Thin Film
Room: 104 A - Session TF-TuA

High Throughput ALD
Moderator: G.N. Parsons, North Carolina State University

2:00pm **TF-TuA1 A Comparison between Conventional- and Spatial ALD; The Effect of Pressure and Exposure Time on Film Properties**, ***P. Poodt***, Holst Centre / TNO, Netherlands **INVITED**

The last few years have seen important developments in spatial Atomic Layer Deposition (ALD), enabling ALD with high deposition rates. Whereas in conventional ALD, precursors are dosed in a time-separated mode using a purge or pump step, in spatial ALD, precursors are dosed simultaneously and continuously at different physical locations. As a result, deposition rates exceeding 1 nm/s have been reported for spatial atmospheric ALD of Al_2O_3. This has led to the development of high-throughput, industrial scale spatial ALD tools for surface passivation of crystalline silicon wafers for solar cells as well as roll-to-roll spatial ALD concepts for flexible electronics.

From the point of view of chemistry, there is no difference between spatial and conventional ALD, as similar precursors and substrates are used to make similar materials. Important differences between spatial and conventional ALD, though, are the time-scales and pressure regime at which spatial ALD is performed. Whereas in conventional ALD, precursor exposure times typically range from a few tenths of seconds to a few seconds, in spatial ALD precursor exposure times can be as short as several milliseconds, during which the physical and chemical processes (e.g. diffusion, adsorption, reaction, crystallization, etc.) responsible for the film growth have to take place. Furthermore, spatial ALD is often performed at atmospheric pressure, where conventional ALD is usually done at low pressure. This especially impacts plasma-enhanced ALD, as the physics and chemistry of atmospheric pressure plasma's can be quite different from the low pressure plasma's typically used in conventional plasma enhanced ALD.

With this in mind, spatial ALD of several different material classes will be discussed, and a comparison with similar, conventional ALD processes, will be made. Similarities, as well as differences, in deposition processes, film properties and their performance in devices will be discussed for

1. Alumina (amorphous dielectric)

2. Zinc oxide (crystalline transparent conductor)

3. Alucone (hybrid material, deposited by spatial Molecular Layer Deposition (MLD))

4. Silver (metal, deposited by plasma enhanced spatial ALD).

Furthermore, possible consequences and opportunities for up-scaling these processes to industrial scales will be discussed.

2:40pm **TF-TuA3 Thin-film Electronics by Spatial ALD**, ***S.F. Nelson***, *C.R. Ellinger, L.W. Tutt*, Eastman Kodak Company **INVITED**

In this talk we describe our approach to thin-film electronics using spatial atomic layer deposition (SALD). ALD has long been known for producing dense conformal films of conductors, insulators, and semiconducting layers from a limited set of precursors. However, in the more common vacuum- and chamber-based ALD processes, the deposition speed has generally been limited. In contrast, the SALD deposition process can be relatively fast. The coating takes place at atmospheric pressure in a localized region of a coating head, with no enclosure except that produced by gas isolation curtains, and thus without any pumping cycles.

Focusing on the field of metal oxide semiconductor thin-film transistors (TFTs), we have demonstrated that SALD produces high quality planar thin film transistors. TFTs with aluminum oxide for the insulator and zinc oxide (ZnO) for the semiconductor have high on/off ratios, and good uniformity of the deposited layers for deposition temperatures at and below 200°C. We show that the regime of fast ALD cycles accessible by SALD produces particularly good performance.

Patterning and alignment of transistors on flexible substrates can present a challenge, especially for short channel lengths. We have investigated novel vertical device architectures enabled by the conformal nature of SALD deposition that unite high performance with generous alignment and resolution requirements. With self-aligned sub-micron channel lengths, these devices demonstrate remarkable current-carrying capability at low voltage.

Finally, we will present a "patterned-by-printing" technique for SALD-grown transistors. By printing an inhibitor ink on the surface, the growth of aluminum-doped ZnO (conductor), aluminum oxide (insulator), and ZnO (semiconductor) can be limited to selected areas of the substrate. The process produces TFTs with the same excellent performance as lithographically patterned TFTs, with high yield, and rapid throughput.

In summary, we will present a range of opportunities in the area of thin-film and "printed" electronics that are enabled by spatial ALD.

4:00pm **TF-TuA7 Roll to Roll PEALD of Mixed Oxide Films for High Barrier Applications**, ***E.R. Dickey***, Lotus Applied Technology **INVITED**

Atomic Layer Deposition (ALD) via substrate motion, rather than pulse-purge cycling on a fixed substrate, is emerging as a promising path to high speed low cost roll to roll deposition of high quality ALD gas diffusion barriers. To date the majority of research in ALD barrier films has been conducted using Al_2O_3 in the thickness range of 20-100nm, with multiple groups reporting Water Vapor Transmission Rates (WVTR) below the detection limits of commonly used testing methods. A smaller body of research has examined TiO_2 films, which in some cases show comparable barrier performance over a similar thickness range. Here we report a Plasma Enabled ALD process incorporating *mixtures* of Al_2O_3 and TiO_2 from TMA, $TiCl_4$, and oxygen-containing plasma, formed by alternating single ALD cycles of each material in a spatial ALD reactor. RBS data indicates the resulting film has a volumetric ratio of Al_2O_3 to TiO_2 of approximately 1.5:1, reflecting the growth rates of each individual material. Use of the mixed material substantially reduces the required film thickness for a given WVTR performance compared to either pure Al_2O_3 or TiO_2. The relationship between barrier performance and ALD film thickness is examined over the range of 2nm to 25nm, with WVTR rates in the range of 10^{-4} $g/m^2/day$ for coatings of 5nm to 10nm thickness, and the mid 10^{-6} range, near the limit of the calcium test employed, for the thickest films. The process has been ramped from the spatial ALD reactor to a Pilot scale roll to roll reactor configured to deposit the mixed film on rolls of polymer 300mm wide by up to 500m long.

4:40pm **TF-TuA9 Spatial Atomic Layer Deposition for New Generation Solar Cells**, ***D. Muñoz-Rojas***, *G. Ercolano, A.T. Marin, C.T. Armstrong, R.L.Z. Hoye, K.P. Musselman, J.L. MacManus-Driscoll*, University of Cambridge, UK

A key factor for the success of new generation PV technologies is the ability to design low-cost, low-temperature, scalable and roll-to-roll compatible fabrication methods. In recent years progressive development of batch type vacuum-free ALD technologies has taken place with novel systems capable of working in the open atmosphere being presented. The key to atmospheric/spatial ALD (AALD/SALD) is that precursors are separated in space rather than in time (as opposed to conventional ALD, which has a sequence of pulse-purge steps), thus allowing orders of magnitude faster deposition rates and low precursor wastage, while keeping the advantages of conventional ALD. We have developed and optimised an AALD system for the deposition of solar cell components and which is compatible with roll-to-roll processing. We will illustrate its potential with several examples, namely, ultrafast deposition of high quality amorphous TiO_2 and ZnO blocking layers for inverted bulk heterojunction solar cells; low temperature deposition of high conductivity Cu_2O films and it use in back-surface-field (BSF) designs for low-cost inorganic solar cells; deposition of doped TiO_2 and ZnO films for application in hybrid solar cells.

5:00pm **TF-TuA10 Spatial Molecular Layer Deposition of Metalcones**, ***M. Smets***, *F. van den Bruele, P. Poodt*, Holst Centre / TNO, Netherlands

Spatial-ALD is emerging as an industrially scalable deposition technology at atmospheric pressure which combines the advantages of temporal ALD, i.e. excellent control of film composition and uniformity on large area substrates, with high growth rates (~ nm/s). Whereas in conventional ALD, precursors are dosed in a time-separated mode using a purge or pump step, in spatial ALD, precursors are dosed simultaneously and continuously at different physical locations. As a result, deposition rates exceeding 1 nm/s have been reported for spatial atmospheric ALD of Al_2O_3. This has led to the development of high-throughput, industrial scale ALD tools for surface passivation of crystalline silicon solar cells as well as roll-to-roll spatial ALD concepts for applications in flexible electronics.

Atomic layer deposition is mostly used to deposit conformal inorganic films. Organic- and hybrid organic-inorganic films can be also be deposited by ALD, which is then referred to as Molecular Layer Deposition (MLD). For example, by combining metal precursors and various organic alcohols, metal alkoxide films or "metalcones" can be obtained. By varying both the

metal precursor and organic precursor, the optical, mechanical, electrical and chemical properties of the film can be tuned.

This presents opportunities for applications such as catalysis, light management, and many others.

We have combined both techniques to do Spatial MLD to deposit several metalcones by combining various metal- and organic precursors. E.g. alucone layers have been deposited using TMA with ethylene glycol, with a growth per cycle (GPC) of about 0.5 nm/cycle and a refractive index of 1.50 at 630 nm. The GPC decreases with increasing deposition temperature and there appears to be an optimum for the ethylene glycol concentration. The optical, chemical and mechanical properties of the films have been investigated by means of e.g. ellipsometry, ATR-FTIR and nano-indentation.

These results show that Spatial MLD is a promising technique to deposit a wide range of new, functional materials at high deposition rates.

Authors Index

Bold page numbers indicate the presenter

— A —

Armstrong, C.T.: TF-TuA9, 1

— D —

Dickey, E.R.: TF-TuA7, **1**

— E —

Ellinger, C.R.: TF-TuA3, 1
Ercolano, G.: TF-TuA9, 1

— H —

Hoye, R.L.Z.: TF-TuA9, 1

— M —

MacManus-Driscoll, J.L.: TF-TuA9, 1
Marin, A.T.: TF-TuA9, 1
Muñoz-Rojas, D.: TF-TuA9, **1**
Musselman, K.P.: TF-TuA9, 1

— N —

Nelson, S.F.: TF-TuA3, **1**

— P —

Poodt, P.: TF-TuA1, **1**; TF-TuA10, 1

— S —

Smets, M.: TF-TuA10, **1**

— T —

Tutt, L.W.: TF-TuA3, 1

— V —

van den Bruele, F.: TF-TuA10, 1