ALD Fundamentals
Room 107-109 - Session AF1-MoA

Precursor and Process I

Moderator: Taek-Mo Chung, Korea Research Institute of Chemical Technology (KRICT)

1:30pm **AF1-MoA-1 Forcing Timescale: Can Monolayer Stability Be Built Into a Precursor?***, Sean Barry,* Carleton University, Canada **INVITED**

Presently, there are two processes for depositing gold metal ALD: the Carleton example uses trimethylphosphinegold (III) to allow gold metal to be deposited under 130°C using plasma-assisted ALD using oxygen, while the Helsinki process uses an aminocarbodithiolatedimethylgold (III) and ozone to deposit gold metal at 180°C. Although both processes are viable, a truly thermal deposition process with a robust and easily synthesized precursor has yet to be developed.

We have been studying Au(I) compounds using a variety of ligands to understand how to improve the thermal stability of gold precursors while maintaining a sufficient volatility and reactivity. Here we maintain the phosphine coordinative ligand but alter the covalent ligand to affect its ability to stabilize a gold compound through electron donicity and protect it using steric bulk. Can the judicious application of these principles allow a gold(I) centre enough kinetic stability at the growing surface to permit saturative growth?

This presentation will discuss the effect of ligand modification on volatility, thermal stability, and deposition kinetics. Volatility and thermal stability were measured using thermogravimetric analysis, while deposition kinetics were measured using a quartz crystal microbalance. These trends will be discussed under the theme of precursor modification, and some general strategies for improving precursor characteristics will be considered.

2:00pm **AF1-MoA-3 Comparative Study on New Heteroleptic Zirconium ALD Precursors***, Sanni Seppälä, K Mizohata,* University of Helsinki, Finland*; W Noh,* Air Liquide Laboratories Korea*; J Räisänen, M Ritala, M Leskelä,* University of Helsinki, Finland

Heteroleptic approach has gained wide interest in the development of ALD precursors in the recent years. By combining different ligands enhancement in properties, such as thermal stability and growth rate, is pursued compared to homoleptic counterparts. For example, replacing an alkoxide ligand of a homoleptic compound with cyclopentadienyl may enhance the thermal stability of the compound. However, it is not always easy to predict the properties of the heteroleptic compounds and sometimes the result can be a combination of the undesirable properties of the different ligands. Thus it is important to study different heteroleptic compounds to understand the benefits they can offer compared to traditional ALD precursors.

Zirconium oxide is a very interesting material for several applications, the most important at the moment being memory devices in microelectronics. In this work, three heteroleptic zirconium precursors, namely cyclopentadienyl N,N-bis(tertbutyl)ethene-1,2-diaminato isopropylalkoxo zirconium Zr(Cp)(^{t}BuDAD)(O^{i}Pr), methylcyclopentadienyl tris[2-(methylamino)ethyl] aminate zirconium Zr(MeCp)(TMEA) and pentamethylcyclopentadienyl triethoanolaminate zirconium Zr(Me_5Cp)(TEA) were evaluated as Zr sources in the atomic layer deposition of ZrO_2. Ozone or water was used as the oxygen source. Films were deposited at 200 – 425 °C with an F-120 ALD reactor (ASM Microchemistry). Growth saturation, crystal structures, compositions and electrical characteristics of the films were thoroughly studied. Zr(Cp)(^{t}BuDAD)(O^{i}Pr) and Zr(MeCp)(TMEA) were found to be more reactive than Zr(Me_5Cp)(TEA) since they produced uniform films with both tested oxygen sources at all studied temperatures whereas with Zr(Me_5Cp)(TEA) films could not be deposited with water below 400 °C. The main crystalline phase of the films was the highest permittivity tetragonal ZrO_2. Very low impurity levels were detected in the films deposited with ozone.

The research leading to these results has received funding from the Finnish Centre of Excellence in Atomic Layer Deposition (Academy of Finland).

2:15pm **AF1-MoA-4 A New Class of ALD Precursors for Aluminum Oxide – Potential Alternative to TMA!***, Lukas Mai, N Boysen, D Zanders,* Ruhr-University Bochum, Germany*; T de los Arcos,* University of Paderborn*; F Mitschker,* Ruhr-University Bochum, Germany*; G Grundmeier,* University of Paderborn*; P Awakowicz, A Devi,* Ruhr-University Bochum, Germany

Due to its chemical inertness and wear resistance, thin films of Al_2O_3 are often employed as protective coatings. In particular gas barrier layers (GBLs) of Al_2O_3 are used in organic light emitting diodes (OLEDs) or on polymers to protect degradable compounds or goods from air. For high quality GBLs, the thin films should be very uniform and conformal over the whole surface especially on demanding geometries. Moreover, the films should be dense and amorphous to avoid diffusion path ways. With atomic layer deposition (ALD) it is possible to fabricate such thin films at low temperatures, as the self-limiting nature of this process leads to highly uniform, conformal and dense films with a precise thickness control. For the ALD of Al_2O_3, trimethylaluminum ([$AlMe_3$], TMA) is the most commonly used precursor. Despite the inherent advantages of TMA in terms of high volatility and reactivity toward a range of co-reactants at low temperatures, there are certain issues with TMA such as its pyrophoric behavior and not well-defined ALD window. Therefore, we attempted the synthesis of alternative Al precursors.

Here, we present the synthesis of the *3-(dimethylamino)propyl* (DMP) substituted aluminum complexes[$AlMe_2$(DMP)] (**1**, DMAD) and[Al(NR_2)$_2$(DMP)] [R = Me (**2**), Et (**3**), ^{i}Pr (**4**)] as an alternative class of precursors for ALD of Al_2O_3.[1]In these complexes, the DMP ligand stabilizes the Al center atom by a dative bond from the amine to the Al (Fig. 1). This yields thermally stable, non-pyrophoric new complexes, whose thermal properties, in terms of evaporation behavior, can be tuned by systematic variation of the alkyl side chains within the ligands (Fig.1). As compounds **1** and **3** exhibits a high evaporation rate at only 45 and 60°C, new plasma enhanced (PE)ALD processes employing oxygen plasma were developed. The two processes are self-limiting at substrate temperatures between 60°C and 220°C on Si(100) with growth rates of 0.92 Å cycle^{-1} using **3** and 0.60 Å cycle^{-1} employing **1** (Fig. 2). The resulting Al_2O_3 thin films are conformal, uniform, smooth, dense and of high purity even at low deposition temperatures. For the investigation of the Al_2O_3 films as GBL, thin films of various thicknesses were deposited on PET substrates at 60°C and the improvement of the gas barrier of the PET by a factor of 90 for a 15 nm thin film using **1** and a factor of 25 for an only 5 nm thin film using **3** was obtained by oxygen transmission rate (OTR) measurements (Fig. 3). The thin film properties are of the same quality as for layers obtained from TMA, rendering our new intramolecular stabilized precursors to be a promising and safe alternative for ALD of Al_2O_3 coatings.

2:30pm **AF1-MoA-5 Atomic Layer Deposition of Aluminum Metal Using a Thermally Stable Aluminum Hydride Reducing Agent***, Kyle Blakeney, C Winter,* Wayne State University

We report the thermal atomic layer deposition (ALD) of highly conductive aluminum metal thin films at temperatures as low as 100°C. The precursors used are $AlCl_3$ and a new aluminum dihydride reducing agent. Self-limiting growth is demonstrated for both precursors with a growth rate of about 3.5 Å/cycle within an ALD window of 120-160°C. Film resistivities were as low as 3.03 µΩ·cm and the films were crystalline by X-ray diffraction. Film composition as determined by X-ray photoelectron spectroscopy showed Al (> 94 at%) with low Cl impurities (<0.5 at%). To our knowledge, this is the first thermal ALD process for aluminum metal films and aluminum has the most negative electrochemical potential ($Al^{3+} \leftrightarrow Al^0 E^\circ = -1.676$ V) of any element deposited by thermal ALD to date. Accordingly, the new aluminum dihydride reducing agent used in this study should enable ALD processes for many challenging elements and materials.

2:45pm **AF1-MoA-6 Low Temperature PE-ALD of Copper Films using Copper Aminoalkoxides Precursors with Hydrogen***, Akihiro Nishida, A Sakurai, T Yoshino, M Okabe, M Enzu, A Yamashita,* Adeka Corporation, Japan

Copper is well-known as an interconnect material for semiconductor devices having a high electrical conductivity, high thermal conductivity, and comparatively good electromigration resistance. Physical vapor deposition (PVD) has been used as the most popular method to deposit thin copper seed layers for microelectronic devices. However, it is difficult to deposit a conformal and continuous film on the high aspect ratio substrate. Copper atomic layer deposition (ALD) is required in order to deposit thin copper seed layers which have good coverage, high film continuity, and low resistivity.

In this study, we have carried out the investigation of several types of copper ALD precursors preferred for industrial uses, and found that some copper aminoalkoxides precursors have low melting points. As an example, the melting point of bis(1-ethylmethylamino-2-propoxy)copper (CTA-5) was observed at 38°C by DSC measurement. CTA-5 showed a very clean TG curve without decomposition and residue at 10 Torr. Additionally, we demonstrated PE-ALD of thin copper metal film using CTA-5 and hydrogen as the co-reactant, and succeeded in making shiny metallic copper films at 40°C. The growth rate was at 0.30 Å/cycle and 0.41 Å/cycle on the Si and SiO_2 substrates, respectively. Each of resistivity was measured at 3.7 μΩ·cm and 4.1μΩ·cm. It was also found that carbon, nitrogen, and oxygen contamination was not detected in each copper metal film by XPS measurement. Regarding film morphology, we verified that continuous films were deposited by FE-SEM measurement. Therefore, we finally conclude that CTA-5 is better suited for manufacturing copper ALD processes compared to conventional copper ALD precursors.

3:00pm **AF1-MoA-7 Atomic Layer Deposition of Rhenium Selenide Thin Films***, J Hämäläinen, K Mizohata, K Meinander, M Mattinen, J Räisänen, M Leskelä,* ***Mikko Ritala,*** University of Helsinki, Finland

2D materials research is evolving at a high pace as new layered materials are synthesized and their properties studied towards various applications. A group of these 2D materials that has raised major attention since 2010 is transition metal dichalcogenides (TMDCs). An addition to this 2D materials family is $ReSe_2$ which was fabricated by CVD only very recently [1]. In many respects $ReSe_2$ is not a typical TMDC material though. It has been reported to have distorted 1T´ structure with low symmetry that leads to anisotropic electronic, optical and mechanical properties similar to ReS_2 [2]. $ReSe_2$ monolayers are more weakly coupled than in typical TMDCs, but not so strongly decoupled as in case of ReS_2 because the structural distortions are not as severe [3].

ALD is a very attractive method for making thin films with precise control on film thickness, composition, and structure. We have recently reported ALD of ReS_2 using $ReCl_5$ and H_2S in a wide deposition temperature range up to 500 °C [4]. Here, we introduce deposition of rhenium selenide thin films by ALD using the same Re metal precursor with bis(trimethylsilyl)selenide as a co-reactant. Successful film growth was achieved at deposition temperatures up to 450 °C. The ALD process development and characterization will be discussed.

[1] M. Hafeez, L. Gan, H. Li, Y. Ma, and T. Zhai, *Adv. Mater.* 28 (**2016**) 8296.

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[3] B. Jariwala, D. Voiry, A. Jindal, B. A. Chalke, R. Bapat, A. Thamizhavel, M. Chhowalla, M. Deshmukt, A. Bhattacharya, *Chem. Mater.* 28 (**2016**) 3352.

[4] J. Hämäläinen, M. Mattinen, K. Mizohata, K. Meinander, M. Vehkamäki, J. Räisänen, M. Ritala, and M. Leskelä, *Adv. Mater.* (**2018**) Early View Online. https://doi.org/10.1002/adma.201703622

3:15pm **AF1-MoA-8 Plasma Enhanced Atomic Layer Deposition of Silicon Nitride Films with Inorganic Disilane Precursors***,* ***Xiaobing Zhou****, B Hwang, X Wang, B Ketola, J Young, C Lee, M Telgenhoff, B Rekken, Y Ahn, W Chung,* Dow Chemicals*; X Meng, Y Byun, J Kim,* University of Texas at Dallas

Di or higher silanes containing one or more than one Si-Si bonds were reported to improve growth-per-cycle (GPC) rates in the atomic layer deposition (ALD) of silicon-based dielectric films. We studied this phenomenon by depositing silicon nitride (SiN) films from two inorganic disilanes without organic functionalities under different plasma enhanced ALD conditions. ALD type of film formation was observed for pentachlorodisilane (PCDS)-ammonia plasma and tris(disilanyl)amine (TDSA)-nitrogen plasma systems at 270 – 360^{o}C. The SiN film properties including refractive indices, compositions and wet etch rates were determined. These results will be discussed in the presentation.

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