, ***Z. Chen****, M.N. Iliev, J.A. Mucha,* University of Houston*, Y.K. Pu,* Tsinghua University, China*, D.J. Economou, V.M. Donnelly*, University of Houston

Nano-crystalline silicon was deposited using a layer-by-layer technique in a novel reactor with two separate reaction regions for amorphous silicon deposition and nano-crystallization. Substrates were rotated between two internal plasma sources, with selectable processing times in each source. A capacitively-coupled plasma (CCP) with SiH_4/He feed gas was used to deposit thin hydrogenated amorphous Si layers that were then immediately exposed to a H_2 or D_2 inductively-coupled plasma (ICP). The reaction of H or D atoms induced crystallization in the films. With 2 or 4 substrates on opposite sides of a circular susceptor, one substrate was in the SiH_4 CCP, while another was in the H_2 or D_2 ICP. These two processes were performed sequentially and periodically to grow thin films. Raman spectroscopy was used to characterize the films and determine the fraction of crystalline (510 and 520 cm^{-1} peaks) material in the a-Si:H layer (480 cm^{-1} peak). For the same total exposure times in each plasma, nearly the same total thickness films were deposited. Many short exposures to both plasmas were more effective in producing nano-crystalline Si than with one long exposure to each plasma. In addition, the fraction of nano-crystalline Si increased with increasing ratio of H_2 ICP-to-SiH_4/He CCP exposure time. Mass spectrometry was also used to monitor products produced in the D_2 plasma. During crystallization, etching was observed and SiD_xH_y peaks were detected, with the strongest coming at m/e=32 (SiD_2^+, SiH_2D^+). These signals decayed to a small background over times that depended on the exposure time in the SiH_4/He CCP. The films were also characterized by spectroscopic ellipsometry and Fourier transform infrared absorption. By utilizing these characterization methods, the kinetics for crystallization was investigated and will be discussed.

5:20pm **PS1-TuA11 Role of PEALD Reactor Wall Conditions on Radical and Ion Substrate Fluxes**, ***M.J. Sowa****, M.J. Sershen, G. Sundaram, J.S. Becker*, Cambridge NanoTech, Inc.

Plasma Enhanced Atomic Layer Deposition (PEALD) relies on plasma generated species as co-reactants for one half of the cyclic, two-step deposition process. Plasma generated species include radicals, ions, electrons, and photons. PEALD research is still in its early stages and the community is just beginning to elucidate the roles of these species in the deposition process and ultimately in the resulting deposited film characteristics.

Plasmas can exhibit quite complex behavior. Without excellent Faraday screening, Inductively Coupled Plasmas (ICPs) will have some component of capacitive coupling between the induction coil and the plasma. This leads to various amounts of extension of the "remote" plasma into the ALD reactor as currents originating at the high capacitive potentials of the plasma source seek out a grounded counter electrode. The sink location for the capacitive currents would be expected to vary substantially depending on if the ALD reactor is coated with a conducting or insulating film.

Ideally the plasma source will deliver a high flux of radicals to the substrate surface. Recombination of radicals on reactor wall surfaces is one of mechanisms by which the radical flux is reduced between the remote source and the substrate. The wall/radical recombination rate is a function of the radical species, the wall material, and the wall temperature.

In a PEALD system which sees multiple film chemistries, at any given time the exposed coating on the reactor walls may be of various conducting or insulating materials. The plasma properties and the radical recombination properties, and thus the flux and characteristics of plasma generated species seen by the substrate, could be substantially different depending on the details of the wall films. Additionally, the wall characteristics could change during the deposition leading to drift in the process over the course of the deposition. This, is turn, could lead to within wafer and wafer-to-wafer non-uniformities.

We have investigated the role of various insulating and conducting wall films on the spatial radical flux and spatial ion flux and energy distribution. Measurements were made on multiple ICP sources designed to deliver radicals to a PEALD reactor in a remote plasma configuration. Measurements were made over a range of rf powers (50-300W), gas compositions (Ar, O2, N2, and mixtures), gas flow rates (10-400sccm), wall films (304L SS, Al2O3, Pt, …), wall temperatures (RT - 200C), and probe/plasma source distances (150 - 450mm). Relative radical flux measurements are derived from the mass loss of photoresist coated QCM crystals. Ion data are derived from Langmuir probe measurements.

5:40pm **PS1-TuA12 Tuning Material Properties in ALD ZnO Films: *In Situ* Plasma Treatments and Doping**, ***M.A. Thomas,*** Stetson University*, J.B. Cui*, University of Arkansas at Little Rock

A variety of techniques has been used to modulate the material properties of atomic layer deposited (ALD) ZnO thin films. The structural, optical, and electrical properties of the various ZnO films were characterized by techniques such as scanning electron microscopy, atomic force microscopy, x-ray diffraction, photoluminescence, transmission/absorption, and resistivity and Hall effect measurements. The electrical properties of ALD ZnO are shown to be readily tunable by combining in-situ plasma treatments with standard thermal-ALD processes. This new ALD technique is labeled plasma enhanced thermal-ALD (PET-ALD) and is capable of significantly reducing or increasing the *n*-type conductivity in ZnO by employing either an O_2 or H_2 plasma, respectively. The resistivity of such PET-ALD films is controllable within more than seven orders of magnitude. Doped ZnO films are also readily obtained by inserting an appropriate number of dopant cycles in between the standard ZnO growth sequence. By adjusting the number of dopant cycles the optical and electrical properties of ZnO can also be well controlled. These ALD films possessing a wide range of structural, optical, and electrical properties, all of which can be easily tuned with appropriate deposition parameters, serve as excellent candidates for use in a variety of electronic and optoelectronic devices.

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