ALD for Manufacturing
Room Auditorium - Session AM1-TuA

ALD for Manufacturing I

Moderators: Hardik Jain, TNO/Holst Center, Maksym Plakhotnyuk, ATLANT 3D Nanosystems

1:30pm **AM1-TuA-1 Atomic Layer Deposition Equipment Used in Industrial Production of More Than Moore Devices***, Taguhi Yeghoyan,* Yole Développement, France

In semiconductor community, Atomic Layer Deposition (ALD) is often associated with upmost advanced nodes, used for manufacturing of logic and memory devices, so called More Moore (MM) applications. For MM, ALD is used in High Volume Production (HVM) already for 20 years, starting with DRAM capacitor coating and logic transistor node shift from 65 nm to 45 nm. From that time on, ALD played a vital role to enable subsequent nodes and transistor architecture evolution, first to FinFet and currently to Gate-All-Around (GAA).HVM of MM devices is done with 300 mm Si wafers, with ALD equipment tailored to a specific process and high throughput. Thus, only few ALD equipment makers are present in MM HVM, generating highest equipment sales revenue.

On the other side of semiconductor industry, More-than-Moore (MtM) device production flourishes with diversified substrates in terms of material, size and sometimes shape. MtM devices encompass MEMS and sensors, Radiofrequency (RF) devices, power devices, CMOS Image Sensors (CIS), photonic devices and various packaging approaches. Among all MtM devices, CIS are manufactured mostly on 300 mm Si wafers on MM-like production lines and require similar ALD equipment. Other MtM devices are manufactured mostly on up to 200 mm production lines at lower volumes and with varied process flow. This MtM devices need flexible ALD equipment able to deposit often thicker films thermally or with plasma assistance, on various substrate sizes and substrate material, i.e. compound, Si, piezoelectric, dies on frame tape among others. Currently, more MtM ALD equipment providers qualify their equipment for Fab production, driven by several applications, where ALD is indispensable. These are for example: GaN HEMT transistors, mini-LEDs and microLEDs as well as wafer level encapsulation.

This presentation aims to give a market research overview on ALD equipment used in industrial production of MtM devices, with market size estimated to $345M in 2020, which is expected to increase to $680.5M in 2026. Moreover, ALD supply chain is outlined: ALD equipment subparts and inspection, process developers and materials suppliers. Finally, commercial MtM devices with identified ALD use are showed.

1:45pm **AM1-TuA-2 Spatial ALD on Large-Area Porous Substrates: How to Avoid Supply Limitation and Maximize Precursor Efficiency?***, Paul Poodt,* SALDtech B.V., Netherlands

One of our greatest challenges for the coming decade is the transition to a sustainable way of generating, storing, and converting energy. High performance batteries, fuel cells, electrolyzers and solar cells are part of the solution, but still face many challenges that need to be solved. Efficiencies and capacities need to increase, the use of scarce and expensive materials needs to reduce and the life-time needs to improve. There are many examples where ALD has been used to improve on these aspects. For example, by applying thin and highly conformal films on porous substrates using ALD, the lifetime of Li-ion batteries can be improved, the loading of expensive catalyst materials in fuel cells and electrolyzers can be reduced and new devices such as 3D solid state batteries are enabled.

In order to enable large-scale mass production of these applications, Spatial ALD can be used for high deposition rates on both large substrates (square meters) and roll-to-roll. Scaling-up Spatial ALD processes on large area porous substrates, however, can lead to problems with supply limitation; i.e. when the required precursor flow to cover a high surface area substrate exceeds the amount of precursor that can actually be supplied, e.g. due to a low vapor pressure. Furthermore, in case of very expensive precursors, it is required to maximize the precursor efficiency to minimize costs.

The dependency of the precursor dose on aspect ratio, sticking coefficient and reactor pressure has been studied in great detail. However, for supply limitation, the effective surface area of porous substrates is the most important parameter. Furthermore, transport of precursor from the inlet towards the substrate and exhausts has to be taken into account. We have developed a numerical model to solve the diffusion-convection-reaction equation for porous substrates in a spatial ALD reactor, named 3D-DCR. The model combines parameters such as the porosity and effective area of the substrate with reactor dimensions, gas flow rates and deposition rate requirements to calculate and optimize the required precursor dose, precursor mass flow and utilization efficiency.

We will discuss several important results from this model, such as: 1) increasing the efficiency means decreasing the deposition rate and vice versa, 2) the required precursor dose does not only depend on pore aspect ratio but also on the reactor dimensions and used flows and 3) precursor efficiencies exceeding 80% are possible for porous substrates. Furthermore we will show how the these results can be used to optimize Spatial ALD processes and equipment for large scale manufacturing of high performance energy devices.

2:00pm **AM1-TuA-3 Atmospheric-Pressure Plasma-Assisted Spatial Atomic Layer Deposition of Silicon Nitride***, Jie Shen,* TNO-Holst Centre, Netherlands*; F. Roozeboom,* University of Twente, Netherlands*; A. Mameli,* TNO-Holst Centre, Netherlands

Silicon nitride is a ubiquitous material in device fabrication, largely employed as an insulating dielectric layer or a gas permeation barrier layer, for example. Despite the effort that has been devoted to the development of effective SiN_x atomic layer deposition (ALD) processes, reports on novel precursors and processes for SiN_x continue to be regularly published. This highlights that some of the challenges such as low deposition rate and poor conformality, to cite the most common ones, are yet to be completely solved, especially at low deposition temperature.[1]

In this work we investigate the feasibility of SiN_x spatial ALD at atmospheric pressure as a possible method for reaching high-quality and high-throughput SiN_x. Deposition temperatures between 150 ^oC and 250 ^oC were explored, resulting in growth per cycle (GPC) values between 0.3 Å/cycle and 0.2 Å/cycle, respectively and in a total ALD cycle time of ~2.4 s. The SiN_x films were grown in a dedicated rotary lab-scale spatial ALD reactor,[2] using either a two-step process, employing bisdimethylaminosilane (BDEAS) and N_2 plasma from a direct dielectric barrier discharge (DBD);[3] or a three-step process, consisting ofBDEAS, followed by a first plasma exposure to N_2/H_2 DBD and a second N_2-only DBD plasma step. The influence of H_2 and N_2 plasma settings, and deposition temperature will be discussed in detail on the basis of the results from X-ray photoelectron spectroscopy (XPS) and Fourier transformed infrared spectroscopy (FTIR).[4] The best results in terms of layer composition and wet etch rate (WER), in 1:100 diluted HF were obtained at a deposition temperature of 250 ^oC. Here, 10% O_2 and 7.4% C contamination levels were detected, for layers with an N/Si ratio of ~ 1.29and a WER of 18 nm/min.

In conclusion we have demonstrated the first atmospheric-pressure spatial ALD process for SiN_x. The results presented herein are therefore very encouraging for low-temperature and high-throughput SiN_x spatial ALD in large-area as well as in roll-to-roll mode. Based on the relevant process details explored in this work, we suggest possible next steps for further improving the quality of the spatial ALD deposited SiN_x layers.

This work was supported in part by Semiconductor Research Corporation (SRC).

References

[1] X. Meng, *et al.*, *Materials*,**9**, 1007 (2016).

[2] P. Poodt, *et al.*, *Adv. Mater.*, **22**, 3564 - 3567 (2010).

[3] Y. Creyghton, *et al.*, Proc. Int. Conf. on Coatings on Glass and Plastics (ICCG 2016), Braunschweig, Germany, June 12-16, 93-97 (2016).

[4] R. Bosch, *et al.*, *Chemistry of Materials*, **28**, 5864–5871 (2016).

2:15pm **AM1-TuA-4 Recent Development of Large Scale ALD for Non-IC industrial Applications***, Wei-Min Li,* Jiangsu Leadmicro Nano Technology Co. Ltd., China **INVITED**

Recent advance in ALD technology has shown prospect of HVM applications in several non-IC industry areas. For instance a breakthrough has been achieved during past few years for high efficiency solar cell HVM thanks to the rapid increase of global clean energy demand. ALD offers not only excellent material properties and functions, but also meets the manufacturing throughput and up-time requirements with significantly reduced manufacturing cost. Growing interests is seen for energy storage and flexible electronics applications as well. The great differences in material chemistry and various substrates to be handled however, calls for continuous innovation for different industrial applications. Author highlights current large scale ALD that are used or with high potential in some of the non-IC industry applications.

In PV industry, both ALD and PEALD have become the enabling technology not only for current mainstream PERC/PERL/PERT, but also finds applications for next generation TOPCon, IBC, HJT, as well as tandem solar cell technology. Batch type ALD and PEALD reactors are exclusively used for wafer based *c*-Si solar cell applications. A record throughput at over 15000 wafers/hour has been achieved with excellent film properties. A typical p-PERC cell efficiency has reached above 23.5%, and novel n-TOPCon solar cell has reached a cell efficiency of above 24.5% in pilot production. While an increase of conversion efficiency can be achieved for ALD enabled high efficiency solar cell manufacturing, the cost-of-ownership is also significantly reduced. With continuous improvement of materials and process integration, further enhancement for high efficiency solar cells are expected.

Significant progress has been achieved as well for ALD industry applications with flexible substrates that requires high permeation barriers properties. A commercial "roll-to-roll" ALD can now handle an effective web width of 1500 mm of PET substrate and achieve WVTR of 10^{-4} mg/day/m^2 at a maximum coating speed of >5 m/min. Large volume powder coating for lithium ion battery and catalyst applications at hundreds kilogram scale is seen approaching commercialization. Nevertheless, novel material and precursor chemistry and innovative reactor design combined with "intelligent manufacturing" to further improve the performance, enhance the productivity as well as reduce the production cost are highly desired.

Recent advances of ALD technology and contribution to some of the key industry areas shows that with continuous innovation and efforts, large scale ALD is becoming a generic and prospective technology for novel non-IC industrial applications.

2:45pm **AM1-TuA-6 An Innovative Method for in Situ Calorimetry of ALD/ALE Surface Reactions***, **Anil Mane**, J. Elam,* Argonne National Laboratory

Calorimetry is an essential analytical technique for determining the thermodynamics of chemical reactions. In situ calorimetry during atomic layer deposition and etching (ALD/ALE) would be a valuable tool to probe the surface chemical reactions that yield self-terminating growth and removal of material at the atomic scale. Additionally, in situ calorimetry would reveal the partitioning of chemical energy between the individual half-reactions that constitute the ALD or ALE cycle. In this study we present an alternative strategy that exploits temperature-induced resistance changes in ALD thin films. Our approach utilizes a thin film ALD nanocomposite resistive layer deposited conformally on the inner surfaces of a borosilicate capillary glass array (CGA) [1]. The ALD nanocomposite has a high resistivity and a well-defined thermal coefficient of resistance (TCR), both of which can be tuned by adjusting the resistive layer composition. In practice, the resistive CGA (RCGA) calorimeter is installed in the ALD system and electrically biased to produce a current in the microamp range that is recorded in real time. During the ALD/ALE surface reactions, heat exchanged with the coating produces transient current features due to the non-zero TCR of the nanocomposite film. These transient features are highly reproducible and can be used to calculate the reaction enthalpies of the individual surface reactions based on the TCR value and the thermos-physical properties of the CGA. Moreover, the RCGA can be calibrated by subjecting the device to well-defined voltage pulses and measuring the resistance changes induced by Joule heating. The RCGA is highly sensitive due to the high surface area of the CGA, the rapid response of the nm-scale resistive coating, and the tunable TCR value. In addition, the device is relatively low cost and easily integrated into ALD/ALE systems. To demonstrate the RCGA calorimetry method, we performed in-situ calorimetry measurements for a range of ALD processes including Al_2O_3, AlF_3, $Al_xO_yF_z$, ZnO, MgO, TiO_2, and ZrO_2. We also studied the nucleation behavior when transitioning between ALD materials and the use of alternative precursors for ALD Al_2O_3, TiO_2, and AlF_3 ALD. We find good agreement between reported enthalpy changes for ALD reactions and the values measured by in situ RCGA calorimetry. We believe that RCGA calorimetry is a versatile in situ method to study the thermodynamics of ALD/ALE surface reactions and a convenient diagnostic for real-time ALD/ALE process monitoring in a manufacturing environment.

1) A. U. Mane et. al., Chem. Vap. Deposition, **19**, 186–193, (2013).

3:00pm **AM1-TuA-7 Production-Suitable 200 Mm Batch ALD/MLD Thin Film Encapsulation Toward Flexible OLED Manufacturing***, **Jesse Kalliomäki**, E. Rimpilä, R. Ritasalo, T. Sarnet,* Picosun Oy, Finland

Organic electronics (OE) have rapidly become a mainstream technology due to their desired properties like low weight, high energy efficiency, flexibility and low manufacturing costs [1]. These advantages can be traced back to the fact that components can be routinely printed on plastics in huge roll-to-roll manufacturing lines. What has changed in the last decade or so is the introduction of thin film encapsulation solutions (TFEs) as a key enabling technology. TFEs can mitigate one of the biggest downsides of OEs - their susceptibility to oxidation by moisture [2]. TFEs allow the devices to stay light, transparent and flexible and help them to achieve their full potential.

TFEs rely heavily on vacuum-based thin film deposition techniques like ALD and MLD, which are not as straightforward to scale to roll-to-roll. Indeed, most of the research on TFEs are carried out on chip-scale and focuses on improving already excellent barrier properties [3]. To avoid bottlenecks in manufacturing, scaling up these TFE processes must be realized. Previously we have reported an industrially viable ALD/MLD process [4], which we have continued to scale with serious production in mind.

We present characterization and scale up results of single-chamber TFEs (Fig 1.). The moisture barrier properties were analysed with tuneable diode laser absorption spectroscopy (Sempa HiBarSense 2.0), delivering excellent results from a very large area (3320 mm^2). Bending properties were analysed by applying tensile stress by bending films deposited on polycarbonate and determining the crack-onset-strain with an optical microscope. Confirming TFEs can resist defects up to 2% tensile stress. All films were deposited using a Picosun P-300B batch ALD tool with batch sizes up to 27 pcs of 200 mm wafers. The process scales to larger chambers and achieves several Å/min growth rates and 2% chip-2-chip uniformities over full wafer batches.

In this work, we have demonstrated that ultra-barrier level TFEs can be coated on surfaces areas meaningfully measured in m^2. The barrier properties are also confirmed from a large enough area, to reflect the performance of the final product.

[1] Chang et al. (2017), doi:10.1109/JETCAS.2017.2673863
[2] Steinmann et al. (2018), doi:10.1557/jmr.2018.194
[3] Li et al. (2019),doi:10.1557/jmr.2019.331
[4] Kalliomäki et al. (2021), ALD2021, conference presentation

3:15pm **AM1-TuA-8 Roll-to-Roll ALD Coatings for Battery Cell Interfaces at Production Scale***, **Andrew Cook**,* Beneq, Finland

ALD is an enabling technology, which has been shown to improve battery performance, through the introduction of thin film coatings to modify interface surfaces on cathodes, anodes and separators. ALD can help to improve thermal stability, stabilise SEI layer, suppress dendrite, inhibit transition metal dissolution, and increase interfacial contact between layers, all of which are current issues facing lithium ion battery technology. This presentation will demonstrate how Beneq use ALD technology to solve these issues and show how this can be scaled to production levels within a Gigafactory environment.

Atomic Layer Deposition (ALD) is an advanced coating technique, which has been extensively studied for more than 10 years for uses in battery applications on small scale batch systems. ALD coatings have been applied to cathode, anode, and separator materials to modify the surface interfaces, and improve battery performance. This presentation will describe the current R2R ALD system, Beneq has developed for high throughput production.

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