ALD Fundamentals
Room Evergreen Ballroom & Foyer - Session AF1-MoP
Precursor Synthesis and Process Development Poster Session

AF1-MoP-1 Atomic Layer Deposition of Molybdenum Films from Molybdenum Pentachloride Precursor*, **Changwon Lee**, S Lee, M Kim,* Versum Materials, Republic of Korea*; S Ivanov,* Versum Materials, Inc.

The lower resistivity WL (Word Line) material is very attractive to the 3DNAND device makers, because they could reduce the cell stack height while maintaining the device speed. Current POR material of 3DNAND WL is tungsten made by tungsten hexafluoride ALD. However, it is well-known that fluorine results in fatal defects in the device critical layer. Fluorine free tungsten precursors such as tungsten pentachloride has been evaluated recently worldwide not only for 3DNAND application but also other memory and logic devices application. Molybdenum is considered as an attractive WL material for next generation 3DNAND devices. Molybdenum has almost same level of low bulk resistivity comparing to tungsten, but it has smaller EMFP (Electron Mean Free Path), so the effective resistivity, a product of bulk resistivity and EMFP, is expected to be lower compare to tungsten for films less than 10nm. Molybdenum chlorides are considered as potential precursors for deposition of molybdenum films from fluorine free precursors.

Here, we report thermal ALD of molybdenum films on PVD titanium nitride substrates up to 500ºC from heated solid high-purity molybdenum pentachloride precursor. Hydrogen was used as a reactant gas under cyclic CVD and ALD conditions. Thickness of molybdenum and titanium nitride films was measured with XRF. Sheet resistance of molybdenum films was measured using 4-point probe technique. The films have been also characterized with TEM and XPS for conformality at aspect ratio 15 trench pattern and impurity depth profile in the film.

We've found that the etching of titanium nitride could be controlled lower than 0.5nm during the molybdenum deposition by variation of molybdenum pentachloride delivery rate. Molybdenum GPC was 0.06 nm per cycle at 500ºC wafer temperature. The dependence of step coverage on deposition conditions was investigated and will be discussed. The properties of molybdenum films deposited from molybdenum pentachloride will be compared to properties of tungsten films deposited from similar tungsten pentachloride precursor. Preliminary results suggest that resistivity of the molybdenum films is lower compare to resistivity of tungsten films at 10-15 nm of film thickness. Rapid thermal annealing at 700ºC further reduced the sheet resistance of the films.

In this paper, we demonstrated thermal molybdenum ALD with fluorine free molybdenum precursor, which shows low etch of titanium nitride substrate and relatively low resistivity compared to tungsten; which is important for next 3DNAND's WL forming application. Details of the deposition study and properties of the molybdenum films will be presented.

AF1-MoP-2 Atomic Layer Deposition of Silver Metal Films: Synthesis and Characterization of Thermally Stable Silver Metal Precursors*, **Harshani J. Arachchilage**, C Winter,* Wayne State University

Silver metal has the lowest resistivity (1.59 μΩ cm) of all metals and has applications in plasmonic devices. Growth by thermal atomic layer deposition (ALD) has been hampered by the low thermal stabilities of virtually all silver precursors. The low precursor thermal stabilities is complicated by the positive electrochemical potential of the silver(I) ion (E° ($Ag^+ + e^- \leftrightarrow Ag$) = 0.7996 V). Herein, we will describe volatile and highly thermally stable silver pyrazolate precursors. The silver pyrazolates $[Ag(3,5\text{-}(CF_3)_2pz)]_3$ and $[Ag(3\text{-}^tBu\text{-}5\text{-}(CF_2CF_2CF_3)pz)]_3$ were synthesized and their volatility thermal stabilities were evaluated by sublimation studies, solid-state thermal decomposition experiments, and thermogravimetric analysis (TGA). $[Ag(3,5\text{-}(CF_3)_2pz)]_3$ was used with 1,1-dimethylhydrazine to deposit silver metal films on SiO_2 substrates at 180 °C with a growth rate of 0.82 Å/cycle. A plot of growth rate versus substrate temperature showed an ALD window of 170 to 220 °C. Saturative self-limited growth was demonstrated in both $[Ag(3,5\text{-}(CF_3)_2pz)]_3$ and 1,1-dimethylhydrazine at 180 °C. The as-deposited films were crystalline. We will also describe the synthesis and characterization of silver pyrazolate complexes containing N-heterocyclic carbene (NHC) ligands. Treatment of $[Ag(3,5\text{-}(CF_3)_2pz)]_3$ and $[Ag(3\text{-}^tBu\text{-}5\text{-}(CF_2CF_2CF_3)pz)]_3$ with three equivalent of the NHC ligands afforded complexes afforded new monomeric complexes of the formula $Ag(R_2pz)(NHC)$. X-ray crystal structures, sublimation data, and the thermal stability of these complexes will also be presented.

AF1-MoP-3 Atomic Layer Deposition of Lanthanum Oxide Using Heteroleptic La Precursors*, **Daehyeon Kim**, J Lee, W Noh,* Air Liquide Laboratories Korea, South Korea

Rare earth-based oxides are of interest for their potential application in future logic and memory technologies, and lanthanum oxide (La_2O_3) is a well known high-k material for metal gate transistors and a dopant for high-k materials. In past studies, heteroleptic precursors which have alkylcyclopentadienyl and amidinate ligands, $La(RCp)_2(R'\text{-amd})$, have been developed to aim to be liquid and to enhance volatility and thermal stability. In this work, three heteroleptic precursors, $La(MeCp)_2(iPr\text{-amd})$, $La(EtCp)_2(iPr\text{-amd})$, $La(iPrCp)_2(iPr\text{-amd})$, were synthesized, and their physical properties were compared. $La(EtCp)_2(iPr\text{-amd})$ and $La(iPrCp)_2(iPr\text{-amd})$ were liquid at RT, and very thermally stable. ALD evaluation of $La(EtCp)_2(iPr\text{-amd})$, which is more promising than $La(iPrCp)_2(iPr\text{-amd})$ in terms of the vapor pressure and the viscosity, was performed with O_3 and H_2O as a co-reactant. Both processes had two plateaus in the ALD windows which were at low and high temperature, respectively. The desired ALD window will be the plateau at higher temperature (>350 ℃), because of low C impurity. The plateau at lower temperature might be useful for another processes. Carbon impurity at the low temperature was drastically decreased below detection limit, after post annealing in N_2 atmosphere. In case of ozone process, the cubic phase was observed at 400 ℃ while all films with water process showed amorphous phase even at 400 ℃.

AF1-MoP-4 Synthesis and Thermal Characterization of New Molybdenum Precursors for Atomic Layer Deposition of Molybdenum Metal*, **Michael Land**,* Carleton University, Canada*; K Robertson,* Saint Mary's University, Canada*; S Barry,* Carleton University, Canada

To keep pace with "Moore's Law" (i.e., the number of transistors in an integrated circuit doubles every 18 months), the size regime of high-performance transistors has now shrunk to ≤ 10 nm. With this decrease of size, traditional metallization materials (e.g., Cu, Al) begin to fail. When microelectronic interconnects – the wiring of integrated circuits – become smaller than 10 nm, the resistivity of the material increases due to electromigration of the metal atoms within the interconnect. Promising metals to replace copper are molybdenum, osmium, iridium, ruthenium, rhodium, and tungsten, because they all have high melting temperature and relatively low bulk resistivities (~4-10 μΩ.cm), leading to lower electromigration.

A method of choice that can be used for the preparation of these small interconnects is atomic layer deposition (ALD). The goal of this project is to develop a chemical precursor compound for the ALD of molybdenum metal. To date, there has only been one reported ALD process for molybdenum metal, however that process utilized harsh co-reagents, and the resulting films had high resistivities. We have chosen the known *bis*(*tert*-butylimido)molybdenum(VI)dichloride as a synthetic starting material, and it has been derivatized with various neutral coordinating ligands, such as ethers, phosphines, amines, and carbenes The ligands were found to have varying effects on the thermal stability of the precursors (up to 300 ºC for the 2,2'-bipyridine adduct), which sometimes came at the cost of poor volatility. However, complexes incorporating less Lewis basic ligands, such as the 1,2-dimethoxyethane adduct, was found to have a large thermal range, with an onset of volatilization of 80 ºC and thermal decomposition at 180 ºC.

These compounds have been characterized in the condensed state, using traditional spectroscopic techniques, and their solid-state structures have been determined using single crystal X-ray diffraction. Their mechanisms of volatilization will also be proposed, based on results from thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), and the resulting sublimation products. Finally, the thermal stabilities of these compounds have been studied using DSC and thermolysis in flame-sealed NMR tubes, and non-volatile decomposition products were characterized using a scanning electron microscope (SEM) with energy-dispersive X-ray spectroscopy (EDS). From these results, mechanisms of thermal decomposition will also be proposed, including methods to prevent low temperature decomposition pathways and furnish viable vapour deposition precursors.

AF1-MoP-6 A Novel Hf Precursor with Linked Cyclopentadienyl-Amido Ligand for Thermal Atomic Layer Deposition of HfO_2 Thin Film*, **Jeong do Oh**, M Nim, J An, J Seok, J Park,* Hansol Chemical, Republic of Korea

HfO_2 thin film has been widely used as gate oxide layer in the complementary metal oxide semiconductor (CMOS) device as well as dynamic random access memory (DRAM) due to suitable band offset with Si, high thermodynamic stability on Si, and high permittivity [1].

In this study, we investigated a novel Hf precursor, CMENHa, which is coordinated by cyclopentadienyl-amido ligand. The physical characteristics of precursor and film properties of the ALD HfO_2 thin films were analyzed via TGA, viscometer, XPS, XRD and TEM. As compare to widely applied CpTDMAH precursor, CMENHa precursor showed higher thermal stability due to chelate effect of bidentate ligand, lower residue (0.6%) and lower viscosity. In addition, CMENHa was observed wide ALD window range up to 400℃ with low carbon impurity contents and good electrical properties such as high dielectric constant and low leakage current density. Base on excellent step coverage, purity and thermal stability, the CMENHa precursor has demonstrated potential as dielectric material for use in CMOS device and DRAM capacitor.

Reference [1] J. Robertson et al., *Rep. Prog. Phys.***69**, 327−396. (2006).

AF1-MoP-7 Atomic Layer Deposition of WS_2 using a New Metal-Organic Precursor and H_2S Molecules*, Deok Hyun Kim*, *D Nandi, S Kim,* Yeungnam University, Republic of Korea

Transition metal dichalcogenides (TDMCs) are exntesively researched in past few years due to their 2D layerd structure similar to graphne . This group of materials offer tunable opto-electronic properties depending on the number of layers and therefore have wide range of applications. Tungten disulfide (WS_2) is one of such TMDCs that has relatively less studied compared to MoS_2. WS_2 has an indirect bandgap of 1.3–1.4 eV in bulk, which have trigonal prismatic coordination around tungsten. The bandgap of WS_2 increases with decreasing thickness and, intriguingly, becomes direct at monolayer thickness with a magnitude of approximately 2.3 eV for the optical bandgap. Such tunability of WS_2 makes it suitable for many semiconductor applications such as field-effect transistors, photodetectors, and photocatalysis, while other promising applications include electrocatalysis and electrochemical energy storage. Atomic layer deposition (ALD) can be adopted very efficiently to control the thickness of WS_2 and hence its properties. Therefore, in this study is WS_2 thin films are grown on several types of substrates by ALD using a new metal-organic precursor [tris(hexyne) tungsten monocarbonyl, $W(CO)(CH_3CH_2C{\equiv}CCH_2CH_3)$ and H_2S at a relatively low temperature of 300°C.The typical self-limiting film growth (growth rate of ~0.13 nm/cycle) is clearly observed with both the precursor and reactant pulsing time. The as-grown films are amorphous with considerable S-deficiency but can be crystallized as WS_2 film with (002) preferential orientation by post-annealing in H_2S/Ar atmosphere at 800 °C. Moreover, the post-annealing helps to reduce the C and O content in the film signififcantly as confirmed by the X-ray photoelectron spectroscopy. Further characterizations of the as-deposited and annealed films are perfomed using several other spectroscopic measurements like Raman, Rutherford backscattering, and UV-vis spectroscopy. The current study thus establishes a new and efficient route to obtain WS_2 thin films which could find several potential applications in future.

Acknowledgements

This work was financially supported by the Ministry of Trade, Industry & Energy (MOTIE; #10080651) and Korea Semiconductor Research Consortium (KSRC) support program for the development of the future semiconductor device. The precursor used in this study was provided by UP Chemical Co. Ltd., Korea.

AF1-MoP-8 Recent Advances in the Development of Metal Organic Precursors for Atomic Layer Deposition*, Anjana Devi*, *L Mai, D Zywitzki, S Beer, N Boysen, D Zanders, J Wree, M Wilken, H Parala,* Ruhr University Bochum, Germany

Atomic layer deposition (ALD) has gained significant attention from the research community and industry due to the distinct advantages in terms of uniform and conformal coating with precisely tunable stoichiometry and thin film thickness. Since ALD is a chemical vapor phase technique, one of the important parameters governing the process is the precursor employed, which most often is in the form of a metal organic complex. The precursor must be volatile and at the same time it must possess a certain thermal stability to avoid decomposition. Furthermore, due to the surface driven reactions the precursor has to be reactive toward the reactive surface sites and in the second reaction step toward co-reactants to achieve a self-limiting behavior to obtain the desired material. However, the library of precursors for various material systems is not very large and for certain metals there are limited precursors commercially available.

This prompts researchers to develop new precursors or fine tune the characteristics of the already adopted precursors to improve upon the properties relevant for ALD. Over the years, our research group focused on developmental precursor chemistry spanning the periodic system and identified several ligand systems bound to the metal center that are well suited for ALD conditions. Herein, we present an overview of our research work including the synthetic strategies for various ligands, namely guanidinates, amidinates, b-ketoiminates, cyclopentadienyls, diazadienes, N-heterocyclic carbenes and alkylamines. Potential precursor solutions for group III, IV, V and VI transition metals as well as lanthanides are presented employing guanidinates and amidinates among which Y, Hf, Mo, W, Gd and Er were already successfully used in ALD processes. For the fourth period transition metals ranging from Fe to Zn, employing b-ketoimines and diazadienes resulted in promising precursors. Noble metals like Cu and Ag can be deposited using N-heterocyclic carbene complexes. Precursors for main group III metals such as Al, Ga and In, were fine tuned for both, low and high temperature ALD processes employing either alkylamines, amidinates or guanidinates. Furthermore, we identified and developed ligand systems which were combined with Sn, Pb for main group IV metals and Sb for main group V, resulting in potential ALD precursors.

In this presentation, precursor systems covering a range of metals will be presented alongside representative examples for the application in ALD processes. We will also demonstrate that this large library is not only suitable for inorganic oxides, or nitrides but also compatible with organic co-reactants in ALD/MLD processes.

AF1-MoP-9 Synthesis of Group VI Oxyhalide Adducts and Mo Metal Film Growth on TiN Surfaces*, David Ermert*, *R Wright Jr., T Baum,* Entegris, Inc.

Molybdenum and tungsten metal films are being widely considered for logic and memory (DRAM/NAND) devices, a result of their low-resistivity and high melting points (low electromigration). Challenges to more widespread adoption of group VI film growth using chemical vapor deposition (CVD) and atomic layer deposition (ALD) stem, in part, from the availability of suitable metal-containing precursors. When considering materials for CVD/ALD applications, halide-saturated MX_n species (e.g. $MoCl_5$, WF_6) offer suitable volatility and can deposit high-quality metal films, but may not be compatible with neighboring films within the device. For example, the resulting HCl or HF byproducts may be detrimental to diffusion barrier performance within the device.

Zero-valent metal carbonyls are logical choices for metal deposition as they display suitable vapor pressures and do not require chemical reduction during thermal decomposition on a surface. Barriers to adoption of these precursors include prohibitively high decomposition temperatures, the formation of metal carbides via incorporation of carbon in the films, and the release of toxic carbon monoxide by-products. In general, volatile organometallic precursors that can be deposited at low temperatures offer attractive alternatives for film deposition provided the deposited films are carbon-free.

Here, we describe a general approach to CVD/ALD precursor design and subsequent growth of molybdenum metal films, at moderate surface temperatures, using a molybdenum oxyhalide species and H_2 co-reactant. Group VI oxychloride adducts of the general formula $MO_2Cl_2L_n$ (where M = Mo, W with L = Lewis base adduct and n = 1, 2) are prepared and screened as potential ALD candidates. Precursor characterization and use in thermal deposition studies will be described. Deposited metal film resistivity approaching 50 μΩ-cm were observed at temperatures below 500 °C. Film composition studies, carried out by XRF spectroscopy, demonstrated a strong substrate temperature-dependence on film identity.

AF1-MoP-10 Gallium Precursor Development for ALD Film Applications*, Atsushi Sakurai*, *M Hatase, N Okada, A Yamashita,* ADEKA Corporation, Japan

Gallium-based films such as gallium oxide and gallium nitride have been attracting the world's attention of those who are looking at future power electric devices with high power, high breakdown voltage, and energy-saving benefit. Although ALD process could be useful for producing many kinds of metal oxide, nitride, carbide thin films with execellent quality and conformality, many studies have not yet been done regarding gallium precursor screening for ALD applications.

Trimethylgallium (TMG) is the well-known gallium precursor to make various kinds of Ga-based thin films such as gallium nitride and gallium arsenide. However, TMG with remote oxygen plasma ALD process still left over some carbon impurity in the gallium oxide film [1]. Furthermore, it has been pointed out that TMG has undesirable pyrophoric nature when exposed to air.

We are looking for various kinds of gallium precursors which have non-pyrophoric nature, good volatility, enough thermal stability, and high ALD reactivity to produce gallium-based thin film even with gentle ALD process conditions. Fig.1 indicates that our new precursor of GNP-7 has the highest vapor pressure of several kinds of N-based gallium molecules. Thermal ALD process using GNP-7 and H_2O co-reactant produced the amorphous gallium oxide film with good ALD process window at low temperature domain (Fig.2). We are also demonstrating gallium nitride films using GNP-7 and NH_3, whose results will be shown in our presentation then.

[1] Xiao Chen et al., ALD 2018 technical program & abstract book, p128, AA3+AF+EM-WeM6

AF1-MoP-11 Design and Optimization of Heteroleptic Zirconium Precursors by Density Function Theory Calculation*, **Romel Hidayat,*** Sejong University, Republic of Korea*; J Cho, H Lim, B Yang, J Park, W Chae,* DNF Co. Ltd, Republic of Korea*; H Kim,* Sejong University, Republic of Korea*; S Lee,* DNF Co. Ltd, Republic of Korea*; W Lee,* Sejong University, Republic of Korea

The stack capacitor of DRAM is continuously developed by decreasing the horizontal dimension, increasing the aspect ratio, and adopting dielectric materials with higher dielectric constants (k). Zirconium oxide (ZrO_2) is a high-k material currently in use in dynamic random access memory (DRAM) devices. The deposition of high-k dielectric materials with excellent conformality and accurate thickness control is required, and the atomic layer deposition (ALD) technology is the best choice. The high-temperature ALD process is desirable for the high dielectric constant and low leakage current density of the deposited film, so the thermal stability of the precursor should be excellent. The reactivity of the precursor is an essential factor to obtain a better conformal film. Also, the precursors must have excellent reactivity for conformal deposition of the film on high-aspect-ratio patterns. A new heteroleptic zirconium precursor for ALD of ZrO_2 has been developed to meet these requirements, and the deposition process and thin film properties using this precursor were presented [1]. The result showed a wide ALD temperature window and excellent step coverage. In the present work, we present the design and optimization of the zirconium precursors by using density functional theory (DFT) calculations. We compared zirconium compounds with different numbers of triamine and dimethylamine ligands to determine the most stable structure. Then, we optimized the alkyl groups in triamine ligand in terms of thermal stability, reactivity, and viscosity. The optimized zirconium compound with a triamine ligand showed better reactivity and stability as compared with the cyclopentadienyl tris-dimethylamine zirconium [$CpZr(N(CH_3)_2)_3$], which is in a good agreement with deposition experiments. DFT calculation is a powerful tool for designing new precursors for ALD process to obtain the desired thermal stability, reactivity, and viscosity.

Figure 1. Lewis base indices and zirconium charge densities of triamine-type zirconium compounds with different combinations of alkyl groups.

[1] H.-D. Lim *et al*., ALD 2018, AF2-TuA13.

AF1-MoP-12 Low Temperature Plasma-Enhanced Atomic Layer Deposition of ZnO from a New Non-Pyrophoric Zn Precursor*, **Lukas Mai**, F Mitschker, P Awakowicz, A Devi,* Ruhr University Bochum, Germany

With its high transparency to visible light and tunable conductivity, zinc oxide (ZnO) is a transparent conductive oxide (TCO) and promising candidate for microelectronic applications such as thin film transistors (TFTs), solar cells or chemical sensors. Furthermore, with a direct band gap of E_g= 3.37 eV it can not only be used for electrical but optical applications e.g. in UV-light emitting diodes (LEDs), too. Owing to its high density, ZnO layers can be employed as protective coating as well and could serve as conductive and protective gas barrier layer (GBL) at the same time on polymers in flexible electronics. For high quality GBLs, the thin films should be very uniform, dense and conformal over the whole surface. With atomic layer deposition (ALD), it is possible to fabricate such thin films at low temperatures with a precise thickness control. For the ALD of ZnO, diethylzinc ([$ZnEt_2$], DEZ) is the most commonly used precursor. Despite the inherent advantages of DEZ in terms of high volatility and reactivity toward a range of co-reactants at low temperatures, there are certain issues with DEZ such as its pyrophoric behavior and not well-defined ALD window. Thus, we attempted the synthesis of an alternative Zn precursor.

Here, we present the synthesis and detailed characterization of bis-3-(dimethylamino)propyl zinc, [$Zn(DMP)_2$] as an alternative precursor for ALD of ZnO. As already demonstrated for aluminum precursors,[1] the DMP ligand stabilizes the zinc center atom by a dative bond from the amine to the metal. This yields a favored 18 electron complex, causing a thermally stable, non-pyrophoric solid compound with a melting point at only 46 °C. The thermal properties are thoroughly characterized showing a high evaporation rate at only 55 °C. Using this precursor, a new plasma enhanced (PE)ALD process employing O_2 plasma was developed. The process is self-limiting at substrate temperatures between 60 °C and 140 °C on Si(100) with growth rates of 0.44 Å $cycle^{-1}$at 60 °C and 0.72 Å $cycle^{-1}$at 140 °C. The resulting ZnO thin films are conformal, uniform, smooth, dense and of high purity even at low deposition temperatures and were analyzed regarding their optical and electrical properties. For the investigation of the ZnO 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 60 for a 10 nm thin film obtained by oxygen transmission rate (OTR) measurements. The thin film properties are of the same quality as for layers obtained from DEZ, rendering the new intramolecular stabilized precursor to be a promising and safe alternative for ALD of ZnO coatings.

AF1-MoP-13 Homoleptic and Heteroleptic Yttrium Precursor: Tuning of Volatility, Reactivity and Stability for ALD Applications*, **Sebastian Markus Josef Beer**, A Devi,* Ruhr University Bochum, Germany

Rare-earth (RE)-based materials in the form of thin films have gained significant attention due to their unique functional properties rendering them suitable for a broad variety of applications. Especially yttrium oxide (Y_2O_3) has been intensively studied for optics, protective coatings or high-k dielectrics. Furthermore, the ability to dope Y into other oxide material systems opens up new avenues for the development of high–performance materials as for instance yttrium doped zinc oxide (Y:ZnO), yttria stabilized zirconia (YSZ) or yttrium doped $SrSnO_3$.[1-3]

Atomic layer deposition (ALD) serves as a superior thin film processing technique enabling precise layer thickness control paired with conformal growth and uniformity fulfilling the main requirements for the fabrication of high-quality thin films. However, ALD processes strongly depend on the performance of the applied precursors. Therefore, the rational design and development of metalorganic compounds comprising optimal physico-chemical characteristics remains a key factor for ALD-based research. Over the years, various Y metalorganic precursors have been developed for ALD processes mainly focusing on homoleptic complexes such as β-diketonates [$Y(thd)_3$], silylamides [$Y(tmsa)_3$], amidinates [$Y(dpamd)_3$], guanidinates [$Y(dpdmg)_3$] or cyclopentadienyls [$Y(Cp)_3$]. Some of these compounds have high melting points, low volatility, reactivity or thermal stability which, in most cases, can be tuned through side-chain variations of the ligand moieties.

Another promising approach is to employ mixed ligand systems to form heteroleptic substituted compounds, ideally combining the characteristics of the respective homoleptic analogues. In earlier reports, RE precursor systems with combination of ligands were demonstrated by Leskelä *et al*[4] and Lansalot-Matras *et al*[5] where liquid precursors were successfully employed for RE oxide thin films. These approaches encouraged us to design and develop new metalorganic Y complexes with advantageous physico-chemical properties such as a high volatility, reactivity and stability thus ensuring applicability in ALD processes.

In our study, we focused on the guanidinate and amidinate ligand classes which provide pronounced reactivity toward co-reactants such as water through their Y-N bonds in combination with the cyclopentadienyl ligand, possessing good thermal stability due to the formation of robust leaving groups. Herein, we present a rational development and detailed characterization of new, spectroscopically pure heteroleptic and monomeric yttrium cyclopentadienyl guanidinate and yttrium cyclopentadienyl amidinate precursors for ALD processes of Y-based thin film materials.

AF1-MoP-14 Gallium ALD Precursor Development based on Mechanistic Study*, M Foody, Y Zhao, **Adam Hock**,* Illinois Institute of Technology

Low temperature deposition of Ga_2O_3 remains a challenge, particularly in the absence of energetic oxygen sources (e.g. plasma or ozone). This is somewhat surprising given the close chemical relationship of aluminum to gallium. For example, trimethylaluminum is an incredibly well-behaved ALD precursor combined with a variety of oxygen sources, trimethylgallium requires the energetic reagent ozone as an ALD partner. We have synthesized a variety of gallium precursors that span the potential chemical space for gallium, e.g. 4, 5, and 6-coordinate complexes, alkyl, amide, and other ligands, etc. and conducted in depth mechanistic analyses of the potential ALD chemistry.

In this talk we discuss the effect of ligand coordination number, identity (N vs C, etc), and ALD partner reagent on nucleation and growth of gallium oxides. This includes QCM measurements under ALD conditions, solution model reactions, and synchrotron studies conducted at the Advanced Photon Source (APS) located at Argonne National Laboratory. The surface reaction of Ga precursors and half-reaction with oxygen sources were also observed by X-ray absorption spectroscopy (XAS). We have found that nucleation of GaOx growth can be achieved on a variety of substrates, however sustained growth of Ga_2O_3 requires forcing conditions for some precursors. The results of these studies were applied to improved gallium oxide processes, including doping strategies. Film characterization will also be discussed as time allows.

AF1-MoP-15 Fluorine Doping of Aluminium Oxide Through In-situ Precursor Synthesis: Theory, Design and Application.*, Ben Peek,* University of Liverpool, UK

Fluorine doped metal oxides are technologically important as conducting thin films, for applications in photovoltaics, flat panel displays, mem resistive devices and power semiconductors. Conventional precursor sources for F-doping involve the use of harmful or toxic reagents such as hydrofluoric acid. Use of these precursors presents challenges in terms of handling and disposal.

Here we report a novel method to synthesise a fluorine precursor, $FAl(CH_3)_2$ in-situ, using mechanisms like those found in atomic layer etching. The method involves a pre-reaction between $Al(CH_3)_3$ and AlF_3 powder to generate the $FAl(CH_3)_2$ immediately before it is injected into the ALD reactor chamber. The intermediate fluorine product has been isolated and analysed using ^{19}F NMR. The effects of key process parameters, including the $Al(CH_3)_3$ dosing and AlF_3 powder bed temperature have been assessed and optimised. The design and fabrication of a system to generate the precursor is presented.

We demonstrate how the precursor has been exploited for the fluorine-doping of aluminium oxide grown by atomic layer deposition. The F-doped Al_2O_3 films have been characterised using low energy ion scattering as a probe of the surface and through-thickness distribution of fluorine in the doped films. This approach is used to elucidate the incorporation mechanisms and the composition of deposited materials.

This in-situ precursor generation technique, potentially opens new routes to doping of a wider range of ALD thin film materials. The full potential of the approach is discussed and other doped systems are considered.

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