Monday Morning, November 7, 2016

Thin Film
Room 105A - Session TF-MoM

ALD Precursors and Surface Reactions

Moderators: Robert Grubbs, Micron Technology, Erwin Kessels, Eindhoven University of Technology, Netherlands

8:20am **TF-MoM1 New Heteroleptic Precursors Enabling Industrial Scale ALD of Next Generation Metal Oxides and Metal Films***, **Nicolas Blasco,*** Air Liquide, France **INVITED**

Thermal and Plasma Enhanced Atomic Layer Deposition (ALD & PEALD) have been major enablers to access new film systems in complex 3D architectures such as sub-14nm logics, sub 20nm DRAM architectures as well as new memory concepts. For example, new oxides film systems could be deposited in a conformal way. Similarly, Ni, Co, Ru metal (PE)ALD drew tremendous attention, with recent efforts towards selective deposition. Chemical functionalization requirements of ALD precursors have been more and more challenging, requiring creative approaches to overcome limitations of previous processes.

Leading groups in 2005-2006 opened the path to the use of “combinatorial” heteroleptic chemicals as ALD precursors. This approach consists in multi-functionalizing the molecule by combining the advantages of several ligand systems, and therefore empirically tailoring its physical and chemical properties (for instance melting point, volatility, thermal stability) - a traditional example being Air Liquide’s ZyALD™ precursor, $ZrCp(NMe_2)_3$. This concept has been extended to multiple ligands and elements. Beyond expected outcome (e.g. physical properties tuning), surprising effects have been observed such as synthesis yield improvement, deposited film crystallinity/stability impact, or even selective deposition.

In this work, achievements using this methodology with new ligand systems and elements will be presented. Specific emphasis will be put on necessary requirements for an industrially viable new precursor, and benchmark with standard molecules.

First, a new set of rare-earth/lanthanide (La, Lu, Sc, Y) precursors will be presented and characterized by various techniques, from a physical & chemical point of view (TGA, DSC, VP), and from deposition behavior point of view (growth rate, film composition). Those novel precursors, for instance combining amidinate ($-(R^1NC(R^2)NR^3)$) and alkylcyclopentadienyl (C_5R_5) ligands, present unique properties which enable access to new material systems via ALD, not only ternary oxides in semiconductor field but also in other areas such as hydrophobic surfaces. This concept will be illustrated with new elements and for example new viable high yield liquid Scandium and lanthanum Oxide precursors will be introduced.

Second, recent improvements in Co, Ni metal ALD/PEALD processes will be presented, especially with the introduction of alkylsilyl ligands for Co precursors chemistry and allyl/amidinate ligands for Ni precursors chemistry. Applicability of those new precursors for advanced logics metal PEALD/ALD/CVD and their comparison with standard molecules (like dicobalt haxacarbonyl tert-butylacetylene - CCTBA) will be presented.

9:20am **TF-MoM4 Time-resolved IR Spectroscopy during ALD of La_2O_3/Al_2O_3 Nanolaminates***, **Brent Sperling**, J.E. Maslar, B. Kalanyan,* National Institute of Standards and Technology (NIST)

Atomic layer deposition (ALD) of La_2O_3-containing films is of interest for high-k dielectric layers in semiconductor manufacturing. Characterization of as-deposited films is made difficult by the tendency of La_2O_3 to form lanthanum carbonates and hydroxides upon exposure to the atmosphere. Previous *in situ* studies have shown evidence for the formation of carbonates during the actual deposition process using an amidinate and water. *Ex situ* studies have found unusual growth behavior that is typically attributed to lanthanum hydroxide formation during deposition. One of the strategies often employed for establishing typical ALD-type growth in La_2O_3-containing films is the incorporation of a second oxide. Although known to be effective, the reasons why are not known. Here, we use time-resolved IR spectroscopy to study surface reactions during La_2O_3/Al_2O_3 nanolaminate formation. A laminar flow reactor using $La(^iPrCp)_3$, TMA, and H_2O as precursors is used. We show that, contrary to previous speculation, non-ideal growth is not due to hydroxide formation. The benefits of incorporating the second oxide is unrelated to suppressing lanthanum hydroxide; alternate explanations must be considered.

9:40am **TF-MoM5 Incomplete Elimination of Precursor Ligands during Atomic Layer Deposition of Metal Oxides***, **Adrie Mackus,*** Eindhoven University of Technology, Netherlands*; C. MacIsaac,* Stanford University*; V. Vandalon, W.M.M. Kessels,* Eindhoven University of Technology, Netherlands*; S.F. Bent,* Stanford University **INVITED**

Atomic layer deposition (ALD) has become an important technique for the deposition of ultrathin and conformal films for a wide variety of applications in nanoelectronics and photovoltaics. Although the reactions mechanisms of several metal oxide ALD processes have been investigated in detail, there are still some open questions regarding the understanding of their growth characteristics. ALD typically relies on two fundamental surface reactions: (*i*) the adsorption of a precursor molecule at specific surface groups (e.g. hydroxyl groups) in the first half-reaction, (*ii*) the elimination of the precursor ligands (while new functional surface groups are formed) in the second half-reactions. In this presentation, it will be shown that the elimination of precursor ligands is often not complete, which has broad implications for the growth characteristics of binary and ternary metal oxide ALD processes.

Experimental evidence for the presence of persisting ligands after the H_2O half-reaction at low temperatures (< 200 ºC) will be presented for the binary ALD processes of Al_2O_3 from TMA, SnO_2 from TDMASn, and ZnO from DEZ. The data for Al_2O_3 was measured using broadband sum-frequency generation (BB-SFG) spectroscopy,[1] while the SnO_2 and ZnO processes were studied using Fourier transform infrared (FTIR) spectroscopy. The incomplete removal of precursor ligands will be explained based on previously reported density functional theory (DFT) studies on cooperative effects during the H_2O half-reaction.[2] In addition, we found that the elimination of precursor ligands is even less effective when ZnO ALD is carried out after SnO_2 ALD, which likely causes the nucleation delay that has been observed for ZnO during the growth of the ternary material zinc-tin-oxide (ZTO).[3,4]

The consequences of the persisting ligands on the growth rate and temperature dependence of the binary ALD processes will be described. Moreover, it will be discussed that the incomplete removal of precursor ligands is expected to play an important role during many other ternary ALD processes, which can explain some of the deviating growth characteristics that have been reported.

1. V. Vandalon and W.M.M. Kessels, *Appl. Phys. Lett.***108**, 011607 (2016)

2. M. Shirazi and S.D. Elliott, *Nanoscale***7**, 6311 (2015)

3. M.N. Mullings *et al.*, *Thin Solid Films***556**, 186 (2014)

4. C. Hägglund *et al.*, *J. Vac. Sci. Technol. A* **34**, 021516 (2016)

10:40am **TF-MoM8 Surface Chemistry of Pt and Al2O3 ALD Studied with Vibrational Sum-Frequency Generation***, **Vincent Vandalon**, W.M.M. Kessels,* Eindhoven University of Technology, Netherlands

The surface chemistry during atomic layer deposition (ALD) of Al_2O_3 and Pt were investigated with vibrational broadband sum-frequency generation (BB-SFG) spectroscopy. These two processes represent examples of two different material classes for ALD: For metal oxides, ALD of Al_2O_3 with $Al(CH_3)_3$ and H_2O as reactants is the prototypical ALD process. Whereas for noble metals, ALD of Pt using $MeCpPtMe_3$ and O_2 as reactants can be considered as prototypical.

Vibrational BB-SFG spectroscopy is excellently suited for in-situ studies of the surface chemistry governing ALD because of its inherent interface selectivity, submonolayer sensitivity, and short acquisition times. It is a nonlinear optical technique which uses the mixing of picosecond visible and femtosecond mid-IR pulses to probe the vibrational response of surface groups. The unique nature of BB-SFG allows the *in-situ* investigation of the surface chemistry on both reflective and transparent substrate without any modifications to the setup.

For ALD of Al_2O_3, both the $-CH_3$ and -OH surface groups ruling the growth mechanism were monitored in-situ with BB-SFG. This study resulted in several new insights into the surface chemistry of this ALD process: Persistent $-CH_3$ groups were observed after the H_2O half-cycle at low temperatures and these significantly influence the growth [Vandalon and Kessels, Appl. Phys. Lett., 2016, Vol. 108] Moreover, the reaction kinetics were studied as a function of temperature and reaction cross sections for both half-cycles were quantified. At low temperatures it was found that the reaction kinetics in the H_2O half-cycle showed a strong dependence on surface coverage. Furthermore, the initial growth of Al_2O_3 on H-terminated silicon was investigated.

ALD of Pt was studied with BB-SFG by probing the C-H stretch region around 3000 cm^{-1}. After precursor exposure, the signature of the C-H stretch mode of the -CH_3 groups was clearly observed. Moreover, a spectrally broad feature was observed in the BB-SFG spectra. This contribution was assigned to unsaturated C chains such as present in the Cp ring. Dosing gas phase MeCp on a Pt and SiO_2 surfaces showed a similar broad feature, supporting this assignment. After O_2 exposure both the -CH_3 and Cp related signals disappeared. These results suggest that after precursor adsorption both -CH_3 and Cp rings (or parts of it) are present at the surface and these groups are removed in the O_2 half-cycle.

11:00am **TF-MoM9 Surface Chemistry of Molybdenum Oxide Atomic Layer Deposition: Role of Precursor Chemisorption on Nucleation Delay and Initiating the ALD Process***, **Charith Nanayakkara**, A. Vega,* The University of Texas at Dallas*; G. Liu, C. Dezelah, R. Kanjolia,* SAFC Hitech*; Y.J. Chabal,* University of Texas at Dallas

Atomic layer deposition (ALD) is an attractive technique for thin film deposition due to its sequential and self-limiting surface reactions leading to conformal and controlled film growth. However, nucleation delays (incubation) can lead to non-uniform island growth, particularly for metal films, often requiring many cycles to obtain a continuous film.

Molybdenum oxide thin films are important for a number of electrical, catalytic, and optical applications. Several Mo precursor-oxidant combinations have been used. For instance, molybdenum hexacarbonyl and ozone (with ALD window between 152 and 172 ^{0}C),[1] and Bis(tert-butylimido)bis(dimethylamido) molybdenum and ozone (with an ALD window between 250 and 300 ^{0}C)[2] gave good film with higher nitrogen content at deposition temperatures less than 250 ^{0}C for the latter.[2] The use of oxygen plasma with bis(tert-butylimido)bis(dimethylamido) molybdenum has shown film growth between 50 - 350 ^{0}C with high elemental H (4 – 11%).[3]

Here, we introduce a new molybdenum precursor, $Si(CH_3)_3CpMo(CO)_2(\eta^3\text{-2-methylallyl}))$ (MOTSMA), which has a good thermal stability (>200 °C), higher volatility with increased vapor pressure (3s exposure results 0.6 Torr gas phase pressure with bubbler at 90 ^{0}C), and increased deposition rates. However, *In-situ* FTIR spectroscopy of the MOTSMA and ozone ALD process reveals that there is a ~15 cycle incubation period at 250°C on OH-terminated oxidized Si(100) surfaces. After this incubation period, i.e. once the steady state ALD process is established, the expected ligand exchange is observed, with formation of surface $Si(CH_3)_3CpMo(\eta^3\text{-2-methylallyl})$ species after the precursor exposure and their removal during the ozone pulse, resulting in $Mo(=O)_2$ surface species. Since this nucleation delay can be reduced by raising the temperature above 300°C, the initial adsorption of the precursor on OH-terminated surfaces was examined as a function of temperature. Indeed, this initial adsorption of MOTSMA on OH-terminated surfaces was found to require higher temperatures. Therefore, we used an initial 350 ^{0}C MOTSMA grafting step in order to overcome the nucleation delay but then performed the ALD process at 250 ^{0}C and 300 ^{0}C. In this manner, steady state film growths with no nucleation delay were obtained at both temperatures, with stoichiometric composition (MoO_3) as confirmed by X-ray photoelectron spectroscopy. The current study highlights the critical role of precursor grafting on eliminating the nucleation delay for ultra-thin ALD grown film deposition.

1. *J. Mat. Chem.* **2011**, *21*, 705
2. *J. Vac. Sci. & Tech. A* **2014**, *32*, 01A119
3. *J. Vac. Sci. & Tech. A* **2016**, *34*, 01A103

11:20am **TF-MoM10 *In situ* FTIR Study of the Surface Reactions during Plasma-assisted Atomic Layer Deposition of SiN_x from Silicon Amides***, **Noemi Leick**, R.A. Ovanesyan, R.J. Gasvoda, P. Walker,* Colorado School of Mines*; K.M. Kelchner, D.M. Hausmann,* Lam Research Corporation*; S. Agarwal,* Colorado School of Mines

Recently, atomic layer deposition (ALD) of silicon nitride (SiN_x) films has been increasingly researched for applications with stringent conformality and processing temperature (≤ 400°C) requirements, such as conformal spacer or etch stop dielectric material in 3-D transistors and air gap interconnect technologies. The necessity for a low-temperature ALD process has shifted focus toward plasma-assisted ALD, mainly using N_2 or NH_3 plasmas. While Cl-based Si precursors have been widely used in ALD of SiN_x films due to their high reactivity, these precursors also form undesirable corrosive byproducts. Silicon amide precursors can overcome these challenges while maintaining a sufficiently high reactivity for ALD.

In this contribution, the focus will be on the growth mechanism of SiN_x films during ALD using $H_2Si(N(C_2H_5)_2)_2$ (BDEAS) and N_2 or NH_3 plasma, at substrate temperatures between 200 – 300 °C. Specifically, we have employed *in situ* attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy to study the film composition, surface reactions during each half-cycle, and the surface species involved in the growth process. From these measurements, we conclude that BDEAS adsorption occurs via a ligand-exchange reaction between one of the diethylamino ligands and surface H, liberating $HN(C_2H_5)_2$ into the gas phase as the main reaction by-product. During the N_2 plasma based ALD process, the N_2 plasma removes the remaining diethylamino ligands from the surface and restores the surface sites necessary for BDEAS chemisorption during the subsequent cycle. The hydrocarbon species on the surface during the N_2 plasma step also leads to the incorporation of C_xN_y species in the SiN_x film. In contrast to the N_2 plasma-based process, NH_3 plasmas in combination with very similar amide precursors have been reported to inhibit SiN_x growth. While our results ultimately confirm these findings, our infrared measurements show that SiN_x growth can initially be achieved with a NH_3 plasma, but attenuates rapidly after the first 5 cycles. The infrared data however suggests that the NH_3 plasma leads to complete removal of the carbon-containing species leading to C-free SiN_x films. Since the composition of SiN_x films deposited by ALD using amide precursors is affected by the nitrogen source in the plasma, a 3-step ALD process involving a NH_3 plasma (to remove C-containing species) followed by a N_2 plasma (to restore surface reactive sites) can potentially optimize the film composition and growth process.

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