Thin Film
Room: 307 - Session TF+PS-MoM

Atmospheric, Roll-to-Roll and other Manufacturing Advances in ALD

Moderator: Paul Poodt, Holst Centre / TNO

8:20am **TF+PS-MoM1 Barrier Properties of Plastic Films Coated with Al_2O_3 by Roll-to-Roll ALD**, ***Charles Dezelah***, Picosun USA, LLC, *T. Hirvikorpi, R. Laine, W.-M. Li*, Picosun Oy, Finland, *M. Vähä-Nissi, E. Salo*, VTT Technical Research Centre of Finland, *V. Kilpi, S. Lindfors*, Picosun Oy, Finland, *J. Vartiainen, E. Kenttä, J. Nikkola, A. Harlin*, VTT Technical Research Centre of Finland, *J. Kostamo*, Picosun Oy, Finland **INVITED**

Atomic layer deposited (ALD) Al_2O_3 has proven to be effective in enhancing the moisture and gas barrier properties of various plastic films and coatings [1-3]. The key challenge in several applications is to find a flexible, reliable, and cost efficient means to protect sensitive goods from ambient atmosphere. In this presentation we describe the first deposition trials on plastic films with a new PICOSUN™ roll-to-roll (R2R) chamber. This study demonstrated that a thin Al_2O_3 layer deposited with this continuous process enhances the barrier performance of these materials with results similar to those obtained in a non-R2R batch processing module.

Silicon wafers, cellophane, polylactic acid, and polyimide film substrates were coated with Al_2O_3 at 100 °C using both a batch PICOSUN™ reactor and a test setup for a R2R ALD fit to the same reactor. The precursors were trimethyl aluminum and H_2O, and 500 deposition cycles were used. The Al_2O_3 deposited samples were characterized for their barrier and surface characteristics. The deposition rate of Al_2O_3 on silicon wafer was similar for the batch and the R2R ALD processes. The results from the oxygen transmission rate (OTR) and water vapor transmission rate (WVTR) measurements in 50 % relative humidity and 23 °C were compared between samples across substrate types and deposition modes. It was found that the R2R chamber provided barrier performance was comparable to traditional batch deposition in several cases, and considerably enhanced relative to uncoated substrates.

The initial mechanical properties of the polymeric substrate were found to be crucial for the barrier properties. For example, an Al_2O_3 coating fabricated on cellophane film was less sensitive to mechanical stresses, and the barrier values obtained were similar to those obtained with batch process for the same substrate. FTIR analyses detected Al_2O_3 covered surfaces after the R2R ALD. AFM images for the batch and R2R produced samples that were quite similar. The relative polarities of surface energy for Al_2O_3 deposited with R2R ALD on all three films were lower than for the batch samples. This indicates some differences in the thin film growth. Implications for manufacturability and scalability will also be discussed.

References:

1. P.F. Carcia, R.S. McLean, M.H. Reilly, M.D. Groner, et al., Appl. Phys. Lett. 89 (2006) 031915.

2. T. Hirvikorpi, M. Vähä-Nissi, T. Mustonen, E. Iiskola, et al., Thin Solid Films 518 (2010) 2654.

3 T. Hirvikorpi, M. Vähä-Nissi, A. Harlin, M. Karppinen, Thin Solid Films 518 (2010) 5463.

9:00am **TF+PS-MoM3 An Industrial Approach to Roll-to-Roll Atomic Layer Deposition**, *M.J. Söderlund, P.T. Soininen*, ***Ville Malinin***, Beneq, Finland

Spatial ALD method has attracted considerable attention lately as means to increase the throughput and coating area of ALD processes to meet industrial requirements. This interest is driven largely by the superior film quality of ALD thin-films, but also by the other foreseen benefits associated with spatial ALD process (in addition to high process) such as high material utilization efficiency and low maintenance requirement. These benefits, enable by the spatial ALD concept, are coming together today specifically for flexible moisture barrier application, driven by need to improve the quality and reduce the costs of ultra barrier films for moisture sensitive devices (e.g. OLEDs). However, for ALD to break into mainstream in roll-to-roll manufacturing of e.g. various different moisture barrier films, the spatial ALD technological approach should be applicable to a wide range of substrates materials (e.g. polymer, metal, paper), as well as meters wide webs and web thicknesses ranging from tens up to hundreds of micrometers.

This paper describes a scalable roll-to-roll ALD system approach, and presents recent results using a commercial WCS 600 R2R ALD system. The approach is based on relative movement between a web, tensioned on a processing drum, and the spatial ALD coating head, which is in oscillating motion around the central process drum. Process for Al_2O_3 based on TMA and H_2O precursors at 100 C demonstrates growth rates between 0.7 - 1.0 Å/cycle with refractive index higher equal or higher than 1.61. Low non-uniformity of less than 10 % is measured across 480 mm effective coating area. Ultra barrier performance of $<5*10^{-4}$ g/(m^2 day) at 38 C/90 % conditions is demonstrated with only 20 nm thick Al_2O_3 films, made on roll-to-roll basis on 500 mm wide PEN film substrate. Prospects for scaling the technology further in web width and speed are discussed.

9:20am **TF+PS-MoM4 Modular Rotating Cylinder Design for Spatial ALD on Porous Flexible Substrates**, ***Kashish Sharma***, *R.B. Hall, S.M. George*, University of Colorado at Boulder

Li-ion batteries (LIBs) have a capacity that typically decays versus number of charge-discharge cycles. Surface coatings on LIB electrodes fabricated using atomic layer deposition (ALD) can dramatically improve the capacity stability. The commercialization of these ALD coatings requires the ability to perform ALD on porous battery electrodes on flexible metal webs. In this work, a new spatial ALD (S-ALD) reactor is developed that is based on a modular rotating cylinder design. The outer cylinder remains fixed and contains a series of slits. The slits can accept a wide range of modules that attach from the outside and accommodate precursor dosing, purging or pumping. The inner cylinder rotates (0-200 RPM) and passes underneath the various slits that are spatially separated. This new S-ALD reactor has been characterized using trimethyl aluminum (TMA) and ozone to grow Al_2O_3 ALD films at 40°C on metallized PET substrates. Spectroscopic ellipsometry measurements obtained Al_2O_3 ALD growth rates of 0.6 -1.1 Å/cycle depending on the O_2 pressure used to prepare the ozone. The Al_2O_3 ALD growth rate was also constant with changing rotation speeds from 60 to 150 RPM. Future experiments will deposit Al_2O_3 ALD films on porous electrodes on flexible metal webs. For these depositions, a "push-pull" design will be utilized where the pressure of the precursor dose will "push" the precursor and carrier gas into the evacuated porous electrode. The reaction products and carrier gas will then be "pulled" from the porous electrode by vacuum pumping. This new spatial ALD reactor has the potential to deposit uniform and conformal thin films on large area and flexible porous substrates at high deposition rates.

9:40am **TF+PS-MoM5 Spatial Atmospheric Atomic Layer Deposition of Oxide and Oxysulfide Semiconductors**, ***Andrea Illiberi****, TNO, Netherlands **INVITED**

Oxide and oxysulfide semiconductors are key components in a wide variety of devices including displays and solar cells. Spatial ALD is emerging as a disruptive deposition technique for the electronic industry because it combines the advantages of temporal ALD, i.e. excellent control of film composition and uniformity on large-area substrates, with high growth rates (up to nm/s) at atmospheric pressure. In this paper we present *spatial atmospheric ALD* of Zn-based multi-component oxides for use as front window in $CuInGaSe_2$ (CIGS)*solar cells* (i.e. i-ZnO, Zn(O,S), Al:ZnO) and as active channel (i.e. InGaZnO) in *TFT-displays*. Films are grown by sequentially exposing the substrate to oxygen and/or sulfur precursors (H_2O, H_2S) and the metal precursor vapors (i.e. DEZ, TMIn, TEGa, or TMAl). By controlling the kinetics of surface reactions between vaporized precursors and reactive sites at the film surface, the composition of the films can be precisely tuned, achieving a constant concentration-depth profiles of the elements along the growth direction, as measured by EDX and XPS analysis.

CIGS solar cells: The front window of CIGS solar cells consists of a stack of CdS/i-ZnO/Al:ZnO layers. Zn(O,S) is emerging as a successful replacement for the CdS buffer layer, being free of toxic elements and having a wider band gap (> 2.4 eV). Both the [S] and [Al] content in ZnO are accurately controlled in the rage from $0 < [S]/[0] < 1$ and $0 < [Al]/[Zn] < 1$, enabling the deposition of the entire front window stack by spatial-ALD. The degradation of the electrical properties of Al:ZnO during damp heat test is prevented by a spatial-ALD Al_2O_3 moisture barrier. The use of spatial ALD Zn(O,S)/i-ZnO/Al:ZnO/Al_2O_3 stack as front windows in CIGS cells is being tested.

TFT-displays: InGaZnO (IGZO) has drawn great attention in the display industry over the last few years, because of its high electron mobility (> 10 cm^2/Vs), as compared to the commonly used amorphous silicon. The growth of IGZO has been investigated by Spectroscopic Ellipsometry,

*** Paul Holloway Award Winner**

while the surface and bulk composition of the films has been measured by Low Energy Ion Scattering and XPS. An initial In-rich phase induces a nucleation phase of about 250 ALD-cycles, followed by film closure. IGZO films have an amorphous structure, as indicated by X-ray diffraction analysis. Spatial ALD IGZO films have been tested as active channel in TFT, achieving a maximum device mobility of 10 cm^2/Vs.

Upscaling: Large area (30 cm wide) spatial ALD of Zn(O,S), Al:ZnO and IGZO will be developed by the roll to roll and sheet-to-sheet technology, respectively, as a new nanomanufacturing platform for the solar and display industry.

10:40am **TF+PS-MoM8 Large Area Atmospheric Spatial Atomic Layer Deposition of Zn(O,S) Buffer Layers for CIGS Solar Cells on Glass Substrates**, *M.D. Bijker, R.S.R. Archer,* Smit Ovens B.V., Netherlands, *P. Poodt,* Holst Centre / TNO, Netherlands, *A. Illiberi,* Solliance / TNO, Netherlands, ***Karel Spee***, Smit Ovens B.V., Netherlands

Spatial ALD (S-ALD) is emerging as a disruptive deposition technique for the electronics and photovoltaics industry because it combines the advantages of ALD, i.e. excellent control of film composition and uniformity, with high deposition rates (up to nm/s) at atmospheric pressure. This allows for a reduction of the Cost of Ownership (CoO) to a level where, for a range of high-volume and low-cost application areas, commercial exploitation is within reach.

S-ALD as developed by the authors makes use of an injector in close proximity (typically less than 100 µm) of a substrate which moves with high speed underneath the injector. This process has been proven to work very well for very flat substrates. Large area glass panels, however, provide quite a challenge as there are large thickness variations over the sheet due to glass thickness variations, surface roughness, bow and warp of the glass. We will present the design and operation of an atmospheric pressure S-ALD sheet-to-sheet tool which can handle 30x40 cm^2 glass panels. The glass panels enter the system through a load lock, pass two heating zones to fast heat-up the substrates and enter a deposition zone. The glass plates are placed on a super flat susceptor and straightened using a vacuum clamp. Sensors detect the remaining thickness variations of each individual glass plate and adjust the injector head proximity for each glass plate. In high speed the glass plate is moved back and forth underneath the injector. Maximum deposition temperatures are 350°C. The injector is equipped with 7 slots, equipped with injectors for trimethylaluminium (TMA), diethylzinc (DEZ), H_2O and H_2S. Each precursor can be entered independently, but also TMA-DEZ premixing and H_2O-H_2S premixing is possible.

The tool will be used for the deposition of Zn(O,S) buffer layers in $CuInGaSe_2$ (CIGS) solar cells as an alternative for Chemical Bath Deposition (CBD) of CdS. This replaces an environmentally polluting process with a Cd-free solution. Several authors have reported CIGS solar cells utilizing Zn(O,S) buffer layers with properties very comparable or even somewhat better (+0,5%) to existing CIGS cells using CdS. Cost of ownership (CoO) calculations show that the production cost using S-ALD are also comparable (~$0,02/Wp).

First Zn(O,S) layers have been prepared using a S-ALD lab-reactor, using DEZ and a mixture of H_2O and H_2S. The composition, optical- and electrical properties of the films can be continuously controlled by different H_2O/H_2S mixing ratios from ZnO. Further experiments are ongoing, including the deposition of Zn(O,S) buffer layer in full CIGS solar cells and its effect of solar cell performance.

11:00am **TF+PS-MoM9 Growth Rates and Mechanisms for Al_2O_3 ALD using TMA/ O_3 at Atmospheric Pressure**, ***MoatazBellah Mousa***, *C.J. Oldham, G.N. Parsons*, North Carolina State University

Under typical low pressure ALD conditions, ozone (O_3) is reported to speed up ALD processes compared to water-based reactions because shorter purge times are needed to fully desorb ozone O_3. Many high-throughput ALD processes are designed to operate at atmospheric pressure where viscous fluid transport can have significant effects. We developed an ALD process using trimethyl aluminum (TMA) and O_3 in a variable-pressure flow tube reactor and measured growth rates, film composition and film uniformity in the growth zone for pressures between ~2 Torr and 760 Torr and temperature ranging from 70°C to ~250°C. We also adjusted overall gas flow rate to study the role of gas residence time. Film thickness was determined by ellipsometry and growth was monitored using an in-situ Quartz Crystal Microbalance (QCM). We observe self-limiting growth between ~150 °C and 250 °C at both ~2 Torr and 760 Torr, and larger growth rate at lower temperature. At high pressure the growth rate is ~20% larger than at low pressure, which is ascribed to slower transport of desorbing product species through the boundary layer at high pressure. We also find that longer O_3 exposure times are needed compared to low pressure growth. This is consistent with a model for the ozone dissociation kinetics showing that higher pressure enhances the rate of ozone loss. The ozone depletion also predicts an observed gradient in film growth rate under sub-saturation conditions along the length of the reactor. During TMA/O_3, O insertion leads to surface methoxy and formate groups at low temperature, whereas surface hydroxyls form at higher temperature. In our reactor, QCM analysis shows evidence for this temperature-dependent surface reaction mechanism at 2 Torr, and it persists at 760 Torr under saturated conditions. Under saturated growth conditions, TOF-SIMS analysis shows films deposited at 2 Torr and 760 Torr have similar composition, with some extra carbon contamination at higher pressure. Overall, similar ALD growth can be achieved for TMA/O_3 at 760 Torr and ~2 Torr, where care must be taken to take into account the faster rate of O_3 dissociation at higher pressures, especially at higher temperature.

11:20am **TF+PS-MoM10 Integration of Feature and Reactor Scales during the Simulation of ALD Scale Up**, ***Angel Yanguas-Gil***, *J.A. Libera, J.W. Elam*, Argonne National Laboratory

As the number of ALD processes, materials and applications increase, it is becoming increasingly important to develop the ability to screen and identify the most prominent candidates for scale up. Precursor pressure, reaction probability, ideality of the surface chemistry, but also other considerations like throughput, surface area, and materials utilization, are critical factors that will determine the feasibility of a particular process. In particular, there are three questions that need to be answered in the transition from lab-scale to manufacturing: 1) what is the impact of a particular precursor chemistry, 2) what are the best processing conditions for a given precursor and substrate, 3) what is the optimal reactor design?

In this talk we will focus on the issue of predicting the scalability and fundamental economics (throughput, precursor utilization) of lab-scale ALD processes. Our approach, developed as part of our work on process development and scale up, combines the experimental characterization of ALD processes in bench-scale reactors, the use of simple analytic models, and the development of new 3D multiscale simulation tools that are optimized to the conditions typically found under ALD conditions, including providing simulated quartz crystal microbalance and mass spectrometry data at any point of the reactor.

Our code, based on open-source libraries, is able to incorporate high-surface area substrates on reactor scale simulations for both cross-flow and roll-to-roll processes, and it takes advantage of the ALD surface chemistry to achieve an extremely efficient two-way coupling between reactor and feature length scales. This method is based on a new approach to simulate feature scale coating that essentially provides the infinite trajectory-limit of the Monte Carlo simulations typically used in the literature.

Besides the description of the model and its implementation, we will exemplify our methodology by presenting results of different metal oxides by ALD, including the validation of the code in a large area reactor. We will also show the results of a parametric study on the impact of non-ideal surface chemistry as well as the presence of high surface area materials / nanostructured features on the substrate. According the results obtained, the presence of high surface area materials makes continuum ALD processes like R2R more efficient. This is a consequence of a more general result of our parametric study, which shows that high reaction probabilities play an important role in ALD scale up.

Authors Index

Bold page numbers indicate the presenter