Area Selective ALD
Room Regency Ballroom A-C - Session AS1-TuA

Polymers

Moderator: Prof. Han-Bo-Ram Lee, Incheon National University

1:30pm **AS1-TuA-1 The Role of Co-Reactant Reactivity and Surface Passivation During Cu-Doping of NiO ALD***, **Matthias Minjauw,*** Ghent University, Belgium*; B. Vermeulen,* Ferroelectric Memory Company, Germany*; A. Illiberi,* ASM, Belgium*; V. Sharma,* ASM Microchemistry Ltd., Finland*; M. Givens,* ASM, Belgium*; J. Dendooven, C. Detavernier,* Ghent University, Belgium

P-type transparent conducting oxides are of high interest for applications in electrocatalysis, optoelectronics, and sensing. Nickel oxide is a viable candidate owing to its chemical stability, wide band gap and excellent transparency in the visual spectrum. However, as for most applications the hole conductivity of NiO is too low, it needs to be increased by doping the NiO with metal cations such as Al, Cu, Co or Zn.[1,2] ALD has proven to be a suitable method for the growth of ultra-thin, precisely doped transition-metal-oxide films on nanostructured devices.
In this work we demonstrate ALD growth of Cu-doped NiO, using the bis(N,N'-di-t-butylacetamidinato)nickel(II) and bis(dimethylamino-2-propoxy)copper(II) precursors. For the $Ni(tBuAMD)_2$-precursor, NiO ALD growth has been demonstrated with H_2O as a co-reactant at 150°C.[2] For the $Cu(dmap)_2$-precursor, using H_2O as the co-reactant at 150°C leads to Cu_2O growth, while using O_3 leads to CuO growth at temperatures of 110°C-175°C.[3] Cu-doped NiO ALD was attempted by combining the two water-based processes in a super-cycle approach. Although the individual NiO and Cu_2O processes display growth rates compatible with literature reports (0.028 and 0.019 nm/cycle resp.), combining both processes in a super-cycle decreases the growth rate significantly (Fig. 1). In vacuo XPS experiments revealed that NiO growth is inhibited on an ALD Cu_2O surface, with negligible deposition even after 145 NiO ALD cycles (Fig. 2). By exposing the Cu_2O to ozone, NiO growth can be initiated from the initial ALD cycles. The effect of this O_3-exposure is two-fold: the Cu_2O is oxidized to CuO, and persistent carbon and nitrogen species are removed from the surface. As exposure of the O_3-treated CuO surface to a single pulse of $Cu(dmap)_2$ blocks NiO growth, but doesn't change the oxidation state of the CuO surface, it must be the $Cu(dmap)_2$ surface ligands themselves that cause the NiO growth inhibition. This is backed up by the fact that there are no ALD NiO literature reports combining $Ni(dmap)_2$ with H_2O. Finally, we demonstrate that Cu-doped NiO ALD growth can be achieved by combining the O_3-based processes in a super-cycle approach, with a growth rate comparable to the growth rates of the unit processes (Fig. 1).

1:45pm **AS1-TuA-2 Elucidating the Role of Functional Groups of Ligands for Selective Metal Blocking via Vapor-Phase Sam Deposition***, **Chandan Das,*** Applied Materials Inc., Singapore*; B. Bhuyan,* Applied Materials Inc.*; Z. Li, J. Wu,* National University of Singapore*; J. Sudijono,* Applied Materials Inc., Singapore*; M. Saly,* Applied Materials Inc.

One of the key areas of area-selective atomic layer deposition (AS-ALD) that the industry is looking for, is the development of fully self-aligned vias (FSAV) for BEOL applications in the advanced nodes. The current study demonstrates the development of ligands possessing suitable volatility for vapor phase SAM growth, additionally being selective to the metals and not on dielectrics. While considering selectivity to the metals by specific azide-, and organophosphorus-based head groups, the tail length and head functional groups have been carefully modified as shown in Fig 1 and 2 (ESI), for delivering the ligands to the chamber for vapor phase SAM growth. Out of various ligands, L_n has shown promising selectivity (WCA ~104°) on metals compared to the SiO_2/Si (WCA ~65°) at 200 °C growth temperature [Fig 3, ESI]. The SAM grown samples have further been annealed up to 300 °C in the presence of organometallic precursors to check the stability under deposition conditions. No loss in the WCA indicates promising stability of Ln SAM, which would be a potential candidate for selective deposition at a relatively higher temperature.

2:00pm **AS1-TuA-3 Integrating Area-Selective Ald with Electrohydrodynamic-Jet Printing to Enable Additive Nanomanufacturing***, **Tae Cho,*** N. Farjam, T. Newsom, C. Allemang, R. Peterson, K. Barton, N. Dasgupta,* University of Michigan, Ann Arbor

The demand for customizable micro/nanoscale patterning of functional materials has led to a strong interest in bottom-up manufacturing of electronics. The current state-of-the-art in fabricating functional devices includes multiple deposition and etching steps in a resource-intensive cleanroom environment. There is yet no universal manufacturing technique that can enable low-cost, high-resolution/quality, and high-throughput additive nanomanufacturing. In this work, we demonstrate the versatility of area-selective ALD with electrohydrodynamic jet (EHD) printing to pattern functional materials and manufacture fully functional devices without the traditional lithographic process.

EHD printing is an additive manufacturing technique which has been previously used to deposit functional materials with solution inks. The printing is performed at atmospheric conditions, and provides an unparalleled combination of high spatial resolution (sub-micron), fast printing speeds, and low cost. However, the materials that can be printed are limited by the solution inks, which are mostly used to print polymers. In this work, we combine EHD printing with ALD in three different manufacturing methods to pattern functional materials: additive and subtractive area-selective ALD (AS-ALD), and acid-based subtractive printing of ALD films. As shown in Scheme 1, ALD films are selectively grown by EHD printing of inhibitors on the surface. We printed polyvinylpyrrolidone (PVP) ink to "passivate" the surface and N-methyl-pyrrolidone (NMP) solvent ink to "activate" the surface towards ALD growth. This enabled additive and subtractive printing with an average linewidth of 312 nm and 9 µm, respectively.

In addition to directly patterning the polymer inhibitors, we also introduce a new subtractive printing process using acid-based inks to directly pattern the metal oxide films deposited by ALD. For this work, we patterned 50 nm thick ZnO ALD by EHD printing acid-based ink to achieve sub-10 µm resolution [2]. Various ink compositions were tested to study the etch and evaporation rates. The printed ALD ZnO features were examined using scanning electron microscopy and atomic force microscopy. Using these integrated techniques, a bottom-gate thin-film transistor (TFT) with an ALD zinc-tin-oxide (ZTO) channel was fabricated without any lithography process [1,3]. This new additive micro/nanomanufacturing platform can enable flexible and customizable patterning of metal oxides without the need for traditional lithography.

2:15pm **AS1-TuA-4 Enhanced ALD Nucleation on Polymeric Separator for Improved Li Batteries***, **Giulio D'Acunto**, S. Shuchi, M. Mattinen, S. Bent,* Stanford University

Lithium batteries are the preferred choice of power sources for portable devices, electric vehicles, and energy storage due to their high energy density. However, despite their widespread use, Li batteries still have several limitations: low thermal stability, limited cycle life, and capacity decay, to name a few. To improve the efficiency of the Li batteries, ongoing research is conducted in several areas, such as battery design and active modification of well-established components. One specific area of focus is the separator, a critical element of all batteries. Its role is to separate the positive and negative electrodes while allowing ion transport.

In this study, separators, which have drawn attention due to their crucial impact on safety and good electrochemical performance, are modified by ALD Al_2O_3 to enhance thermal stability and increase the cycle life of batteries. After optimizing the surface pre-treatment, Al_2O_3 deposition is performed with trimethylaluminum (TMA) and water at 80 ºC, below the shrinkage temperature of the separator, with a long exposure time and on a custom-made reaction bed, allowing uniform and conformal deposition all around the separator.

A Celgard 2325 separator - polypropylene (PP)/polyethylene (PE)/PP - is modified using different exposure times of UV ozone (UVO) to functionalize the inert carboxyl group. X-ray photoelectron spectroscopy (XPS), water contact angle (WCA), and scanning electron microscopy are used to characterize the membranes and test the effectiveness of the UVO functionalization as well as its role in the nucleation of Al_2O_3. Moreover, electrochemical measurements, such as Li-ion conductivity and long-term cycling tests on Li|Cu half-cells, are performed.

The more hydrophilic nature of the membrane after ozone treatment, which saturates after 4.5±1.0 min of exposure to UVO, is confirmed by XPS and WCA. The thickness of ALD Al_2O_3, with 20% $Al(OH)_3$, strongly correlates to the oxygen content present on the membrane after UVO exposure. The deposition on the polymeric separator also leads to a notably lower growth rate (0.8±0.2 Å/cycle), in contrast to the well-established 1.1 Å/cycle determined on SiO_2.

Overall, we show how a controlled UVO pre-treatment can enhance the growth of ALD Al_2O_3 on the separator. We also show that adding ALD Al_2O_3 can improve battery cycle life. The resistive Al_2O_3 overlayer does not affect the Li-ion conductivity of the separator but improves its thermal stability. This work shows how a readily-accessible treatment can enhance the nucleation and control the deposition of a metal oxide by ALD, opening new possibilities to develop better Li batteries.

2:30pm **AS1-TuA-5 Improved Metal Selectivity via Inherent Orthogonal ASD: Polymer ASD Improves Nucleation Inhibition for Metal ASD***, **Hwan Oh,*** North Carolina State University, Republic of Korea*; H. Margavio,* North Carolina State University*; H. Yang,* North Carolina State University, Republic of Korea*; G. Parsons,* North Carolina State University

Despite recent achievements in area-selective deposition (ASD), the current focus on ASD is limited to single-material ASD. The integration of discrete ASD processes into a sequential process, *i.e.,* multi-material ASD has great potential to provide additional leeway in fabricating semiconductor devices.[1] Specifically, combining organic and inorganic ASD processes in an orthogonal sequence, in which the organic ASD layer can act as a sacrificial layer, can extend the functionalities of individual ASD processes. In this work, we demonstrate a multi-material ASD using individual inherent ASD processes in an orthogonal sequence: 1) poly(3,4-ethylenedioxythiophene) (PEDOT) ASD on SiO_2*vs.* Si-H [2] *via* oxidative chemical vapor deposition (oCVD) using 3,4-ethylenedioxythiophene (EDOT) as a monomer and antimony pentachloride ($SbCl_5$) as an oxidant, and 2) W ASD on Si-H *vs.* SiO_2 [3] *via* atomic layer deposition (ALD) using tungsten hexafluoride (WF_6) and highly diluted silane (2 wt% SiH_4 in Ar). Herein, PEDOT ASD on SiO_2 (*vs.* Si-H) serves as a potential sacrificial layer to inhibit undesired nucleation of W on SiO_2. The cross-sectional scanning transmission electron microscopy (STEM) and energy-dispersive X-ray spectroscopy (EDX) analyses show that without a pre-deposited PEDOT layer on SiO_2, 10 cycles of W ALD result in ~ 7.7 nm of W ASD on Si-H with growth per cycle (GPC) of 7.7 Å/cy, but the formation of undesired W nuclei (*i.e.,* selectivity loss) is also observed on SiO_2 (Figure 1a and 1b). On the other hand, with a pre-deposited PEDOT layer on SiO_2, the same W ALD process leads to similar growth of W ASD on Si-H, but no growth of W is confirmed on SiO_2 (Figure 1c and 1d). This result indicates that pre-deposited PEDOT (first ASD) can improve the selectivity window of W (second ASD) by inhibiting unwanted nucleation of W. This study can be extended to other material pairs or other multi-material configurations. For example, a polymer ASD can be achieved on metal (*vs.* dielectric) for another subsequent ASD of interest, such as low-k ASD on dielectric (*vs.* metal). Overall, weanticipate that multi-material orthogonal ASD canbring a new paradigm to future microelectronics manufacturing beyond sing-material ASD processes.

2:45pm **AS1-TuA-6 Self-Aligned Patterning by Area-Selective Etching of Polymers and ALD***, V. Lasonen, C. Zhang, M. Vehkamäki, A. Vihervaara,* University of Helsinki, Finland*; L. Mester,* attocube systems AG, Germany*; M. Karimi,* AlixLabs AB, Sweden*; Y. Ilarinova,* AlixLabs, Sweden*; R. Jafari Jam, J. Sundqvist,* AlixLabs AB, Sweden*; **Mikko Ritala,*** University of Helsinki, Finland

We have recently presented area-selective etching of polymers as a new approach for self-aligned thin film patterning [1]. The area-selective etching is based on different catalytic properties of surfaces under the polymer film being patterned. When annealed at a proper temperature in presence of a proper etching gas, the polymer is decomposed away from catalytically active surfaces whereas on catalytically inactive surfaces the polymer remains. The process is made possible by the small etching gas molecules (O_2 and H_2) being able to diffuse through the polymer layer and become activated by the catalytic surface. With some catalyst - polymer combinations no etching gas is needed as the polymer decomposition occurs by catalytic thermal cracking.After the self-aligned patterning of the polymer, it may remain as part of the device or, more likely, used as the growth directing template in various deposition processes, such as area-selective ALD and CVD, and line-of-sight PVD followed by lift-off.

A critical question is how accurate line edges can be made with the area-selective etching process. An obvious concern is that spill-over of activated etching gas atoms or polymer flow can blur the interface between the decomposed and non-decomposed polymer area. In this research we have explored the capabilities of the method by using about 100 nm diameter metal dots as the starting pattern. These dots were made by a lift-off process using Talbot displacement lithography and electron beam evaporation. Polyimide deposited by molecular layer deposition and poly(methyl methacrylate) (PMMA) deposited by spin coating were used as polymers. Nano-FTIR spectroscopy verified accurately defined selective removal of PMMA from Pt. After the area-selective removal of the polymers from the Pt dots, ALD Ir and Ni processes were conducted. In the case of Ir, perfect area-selective deposition was achieved, while the nickel process resulted in some scattered deposition also on the polymer but these nuclei were removed upon removal of the polymer.

Reference

1. C. Zhang, M. Leskelä and M. Ritala, Coatings, **11**, 1124 (2021).

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