

Thin Films Division

Room 21 - Session TF-ThM

Area-selective Deposition and Infiltration Growth Methods

Moderator: James Fitz-Gerald, University of Virginia

8:00am TF-ThM-1 Thin-Film Encapsulation Based on ALD Technology for Organic Light-Emitting Diodes, *Tony Maindron*, CEA-Leti, France **INVITED**

Thin-film encapsulation of organic electronic circuits like Organic Light-Emitting Diodes (OLED) consists in the addition of vacuum deposited thin mineral barrier directly onto the organic circuit. The main challenge today is to achieve high encapsulation levels with WVTR $\sim 10^{-6}$ g/m²/day. The ALD technology is well-suited to reach that goal because the technology allows the deposition of defect-free thin barrier films, mainly of Al_xO_y. However, the main limitation of the ALD technology is the relative stability of the Al_xO_y layer when it is exposed to hot humid atmospheres. Due to its high C and H atoms content, resulting from the low temperature deposition used to deposit onto the fragile circuits (maximum process temperature allowed for OLED ~ 100 °C), the Al_xO_y layer corrodes very quickly and loses its barrier properties prematurely. An additional passivation is therefore mandatory in order to protect the Al_xO_y from water condensation onto its surface. Different works have illustrated the benefits of depositing an additional ALD layer on top of the Al_xO_y, an additional PECVD or PVD layer on top of the Al_xO_y or using hybrid ALD/MLD (Al_xO_y/metalocene) nanocomposites. In each case, the stability of the aluminum oxide is improved because it is not exposed directly to moisture condensation. Alternatively for thin-film encapsulation purposes, other materials of interest can be deposited by low-temperature ALD: ZrO₂, TiO₂, SnO₂, SiN_x, ZnO, or ZnO:Al (AZO). After a review of solutions to stabilize Al_xO_y films, performances of new single barrier materials will be described in this work and compare to Al_xO_y. It is well-known also that the quality of the encapsulation relies also on the cleanliness of processes. Defects can be described as exogenous particles but they can be seen also as the circuit's surface topography, as well as its surface nature. Getting rid of defects is an important feature for thin-film encapsulation. ALD can provide high surface conformity and can be deposited almost onto every surface. However, as thin-film barriers deposited by ALD remain very thin (dozens of nm), it is mandatory to grow them onto a particle-free surface to ensure a reliable encapsulation. Otherwise, particles can create pinholes that act as a pathway for moisture to reach the fragile device underneath. In the case of OLEDs, black spot features then appear. Other encapsulation processes, based on other deposition technologies like PECVD or PVD, described the use of thick planarization layers to fix the particle issue. Similar strategies can be applied with ALD. The technology developed at CEA-Leti will be presented in the second part of this work.

8:40am TF-ThM-3 Vapor Phase Infiltration: Unifying the Research Community Around Processing Science Fundamentals, *Mark Losego*, Georgia Institute of Technology

Vapor phase infiltration (VPI) and its sister processing routes—sequential vapor infiltration (SVI), multiple pulse infiltration (MPI), and sequential infiltration synthesis (SIS)—are exciting, new chemical vapor processing technologies for synthesizing unique organic-inorganic hybrid materials. Because each of these processes were developed independently at various laboratories around the globe and designed to solve different technological problems, a common language has yet to emerge. This lack of a common lexicon introduces unnecessary complexity to the literature and slows the cohesive advancement of the science. This talk seeks to unify the research community around the fundamental science of these processes and demonstrate its uniqueness amongst other chemical vapor processing routes. While VPI/SVI/MPI/SIS emerged from the atomic layer deposition (ALD) research community, its kinetics is substantially different from ALD and truly unique amongst all chemical vapor processes. Unlike ALD and CVD, VPI/SVI/MPI/SIS is not a deposition process but rather an infiltration process composed of three distinct steps: (1) sorption (dissolution) of the gaseous precursor into an organic (polymeric) material, (2) diffusion of that precursor within this host material, (3) entrapment (reaction) of the precursor within the host material (Fig. 1). These unique processing kinetics are similar (identical?) for all of these infiltration processes and rich in fundamental science that intersects with a surprising number of disparate fields including gas membrane separations and solvent vapor annealing. For decades, understanding the fundamental kinetics of ALD and CVD has been the driver for advancing these technologies' processing capabilities; it is now time to do the same for these chemical infiltration processes, such

that rationale design physics can be established to devise processing schemes that precisely control the depth and quantity of inorganic infiltration. To guide this unification, this talk will introduce (1) a kinetics-based taxonomy scheme for classifying chemical vapor processes, (2) a basic framework for a common kinetics theory, and (3) a series of common, fundamental scientific questions that, if solved, could significantly advance the utility and expand the use of VPI processing technology.

9:00am TF-ThM-4 Vapor Phase Infiltration (VPI) of Polymers with Intrinsic Microporosity, *Emily McGuinness, F Zhang, R Lively, M Losego*, Georgia Institute of Technology

PIM-1, a polymer with intrinsic microporosity, is commonly used for membrane-based chemical separations. However, PIM-1 undergoes detrimental microstructural changes over time and after exposure to certain solvents. In this talk, we will discuss our efforts to use vapor phase infiltration of inorganic components as a means to maintain the microstructure of PIM-1. Vapor phase infiltration (VPI) is a process by which metalorganic precursors are diffused into organic polymer materials to transform them into organic-inorganic hybrids. In this work, we investigate how utilizing VPI can increase PIM-1 durability. We examine VPI of several metal-organic precursors including diethylzinc, trimethylaluminum, and titanium tetrachloride. VPI has been effective in diffusing and trapping inorganic species to a depth of more than 10 microns in PIM-1 material (Figure 1). Gas sorption measurements (BET) indicate that the infiltration process does not significantly decrease the surface area nor the permeability of these PIM-1 membranes (Figure 2). These treatments are also found to improve the chemical stability of PIM-1 when exposed to organic solvents. The kinetics of the VPI process on PIM-1 materials will also be discussed.

9:20am TF-ThM-5 Organic Solvent Resistance of Hybrid Organic-Inorganic Films Synthesized via Vapor Phase Infiltration, *Collen Leng, M Losego*, Georgia Institute of Technology

We have observed that poly(methyl methacrylate) (PMMA) films infiltrated with trimethylaluminum (TMA) precursors no longer dissolve in toluene, a PMMA solvent. TMA chemically reacting with carbonyl groups in PMMA could be the reason for this solubility resistance. However, films with only a small amount of TMA infiltration will swell significantly inside toluene (over 20% of pre-immersion thickness) and buckle. Interestingly, PMMA films can swell over 50% when infiltrated by TMA at 60 °C without buckling. We attribute this difference to potential crosslinking of PMMA chains during TMA reactions, resulting in a more rigid film and less polymer chain mobility.

For our experiments, the films are spun-cast on silicon and have thicknesses ranging from around 200 nm to 2 microns. The samples are then treated using VPI, with processing temperatures ranging from 60 to 120 °C and exposure times ranging from 1 second to full infiltration (on the scale of hours). Spectroscopic ellipsometry is used to track film thickness changes as the treated films are immersed in toluene for times up to several days.

At a processing temperature of 90 °C, films exposed to TMA for more than 10 minutes no longer dissolve entirely in toluene, but significant film swelling has caused the films to buckle and create micro-folds. Partial delamination of the films from the silicon substrates are also observed due to the buckling actions as well as from small scratches and holes in the films that allow toluene to penetrate and remove the bottom section of the film, where not enough TMA has reacted with PMMA. We find delamination, swelling, and buckling to not be issues for films that are fully treated, which we define as having enough precursor exposure to allow TMA to interact with the entire bulk of the PMMA film. Films that are fully infiltrated remain stable when immersed in toluene for over 10 days.

The results of this study will provide a better understanding of new properties for these polymer films treated by metalorganic precursors. The findings on solubility may be applicable in coatings for various applications.

9:40am TF-ThM-6 Surface Selective CVD of Metallic Thin Films Using Inhibitor Molecules, *Elham Mohimi*, University of Illinois at Urbana-Champaign; *Z Zhang*, University of Illinois at Urbana-Champaign, US; *S Liu, B Trinh*, University of Illinois at Urbana-Champaign; *J Mallek*, MIT Lincoln Laboratory; *G Girolami, J Abelson*, University of Illinois at Urbana-Champaign

In the fabrication of nanoscale devices, the top-down process of lithography and etching is time consuming and expensive. A proposed bottom-up approach – area selective growth – would enable device fabrication beyond conventional patterning limits: thin films would

Thursday Morning, November 2, 2017

preferentially deposit onto pre-existing portions of a structure with no nucleation and growth on other surfaces. However, a selective process is subject to statistical failure – the nucleation of unwanted material – when it relies on the initial characteristics of the non-growth surface, either the inherent chemical properties or passivation pre-treatments. A robust process requires dynamic control of selectivity to ensure that no stray nucleation occurs on the intended non-growth surfaces for the total time required to deposit film on the device areas.

Here, we present a perfectly selective CVD method which involves adding a neutral molecule “inhibitor” to the process gas mixture: the inhibitor dynamically populates oxide surfaces and prevents nucleation while permitting the deposition of film on metal surfaces, where the inhibitor effect is weaker. Because the inhibitor concentration on the oxide surfaces is continuously replenished, it completely eliminates film nucleation on defects or impurity sites.

We previously demonstrated perfectly selective copper CVD using the Cu(hfac)VTMS precursor with additional VTMS as the inhibitor: no nucleation occurs on thermal SiO₂ or on porous, carbon doped oxide, while copper growth occurs on areas covered with a ruthenium seed layer [1]. The excess VTMS scours Cu(hfac) intermediates off the dielectric surface prior to the disproportionation (growth) reaction. Here, we extend the method by using a different class of inhibitor molecules to afford the selective CVD of transition metals and their compounds on a wide variety of oxide substrates; and we explain the mechanism of selectivity.

1. S. Babar, E. Mohimi, B. Trinh, G. S. Girolami and J. R. Abelson, "Surface-selective chemical vapor deposition of copper films through the use of a molecular inhibitor," *ECS J. Solid State Sci. Tech.* 4(7), N60-63 (2015)

11:00am **TF-ThM-10 Toward Area Selective Atomic Layer Deposition on Co, W and Ru Metal/Silicon Patterns**, *Dara Bobb-Semple*, *S Bent*, Stanford University

Modern electronic devices have achieved significantly smaller sizes and increased structural complexity in recent years. Device fabrication today is based on ‘top-down’ processes with multiple lithography and etching steps which serve as a bottleneck as well as a source of errors for device miniaturization. Area-selective atomic layer deposition (AS-ALD), which combines a surface modification technique and atomic layer deposition (ALD) in a ‘bottom-up’ approach to nanopatterning, shows great promise in addressing these issues. Most work on AS-ALD typically uses tightly-packed, self-assembled monolayers (SAMs) to modify the substrate surface and block ALD. Past studies have demonstrated AS-ALD on Si/SiO₂ substrates patterned with SAMs and, more recently, our group has demonstrated AS-ALD using octadecylphosphonic acid SAMs and alkanethiol SAMs on Cu/SiO₂ substrates.

Incorporating the AS-ALD process into any fabrication scheme requires understanding how SAMs interact with different materials. In this work, we have extended our previous studies on Cu substrates to perform comparative studies on the formation of octadecylphosphonic acid and alkanethiol SAMs on three metal substrates: Co, W and Ru. After SAM deposition, model metal (Pt) and metal oxide (ZnO) ALD processes were performed to assess the quality and blocking ability of the SAM layer on the different substrates. X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy, X-ray reflectivity, water contact angle (WCA) goniometry, and atomic force microscopy were used to characterize modified samples before and after ALD.

Overall, we observed that the most passivating SAMs of both alkylphosphonic acids and alkanethiols are consistently formed on Co and Ru; SAMs formed on W are less well-packed and hence less reliable in blocking ALD. In fact, XPS results did not show evidence that a SAM was formed on the W substrate following deposition of ODPA in t-butanol, even though increased WCA was observed. Moreover, the solvent was found to play an important role. We found that after a 48h deposition, the Co and Ru substrates passivated using ODPA in t-butanol showed WCA 5° higher on average than when passivated in a toluene solution. Conversely, W substrates showed WCAs < 90° when t-butanol was used as a solvent, but >100° when toluene was used. These results may be explained in terms of the poor Lewis acid character of the W substrate and may indicate a larger role of solvent-substrate interactions in SAM deposition. These studies provide insights that are important for consideration in the development of fabrication processes which incorporate SAMs for AS-ALD.

11:20am **TF-ThM-11 Area-selective ALD of Ru by Combining an ABC-type ALD Process and O₂ Plasma Etching**, *S Chopra*, Eindhoven University of Technology, The Netherlands; *M Vos*, Eindhoven University of Technology, The Netherlands, Netherlands; *J Ekerdt*, The University of Texas at Austin; *E Kessels*, *Adrie Mackus*, Eindhoven University of Technology, The Netherlands, Netherlands

Area-selective atomic layer deposition (ALD) is expected to be an enabling technology for the fabrication of future nanoelectronics with sub-10 nm dimensions. In practice it is extremely difficult to achieve high selectivity for area-selective ALD because of undesirable growth initiation on defects and impurities. Given that many processes exist for etching materials, novel combinations of area-selective ALD and etching are currently being considered to eliminate this unwanted growth.¹ In this work, the selectivity of area-selective ALD of Ru on Pt patterns (metal-on-metal deposition) is improved by etching Ru using an O₂ plasma after or during the deposition.

ALD of Ru was carried out using an ABC-type process consisting of ethylbenzene-cyclohexadiene Ru(0) precursor, O₂ gas, and H₂ gas steps. The additional H₂ dosing step ensures that metallic Ru is deposited by reducing the RuO₂ top layer every cycle. This ABC-type ALD process allows for Ru deposition at low temperatures to exploit the larger differences in growth rates on SiO₂ versus Ru or Pt for achieving area-selective ALD. However, even at the low temperature of 150 °C, for which 500 Ru ALD cycles on Ru resulted in 17.5 nm growth, undesirable Ru islands were observed on the SiO₂ non-growth substrate.

When Ru is exposed to O₃ or to an O₂ plasma, RuO₄ is formed as a volatile reaction product. Because O₂ plasma has a high selectivity toward Ru etching, it can be used in a post-deposition treatment to eliminate residual Ru islands from the SiO₂ non-growth substrate. Area-selective ALD with an almost perfect selectivity was obtained when performing supercycles consisting of Ru ABC cycles and an O₂ plasma etch step every 100 cycles. The selectivity of the growth was investigated by performing Ru ALD on Pt-containing seed layers patterned by electron beam induced deposition (EBID) on SiO₂ substrates.² The O₂ plasma etch does not significantly influence the properties of the Ru on the seed layer patterns as will be shown in the presentation.

1. R. Vallat, R. Gassiloud, B. Eychenne, and C. Vallée, *J. Vac. Sci. Technol. A*, **35**, O1B104 (2017)

2. A.J.M. Mackus, S.A.F. Dielissen, J.J.L. Mulders, and W.M.M. Kessels, *Nanoscale* **4**, 4477 (2012).

11:40am **TF-ThM-12 Enhancing the Inherent Area-selective ALD of TiO₂ using BCl₃**, *Seung Keun Song*, *P Lemarie*, *G Parsons*, North Carolina State University

Area selective deposition of thin film becomes increasingly important as semiconductor industries require shorter node than 10nm scale to alleviate trade-offs between performance and power consumption. Since inherent substrate-dependent selectivity shows relatively narrow selective window, enhancing procedure is required. TiO₂ atomic layer deposition (ALD) using titanium tetrachloride (TiCl₄) and water has been observed to selectively deposit TiO₂ on Si-OH preferentially over Si-H surfaces. However, the selectivity is lost after initial incubation cycles. In an attempt to better understand selectivity loss mechanisms, we studied the role of surface hydrophobicity and found that the incubation period increased as the contact angle of the initial substrate surface also increased. Furthermore, we incorporated BCl₃ into our TiO₂ ALD sequence to further enhance the overall selectivity. Through the ellipsometry thickness measurement, TiO₂ ALD with BCl₃ shows more delayed TiO₂ growing on Si-H without delaying on Si-OH. Using quartz crystal microbalance (QCM) we show that BCl₃ appears to impede TiO₂ growth, rather than significantly etching TiO₂. Finally, we provide evidence that the ability to effectively impede TiO₂ deposition on Si-H without significantly reducing deposition on the Si-OH surface depends on the amount and frequency of BCl₃ dosing. This work ensures better selectivity than previous result.

12:00pm **TF-ThM-13 Selective ALD by Intercalation of Etching Cycles in PEALD Process**, *Rémi Vallat*, *R Gassiloud*, CEA/LETI-University Grenoble Alpes, France; *C Vallée*, Université Grenoble Alpes & CEA, LETI, Minatec Campus, Grenoble, France

Therefore complementary techniques are needed to continue extreme scaling and extend Moore’s law. Selective deposition processes can be used to increase and enhance patterning capabilities at very low cost. In our lab, a new selective Plasma Enhanced ALD process has been developed by adding etching steps in the PEALD flow. To be effective, 3 conditions must be satisfied (Figure 1):

Thursday Morning, November 2, 2017

- A different nucleation delay on different substrates
- A nm scale etching of the thin film
- The etching step must add a new nucleation delay

We used this process for the selective deposition of Ta₂O₅ with TBTDET (TertButylimido Tris(DiEthylamino Tantalum) precursor and a plasma gas mixture of O₂/Ar/NF₃ for deposition and etching steps. Ta₂O₅ has been selectively deposited on a metal substrate (TiN) versus SiO₂ and Si substrates (no deposition on these substrates). For this process, the different substrates have been patched onto a Si wafer and introduced simultaneously into the PEALD reactor. ^[1]

For this presentation we will present the selective process developed for TiO₂ with TDEAT (Tetrakis DiEthylAmido Titanium) precursor. The ALD selective process has been successfully developed for the deposition of TiO₂ on three different metallic substrates (TiN, NiPt and W). As for Ta₂O₅ deposition, a thin TiO₂ film is deposited on the different metal substrates but not on Si and SiO₂ substrates although all substrates are introduced simultaneously in the deposited chamber. Details on the process will be given during the presentation with a focus study on precursors and radicals interactions with the different surfaces after each step of the process. In this study, quasi in situ XPS was used. Figure 2 shows Ti2p peak for one titanium pulse on silicon substrate with or without etching step. Fluorine treatment lead to thinner layer. This difference is explained by Si-F and Si-O-F bonds presence at the surface. This fluorine bonds blocks the titanium growth.

The thin oxide films selectively deposited will be used in 3D nonvolatile memory devices. Our objective is to realize a crosspoint memory in backend level from a pattern area or a trench area without the photolithography step. Therefore, electrical properties of the Ta₂O₅ and TiO₂ oxides deposited with the standard PEALD process are compared to those of thin films selectively deposited thanks to C(V), C(f) and I(V) measurements. We will show that the selective ALD process does not degrade the dielectric properties of the films in terms of leakage current and electrical field breakdown. Resistive memories cycles are also compared and discussed. Finally, 3D structures with the selective deposition process will be shown.

Author Index

Bold page numbers indicate presenter

— A —

Abelson, J: TF-ThM-6, **1**

— B —

Bent, S: TF-ThM-10, **2**

Bobb-Semple, D: TF-ThM-10, **2**

— C —

Chopra, S: TF-ThM-11, **2**

— E —

Ekerdt, J: TF-ThM-11, **2**

— G —

Gassilloud, R: TF-ThM-13, **2**

Girolami, G: TF-ThM-6, **1**

— K —

Kessels, E: TF-ThM-11, **2**

— L —

Lemarie, P: TF-ThM-12, **2**

Leng, C: TF-ThM-5, **1**

Liu, S: TF-ThM-6, **1**

Lively, R: TF-ThM-4, **1**

Losego, M: TF-ThM-3, **1**; TF-ThM-4, **1**; TF-ThM-5, **1**

— M —

Mackus, A: TF-ThM-11, **2**

Maindron, T: TF-ThM-1, **1**

Mallek, J: TF-ThM-6, **1**

McGuinness, E: TF-ThM-4, **1**

Mohimi, E: TF-ThM-6, **1**

— P —

Parsons, G: TF-ThM-12, **2**

— S —

Song, S: TF-ThM-12, **2**

— T —

Trinh, B: TF-ThM-6, **1**

— V —

Vallat, R: TF-ThM-13, **2**

Vallée, C: TF-ThM-13, **2**

Vos, M: TF-ThM-11, **2**

— Z —

Zhang, F: TF-ThM-4, **1**

Zhang, Z: TF-ThM-6, **1**