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

ALD Surface Reactions and Precursors
Moderator: Andrew Cavanagh, University of Colorado, Boulder

2:00pm **TF+PS-MoA1 Broadband Sum-frequency Generation: Studying the Initial Growth of ALD Al_2O_3 by Nonlinear Surface Vibrational Spectroscopy**, ***Vincent Vandalon**, R.H.E.C. Bosch, W.M.M. Kessels*, Eindhoven University of Technology, Netherlands

The understanding of the atomic layer deposition (ALD) processes has advanced significantly through the insight obtained with in situ linear vibrational surface spectroscopy, in particular by Fourier transform infrared (FTIR) spectroscopy. In this work we apply a nonlinear vibrational spectroscopy technique, the so-called broadband sum-frequency generation (BB-SFG) method, to study the ALD surface chemistry in situ. BB-SFG is a laser based technique, new to the field of ALD, in which a short visible spectrally-narrow laser pulse (~1 ps) is combined with an ultrashort broadband IR pulse (~90 fs) impinging simultaneously on the sample. The generated sum-frequency spectrum, detected in the visible, contains a part of the vibrational fingerprint of the IR region (bandwidth ~100 cm-1) which can detected "background-free" with a high sensitivity even at short integration times (1-100 s). Moreover, the surface selective nature of BB-SFG is uniquely suited for the study of the ALD surface chemistry in which the surface groups can be monitored accurately. In this presentation, first the BB-SFG method developed in our group in the last few years will be explained. Subsequently, the application of the method during ALD Al2O3 (from Al(CH3)3 and H2O) will be addressed. In particular the initial film growth of Al2O3 on H-terminated Si(111) will be followed by probing the Si-H stretch mode (2084 cm-1) with BB-SFG. The decrease in Si-H signal due to Al(CH3)3 and H2O exposure will be correlated with the increase of the second-harmonic signal [1], revealing insight into the kinetics of initial film growth as well as the surface chemistry during steady-state growth. The results will be combined with observations by FTIR studies from our own work and from literature [2]. The surface reactions during the initial growth of Al2O3 by ALD will be addressed.

References:

[1] Höfler, APPL PHYS A-MATER 63, 533-547, 1996

[2] Frank, Chabal, Wilk, APL 82, 4758, 2003

2:20pm **TF+PS-MoA2 *In Situ* FTIR Analysis of Reaction Mechanisms between Trimethylaluminum and Carbonyl-Containing Polymers During ALD**, ***Philip Williams**, E.C. Dandley, A. Brozena, C. Needham, C.J. Oldham, G.N. Parsons*, North Carolina State University

New methods to modify polymers are of interest for numerous applications. The chemical mechanisms during trimethylaluminum (TMA) and water exposure during Al_2O_3 ALD onto polymers depends strongly on the polymer substrate and ALD conditions. Under some conditions, a solid oxide film can form with a relatively abrupt polymer/oxide interface. Typically however, TMA can diffuse sub-surface and react with the polymer in the substrate near-surface or bulk. Recently, we studied mechanisms during TMA vapor infiltration into various polymers using *in situ* infrared spectroscopy. In many polymers, the TMA coordinates with a polymer functional group, either on the backbone or on a side-chain, to form a Lewis acid/base adduct. For example, in poly(vinylpyrrolidinone) (PVP), the carbonyl of the amide moiety (~1780 cm^{-1}) is observed to coordinate strongly with trimethylaluminum and shift to ~1725 cm^{-1}, and the adduct remains stable until water exposure. After water treatment, the adduct mode decreases and the original amide carbonyl signal appears to return. This could indicate release of TMA, but aluminum oxide formation in the polymer shows clearly that the TMA reacts within the polymer. Ab initio calculations (B3LYP) were performed to support mechanistic analyses of TMA within the polymer. A similar TMA/carbonyl adduct formation/release mechanism is observed during TMA/water exposure to poly(methyl methacrylate). On the other hand, when poly(acrylic acid) is exposed to TMA, the carbonyl mode disappears then does not reappear after water exposure. This suggests that in PAA, the TMA reacts with the carbonyl to form a stronger covalent bond that does not change upon water exposure. This difference in reactivity for TMA in the polyacid is likely associated with the presence of acidic hydrogens aiding in the formation of the methane byproduct and more stable covalent aluminum-oxygen bonds. These results help expand understanding of ALD onto polymers and can enable better control of coating and infiltration processes.

2:40pm **TF+PS-MoA3 Time-resolved FT-IR Spectroscopy during ALD using $La(^{i}PrCp)_3$ and H_2O**, ***Brent Sperling**, J.E. Maslar, W.A. Kimes*, NIST

In situ Fourier transform infrared (FT-IR) spectroscopy has provided many valuable insights into various chemistries used for atomic layer deposition (ALD). Frequently, it is used to observe the molecular fragments remaining on a surface after exposure to each precursor or the phonon modes of films as they are deposited layer-by-layer. The limitations of FT-IR spectroscopy, however, have restricted it to quasi-static conditions that differ dramatically from most growth studies. Spectra cannot easily be obtained with the temporal resolution needed to keep pace with typical ALD cycle times. We have developed a method that signal averages time-resolved spectra over multiple ALD cycles to improve the rate of data acquisition to around 150 ms. Additionally, by using external reflection from a metal surface, absorption by surfaces species is enhanced; alternating polarization states allows the surface to be differentiated from gas-phase species and deposition on the windows. We apply this method to $La(^{i}PrCp)_3/H_2O$ chemistry ($^{i}PrCp$ = isopropyl-cyclopentadienyl), which has proved to be difficult to understand from growth studies. We present our attempts to recreate literature conditions in our laminar flow reactor with *in situ* FT-IR spectroscopy to observe surface and gas-phase species.

3:00pm **TF+PS-MoA4 Surface Reactions and Interface Evolution during the ALD of HfO_2 on GaAs Surfaces Studied by *In Situ* ATR-FTIR**, ***Liwang Ye**, T. Gougousi*, University of Maryland, Baltimore County

In situ attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy was utilized to study the surface reactions and interface evolution during the Atomic Layer Deposition (ALD) of HfO_2 on GaAs(100) surfaces. The chemistry studied involves the use of tetrakis (dimethylamino) hafnium (TDMAH) and H_2O. The experiments were performed on chemical oxide and HF etched GaAs(100) starting surfaces. For the deposition of HfO_2 on chemical oxide GaAs surface at 275°C, which corresponds to the optimal ALD process temperature, considerable arsenic oxide consumption was observed at the 1st TDMAH exposure. The arsenic oxide removal continued during subsequent ALD cycles albeit at a reduced rate. For similar experiments performed at 200°C, the arsenic oxide consumption was significantly lower than that at 275°C in agreement with the observations of Suri et al.[1] A clear ligand exchange process is identified through the alternate appearance of the CH and OH terminated surfaces. However, additional byproducts that contain -C=N- bonds are produced during the water pulse and accumulate in the film. Isotope exchange experiments indicate that these species are compatible with the formation of methylmethyleneimine (MMI) that may be produced through a beta hydride elimination pathway. [2,3]

[1] R. Suri, D. J. Lichtenwalner, and V. Misra, Appl. Phys. Lett. **96**, 112905 (2010).

[2] C. M. Truong, P. J. Chen, J. S. Corneille, W. S. Oh, and D. W. Goodman, J. Phys. Chem. **99**, 8831 (1995).

[3] M. Bouman and F. Zaera, J. Electrochem. Soc. **158**, D524 (2011).

3:40pm **TF+PS-MoA6 Precursor Design: Controlling Melting Point, Volatility, Reactivity and Other Important Characteristics of CVD and ALD Precursors**, ***Seán Barry***, Carleton University, Canada **INVITED**

Chemical vapour deposition methods (CVD) including atomic layer deposition (ALD) are relatively forgiving processes in many respects: the pressure does not have to be very low or strictly controlled, and to some extent the temperature of deposition likewise can have a certain amount of error. These forgiving conditions are largely due to the fact that growth of a film by CVD and ALD is controlled by the surface chemistry of the precursor used, as well as the behaviour of the precursor under thermal stress and in the gas phase. It is often said that precursor "design" is important in these fields: this refers to the control over several key characteristics of the precursor with respect to thermal and chemical behaviour.

My research hinges on the design of precursors with respect to four key characteristics, and each will be discussed using examples. Control of melting point is important to allow better kinetics of evaporation, and this can be tuned by ligand design and asymmetry in the precursor compound. Volatility is a key factor for a precursor, and this can be controlled many ways, including the coordinative saturation of the central (typically metal) atom of the precursor. Thermal stability and chemical reactivity are intimately related, and here choice of ligand, and knowledge of gas phase and surface chemistry is critical for fine control over the difference between a CVD precursor (which undergoes continual deposition) and an ALD

precursor (which requires at least a measure of surface stability to allow for self-limiting behaviour).

4:20pm **TF+PS-MoA8 Characterizing Vapor Delivery of μ^2-η^2-(^{t}Bu-Acetylene)Dicobalthexacarbonyl (CCTBA) for Deposition Processes**, ***James Maslar**, W.A. Kimes, B.A. Sperling,* National Institute of Standards and Technology (NIST)*, R. Kanjolia*, SAFC Hitech

Cobalt metal is a promising material for the formation of enhanced copper barrier and/or seed layers for copper interconnects in integrated circuits. For these applications, atomic layer deposition of cobalt using a gas-phase precursor can provide advantages in the device fabrication process. μ^2-η^2-(^{t}Bu-acetylene)dicobalthexacarbonyl (CCTBA) is a cobalt precursor that can be delivered as a vapor in a carrier gas. However, CCTBA exhibits a relatively low vapor pressure at ambient conditions and typically must be delivered at elevated temperatures to increase the amount of material delivered to the growth surface. As is typically the case for deposition precursors, prolonged heating can lead to decomposition of CCTBA. Therefore, this work was undertaken to help identify optical delivery conditions for CCTBA by investigating 1) the decomposition of CCTBA in an ampoule at various ampoule temperatures and 2) the delivery of CCTBA from an ampoule as a function of carrier gas flow rate, system pressure, and ampoule temperature. CCTBA decomposition in an ampoule was investigated by using Fourier transform infrared (FT-IR) spectroscopy to identify the species present in the headspace of a CCTBA-containing ampoule as a function of time and ampoule temperature. CCTBA delivery was investigated using two optical techniques installed onto a delivery line from the ampoule. Optical access to the delivery line was achieved using two custom-built in-line optical flow cells that were designed to minimize perturbations to the gas flow. One flow cell was utilized for time-resolved FT-IR spectroscopy. This technique was used to identify the species entrained in the carrier gas. However, time response was limited to ~150 ms which is insufficient to resolve many thermal processes impacting CCTBA entrainment. In order to improve time resolution, a CCTBA-specific region of the mid-IR spectrum was identified and a direct optical absorption technique designed for CCTBA. This techinque employed a broadband infrared source with a mid-IR bandpass filter for isolating CCTBA-specific absorption features. This technique was installed on the second optical flow cell and used to measure the time-dependent CCTBA partial pressure as a function of gas flow rate, system pressure, and ampoule temperature for each CCTBA pulse with a time resolution of ~5 ms. In this manner, the dependence of CCTBA partial pressure on delivery conditions was identified. From these data and the time-dependent partial pressure data obtained with this optical measurement, the dependence of the actual amount of CCTBA delivered on delivery conditions was calculated.

4:40pm **TF+PS-MoA9 Effect of Precursor on Coating Uniformity in Mesoporous Metal Oxide Films during Steady and Hold-Step ALD Processes**, ***Berç Kalanyan**, M.D. Losego, G.N. Parsons*, North Carolina State University

Mesoporous film substrates with surface areas greater than 100 m^2/g see use in a variety of applications, most notably in photovoltaic and photoelectrochemical energy conversion. Pastes composed of 10-20 nm diameter metal oxide particles (ITO, FTO, ATO, TiO_2) are cast as a thick film and sintered to form conductive substrates. Atomic layer deposition (ALD) is uniquely suited to apply conformal coatings into these types of mesostructured films. To date, ALD coatings have been used in this fashion for dye sensitized solar cells, photoelectrochemical cells, and thermal photovoltaic devices. Beyond common “steady” or “continuous-flow” ALD processes, several research groups have explored the use of “gas hold steps”, where the reactor is isolated from the pump for some period of time during the precursor exposure, for example, to enhance precursor infusion into high surface area or porous substrates.

In this study we examine ALD processing under steady and hold-step sequences for applying TiO_2 coatings into mesoporous Sn-doped indium oxide (ITO). Typical mesoposous films are up to 10 µm thick, which represents the minimum distance (without tortuosity) that precursor vapors need to travel in order to reach the bottom of the mesostructure. We choose two Ti-containing precursors, titanium tetrachloride ($TiCl_4$) and titanium tetraisopropoxide (TTIP), to understand the influence of bulky functional groups on precursor diffusion. The TTIP diffusivity will be smaller than $TiCl_4$, but it is also sterically hindered by its larger molecular size. We characterize film uniformity in mesoporous substrates by dynamic time-of-flight secondary ion mass spectrometry (TOF-SIMS), in-situ quartz crystal microbalance (QCM), and Krypton gas adsorption experiments.

We show that the $TiCl_4/H_2O$ process can readily infiltrate into nanoporous ITO films as thick as 15 µm using a typical ALD process sequence, without gas “hold” steps. On the other hand, SIMS analysis shows that TiO_2 films deposited using TTIP and H_2O under the same exposure condition reach a depth of only 6 µm before exhibiting a large decay in TiO^- secondary ion intensity. While the $TiCl_4$ shows much better coverage, the process suffers from potential contamination, for example, from Cl which is observed in SIMS analysis. Therefore the use of bulky precursors such as TTIP is critical for ALD infiltration into mesoporous substrates, especially under conditions where coating impurity content is an important concern.

5:00pm **TF+PS-MoA10 Study of the Growth of Zinc Tin Oxide As Model System for Ternary Metal Oxide Atomic Layer Deposition**, ***Adriaan Mackus**, R.W. Johnson, W.-H. Kim, S.F. Bent*, Stanford University

In recent years there is increasing interest in atomic layer deposition (ALD) processes that go beyond traditional AB cycles to enable the deposition of alloyed, doped, or ternary materials. The composition of a ternary material can be tuned by mixing the cycles of two different AB processes in a certain ratio ($(AB)_n(CD)_m$). However, in practice, the composition and the growth rate tend to deviate from what is expected based on the cycle ratio n/m, whereas the formation of a certain crystallographic phase strongly depends on the mixing of ALD cycles and post-deposition anneal conditions. A detailed understanding of how to deposit ternary metal oxides with control of composition and crystallographic phase is currently lacking.

In this work, the material zinc tin oxide (ZTO) has been selected as a model system for studying ternary metal oxide ALD, motivated by its applications as transparent conducting oxide (TCO)[1] or buffer layer[2] in solar cells. For these applications it is important that ZTO consists of earth-abundant non-toxic elements, and therefore has the potential to replace indium-based TCOs or Cd-based buffer layers. ZTO films were deposited by combining the ALD processes of ZnO from diethylzinc (DEZn) and water, and SnO_2 from tetrakis(dimethylamido)tin (TDMASn) and water.[1,3] Synchrotron-radiation X-ray diffraction (SR-XRD) has been performed at the Stanford Synchrotron Radiation Lightsource (SSRL) to investigate the crystallographic phase of the films as a function of composition, cycle ratio, and anneal conditions. It was found that the zinc orthostannate (Zn_2SnO_4) phase forms upon high-temperature annealing, thereby confirming the deposition of ZTO. In addition, Fourier transform infrared spectroscopy (FTIR) was employed to elucidate the surface chemistry of the ZTO ALD process.

1. Mullings *et al.*, Thin Solid Films **556**, 186 (2014)

2. Lindahl *et al.*, Prog. Photovolt: Res. Appl. **21**, 1588 (2013)

3. Mullings *et al.*, J. Vac. Sci. Technol. A **31**, 061503 (2013)

Authors Index

Bold page numbers indicate the presenter

— B —

Barry, S.T.: TF+PS-MoA6, **1**
Bent, S.F.: TF+PS-MoA10, 2
Bosch, R.H.E.C.: TF+PS-MoA1, 1
Brozena, A.: TF+PS-MoA2, 1

— D —

Dandley, E.C.: TF+PS-MoA2, 1

— G —

Gougousi, T.: TF+PS-MoA4, 1

— J —

Johnson, R.W.: TF+PS-MoA10, 2

— K —

Kalanyan, B.: TF+PS-MoA9, **2**
Kanjolia, R.: TF+PS-MoA8, 2
Kessels, W.M.M.: TF+PS-MoA1, 1
Kim, W.-H.: TF+PS-MoA10, 2
Kimes, W.A.: TF+PS-MoA3, 1; TF+PS-MoA8, 2

— L —

Losego, M.D.: TF+PS-MoA9, 2

— M —

Mackus, A.J.M.: TF+PS-MoA10, **2**
Maslar, J.E.: TF+PS-MoA3, 1; TF+PS-MoA8, **2**

— N —

Needham, C.: TF+PS-MoA2, 1

— O —

Oldham, C.J.: TF+PS-MoA2, 1

— P —

Parsons, G.N.: TF+PS-MoA2, 1; TF+PS-MoA9, 2

— S —

Sperling, B.A.: TF+PS-MoA3, **1**; TF+PS-MoA8, 2

— V —

Vandalon, V.: TF+PS-MoA1, **1**

— W —

Williams, P.: TF+PS-MoA2, **1**

— Y —

Ye, L.: TF+PS-MoA4, **1**