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 ^{o}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 ^{o}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 ($Al^{3+} \leftrightarrow Al^0 E° = -1.676$ 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.

[2] M. Hafeez, L. Gan, A. S. Bhatti, T. Zhai, Mater. *Chem. Front.* 1 (**2017**) 1917.

[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°C. The SiN film properties including refractive indices, compositions and wet etch rates were determined. These results will be discussed in the presentation.

ALD Fundamentals
Room 107-109 - Session AF2-MoA

Mechanism and Surface Science

Moderators: Charles H. Winter, Wayne State University, Sang Woon Lee, Ajou University

4:00pm **AF2-MoA-11 Different Growth Mechanism of SiO_2 Layer on Various High-*k* films by PE-ALD using Tris(dimethylamino)silane and Oxygen Plasma**, ***Toshihide Nabatame***, *M Inoue,* National Institute for Materials Science, Japan*; M Takahashi, K Ito,* Osaka University, Japan*; N Ikeda, A Ohi,* National Institute for Materials Science, Japan

GaN power devices with metal-oxide-semiconductor (MOS) structure have been widely investigated to suppress the leakage current properties. Various silicate materials such as $HfSiO_x$ and $AlSiO_x$ have been characterized as gate insulator. To fabricate silicate films, a HfO_2/SiO_2 laminate was generally deposited by atomic layer deposition (ALD). The SiO_2 films grown by ALD using Tris(dimethylamino)silane (TDMAS) precursor and ozone oxidant gas had high-quality as gate insulator [1]. However, the growth mechanisms of the SiO_2 film on various High-*k* materials have not been fully understood. In this study, we systematically investigate growth rate of SiO_2 layer on various High-*k* layer by plasma-enhanced ALD (PE-ALD) using TDMAS precursor and oxygen plasma gas, and also discuss about different growth rate.

The SiO_2 films were deposited on SiO_2, HfO_2, Al_2O_3, and TiO_2 films/Si substrates by PE-ALD at 300 degree C. The HfO_2/SiO_2 laminate films were also grown by PE-ALD at 300 degree C with Tetrakis(dimethylamino)hafnium and TDMAS precursors. The various composition ratios (Hf/Si = 3/1, 2/1, 1/1, 1/2, and 1/3) of the HfO_2/SiO_2 laminate films were prepared by changing each number of ALD cycle.

The growth per cycle (GPC) of the HfO_2 and SiO_2 films on SiO_2/Si substrates were found to be 0.083 and 0.038 nm/cycle, respectively, from the relationship between the number of ALD cycles and the film thickness. On the other hand, the experimental data of the HfO_2/SiO_2 laminate thickness as a function of the number of ALD cycle satisfied a linear relationship regardless of Hf/Si composition ratio. The GPC was 0.082 nm/cycle. Considering to the GPC of the HfO_2 (0.083 nm/cycle), the estimated GPC of a SiO_2 layer was 0.081 nm/cycle, which was unexpected, but increased by about 2 times compared to a single SiO_2 film. To recognize the different GPC of the SiO_2 layer between HfO_2/SiO_2 laminate and a single SiO_2 films, the GPCs of the SiO_2 films on SiO_2/Si and HfO_2/Si substrates were examined up to 10 cycles. Noted that the GPC of the SiO_2 films on HfO_2/Si substrate was much higher than that on SiO_2/Si substrate. Furthermore, the Hf content of HfO_2/SiO_2 laminate film with Hf/Si=1/3 shifted to the Hf rich side from the relationship between the designed Hf/Si composition ratio and the estimated Hf/Si ratio of the deposited film using TEM and EDS analysis. These suggest that an initial adsorption of TDMAS precursor on the surface of SiO_2 and HfO_2 films must be different and strongly affects to the GPC.

Reference

[1] L. Han, and Z. Chen, ECS J. of Solid Sate Sci. and Technol., 2 N228 (2013).

4:15pm **AF2-MoA-12 In-situ Surface Science Studies of Atomic Layer Processes of GaN Surfaces in Preparation for Atomic Layer Epitaxial Growth**, ***Samantha Rosenberg***, U.S. Naval Research Laboratory*; D Pennachio,* UCSB*; M Munger,* SUNY College at Brockport*; C Wagenbach,* Boston University*; V Anderson,* Kennesaw State University*; S Johnson, N Nepal, A Kozen, J Woodward,* U.S. Naval Research Laboratory*; Z Robinson,* SUNY College at Brockport*; J Hite,* U.S. Naval Research Laboratory*; K Ludwig,* Boston University*; C Palmstrøm,* UCSB*; C Eddy, Jr.,* U.S. Naval Research Laboratory

We have previously shown that using our low temperature plasma-assisted atomic layer epitaxy (ALEp) method we can grow AlN and InN for various applications.[1-3] The materials we have grown using our ALEp method have shown good crystalline quality, but suffer from an incorporation of carbon. Theory has led us to believe that the substrate preparation plays a significant role in the remediation of carbon, as that surface becomes the interface for the growth of the III-N film. Therefore, using surface science techniques, we strive to develop not only a fundamental understanding of the ALEp growth process but also atomic layer processes that will result the best cleaning method for a pristine starting surface for ALEp.

Here we employ *in-situ* surface studies of *in-situ* and *ex-situ* GaN substrate preparation and InN ALEp growth to advance fundamental understanding of the ALEp process. We conduct *in-situ* grazing incidence small angle x-ray scattering (GISAXS) experiments at the Cornell High Energy Synchrotron

Source utilizing morphological evolution monitoring to investigate the growth surface during sample preparation, a gallium-flash-off atomic layer process (ALP) at varying temperatures, and film deposition. GISAXS information is complemented with *in-vacuo* x-ray photoelectron spectroscopy, reflection high-energy electron diffraction, and *ex-situ* atomic force microscopy studies conducted at the Palmstrøm Lab at UCSB, where we consider different *ex-situ* sample preparation methods in contrast to our standard preparation method as a way to produce the most suitable GaN surface for our ALP/ALEp-based approach. We have been able to determine with GISAXS that ALP-based gallium-flash-off experiments performed at higher temperatures (500°C) produce a smoother starting surface than lower temperatures. Additionally we have determined that we should only perform ~10 cycles instead of 30 as was empirically chosen previously. We have also been able to observe repeating cycles in our ALEp process with GISAXS, leading us to insights on the underlying chemical process of the gallium-flash-off ALP. With the Palmstrøm Lab at UCSB, we have determined with *in-vacuo* XPS and *ex*-situ AFM that a combination of UV/ozone exposure followed by an HF dip produces the cleanest and smoothest GaN surface. Combining these two results, *ex-situ* and *in-situ* cleaning preparation, should lead us to the best GaN starting surface to grow high quality crystalline III-N materials.

[1] N. Nepal, et al., Appl. Phys. Lett. 103, 082110 (2013)

[2] C. R. Eddy, Jr, et al., J. Vac. Sci. Technol. A 31(5), 058501 (2013)

[3] R. S. Pengelly, et al., IEEE Trans. Microwave Theory Tech. 60, 1764 (2012)

4:30pm **AF2-MoA-13 Surface Chemistry during Atomic Layer Deposition of Zn(O,S)**, ***Bonggeun Shong***, Hongik University, Republic of Korea

Ternary compound zinc oxysulfide (Zn(O,S)) is a semiconductor whose band gap is tunable with the composition. Thin films of Zn(O,S) can be deposited with atomic layer deposition (ALD) using diethylzinc ($Zn(C_2H_5)_2$) and mixed pulses of H_2O and H_2S as O and S sources, with an advantage of tunable O to S atomic ratio. However, it is known that the fraction of S incorporated in the ALD Zn(O,S) thin films is higher than its ratio in the reactant pulses [1]. Recently, the reason for such growth behavior has been suggested as exchange reactions between *ZnOH and H_2S to yield *ZnSH at the surface of the growing film [2]. In this work, the surface chemical reactions involved in ALD of Zn(O,S) is investigated using density functional theory (DFT) calculations. It is observed that while ALD reactions of both ZnO and ZnS would be facile, the reactions involving H_2S are both kinetically and thermodynamically favored over those with H_2O. As a result, surface *ZnOH can be replaced by H_2S, but reaction of *ZnSH with H_2O is less likely. Our results confirm the chemical mechanism governing the composition of ALD Zn(O,S), and suggest factors needs to be considered in ALD of ternary compounds.

[1] Bakke et al., JVSTA 2012

[2] Lancaster et al., JPCC 2017

4:45pm **AF2-MoA-14 Surface Reaction Mechanism of Atomic Layer Deposited Metal on Organic Textiles**, ***Jong Seo Park,*** Yonsei University, Republic of Korea; *H Lee,* Incheon National University, Republic of Korea

Electronic textiles (e-textiles) are electrically conductive textiles which are potentially important for future wearable electronic systems. Recently, we reported that atomic layer deposition (ALD) could be a good route to functionalize conventional non-conductive textiles to conductive textiles just by depositing Pt on Cotton without any damage. In this work, we deposited Pt via ALD on various thermally weak textiles, such as Cotton, Silk, Nomex, Nylon, Wool and Kevlar fibers. Pt was successfully deposited on Cotton, Silk, Nomex, Wool, Kevlar fibers except Nylon fibers. We investigated the growth characteristics and surface reactions mechanism of ALD Pt on various textiles by using different techniques, such as X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and density functional theory (DFT) calculation. Pt ALD on the various textiles seems to be hard since it has rare reactive sites of ALD reaction such as surface hydroxyl group. From results of XPS and DFT calculation, it was found that Pt precursor molecules directly react with chemical species of the reactive sites of Cotton and Silk fibers, while Nylon fibers did not react with Pt precursor molecules. The activation energies for the reactions of the Pt precursor with cellulose of Cotton (26.3 kcal/mol for –OH) or Silk fibroin (19.5 kcal/mol for –OH, 26.1 kcal/mol for –NH) are smaller compared to that with Nylon 66 (36.9 kcal/mol). Therefore, the reactivity of Nylon toward adsorption of HDMP is considerably smaller than those of Cotton and Silk. Thus, we found that ALD Pt layer forms with very high durability on surface of Cotton and Silk fibers through organic-inorganic hybridization. We believe that the functionalized flexible textiles which were obtained by Pt ALD are promising candidates for various wearable and smart fabric industries as a new platform for future textile electronics.

5:00pm **AF2-MoA-15 Insight in Surface Dependence and Diffusion-mediated Nucleation Mechanism of Ruthenium Atomic Layer Deposition on Dielectrics**, ***Job Soethoudt,*** KU Leuven, Belgium; *Y Tomczak,* IMEC, Belgium; *F Grillo, R Van Ommen,* Delft University of Technology, Netherlands; *E Altamirano Sanchez,* IMEC, Belgium; *A Delabie,* KU Leuven, Belgium

Area -Selective Deposition (ASD) is of interest for a variety of applications including bottom-up patterning for nano-electronic device fabrication, yet its industrial implementation has been limited by unwanted nucleation on the non-growth surface. ASD of Ruthenium is of interest for bottom-up patterning, as a thin Ru hardmask is not attacked by etchants typically used to pattern dielectrics or TiN hardmasks (eg. C_xF_y, NF_3, BCl_3). In order to control and reduce defectivity in Ru ASD, the surface dependence and nucleation mechanisms of Ru Atomic Layer Deposition (ALD) need to be understood.

We have investigated the nucleation mechanism of (ethylbenzyl)(1-ethyl-1,4-cyclohexadienyl)ruthenium (EBECHRu) and O_2 ALD at 325ºC on different dielectric surfaces. The Ru nucleation behaviour is strongly affected by the dielectric surface, and is governed by adsorption, diffusive aggregation and coalescence. Precursor chemisorption proceeds most rapidly on -OH terminated dielectrics, followed by Si-O-Si bridges and finally Si-CH_3 terminated organosilicate glass (Figure 1). On hydrophilic and hydrophobic SiO_2 the average nucleus is significantly larger compared to values predicted from the inherent deposition rate on existing Ru nuclei (0.03nm/cycle), indicating Ru species aggregate through surface diffusion during nucleation resulting in an island growth mode (Figure 2a, b, c). Less reactive surfaces not only result in fewer, larger nuclei because of the reduced adsorption rate on the substrate, but the nucleus size distribution also becomes more polydisperse because surface diffusion promotes aggregation (Figure 2d). The nucleation behaviour on organosilicate glass is explained through a growth model [1, 2] which takes into account the impact of diffusive aggregation on the nucleus size distribution (Figure 3). The experimental results are best described if the Ru precursor adsorption initially occurs only on the organosilicate glass substrate, and the Ru nuclei are active towards precursor chemisorption only after reaching a critical size (~0.85 nm). This result is consistent with the notion that catalytic decomposition of the ligands by oxygen requires a minimum Ru island size. The initial stages of growth are therefore dominated by the diffusive aggregation of Ru nuclei rather than direct Ru growth on the islands. These findings provide new fundamental insight in the nucleation mechanism of Ru ALD. Moreover, the impact of surface diffusion may be relevant for ASD as surface diffusion could mitigate defectivity caused by nucleation on dielectrics.

[1] F. Grillo et al., J. Phys. Chem. Lett. 8, 975-983 (2017).

[2] F. Grillo et al., Catal. Today (2018)

5:15pm **AF2-MoA-16 Surface Oxidation Model in Plasma-enhanced ALD for Silicon Oxide Films Including Various Aminosilane Precursors**, ***Kosuke Yamamoto***, *A Suzuki, M Kagaya, M Matsukuma, T Moriya,* Tokyo Electron Technology Solutions Ltd., Japan

Plasma-enhanced atomic layer deposition (PEALD) attracts much attention for semiconductor manufacturing processes because it permits both low process temperature and high film uniformity. Deposition of silicon oxide (SiOx) films is one of the most successful applications in PEALD. The conformal, uniform and low-temperature deposition of PEALD-SiOx thus enables self-aligned multiple patterning in high volume manufacturing. Based on this technical and industrial significance, many research groups have already discussed surface reaction mechanisms of PEALD-SiOx deposited by using aminosilanes and O_2 plasma. However, previous researches mainly focused on the adsorption step of the silicon precursors and there are fewer studies published on the oxidation step. In this work, we therefore aim to clarify the surface oxidation mechanism of PEALD-SiOx processes by employing both experimental and computational approaches.

Firstly, we calculated the main chemical species present in an Ar/O_2 plasma by using numerical simulation in order to narrow down the potential reactions between oxidants and surface functional groups. We determined that triplet oxygen atom (^3O) and singlet oxygen molecule ($^1O_2$) are expected to be the main oxidants under our experimental condition. To compare the energy barriers for the specified reactions with ^3O and $^1O_2$, we analyzed oxidation pathways by using density functional theory (DFT)

calculations, as shown in Figure 1. No energy barrier was observed in the ^3O oxidation pathway in contrast with $^1O_2$ oxidation, which has an energy barrier of 0.1~0.6 eV. These computational results support the conclusion that surface oxidation is dominated by ^3O; in view of both the generation of oxidizing species and the energy barrier for oxidation. Subsequently, PEALD experiments were systematically examined with various aminosilanes, substrate temperatures (T_{subs}) and oxidation times, as shown in Figure 2. We found that the number of amino ligands (R) on the precursors affected saturation trends with oxidation time. Moreover, a more rapid increase was observed with increasing substrate temperature for SiH_3R precursors compared to the results for precursors which have more amino ligands. We have thus developed a surface oxidation model for explaining these experimental results considering just two reactions: Si-H bond oxidation and Si-R bond oxidation. Even with this simple reaction model, the differences in surface oxidation trends can be explained simply by considering the ratio of surface densities of Si-H and Si-R groups before the oxidation step.

5:30pm **AF2-MoA-17 Thermal and Plasma Enhanced Atomic Layer Deposition of Al_2O_3 and HfO_2 Films Investigated by using in situ Auger Electron Spectroscopy***, **Haiping Zhou**, Y Fu, M Mirza, X Li,* University of Glasgow, UK

Al_2O_3 and HfO_2 are well-established high-k materials to replace SiO_2 in transistor and capacitor applications. To grow high quality atomic layer deposition (ALD) films with high dielectric breakdown electric field and low leakage current, it is important to understand the impact of both plasma enhanced ALD (PEALD) using O_2-plasma and thermal ALD using H_2O on the interface between ALD film and substrate surface, and also the impact of the interface on the quality of ALD films.

We have studied the influence of both thermal and PEALD processes on the electrical properties of Al_2O_3 and HfO_2 films, and found that both the Al_2O_3 and HfO_2 films grown by the PEALD with O_2-plasma have higher dielectric breakdown electric fields and lower leakage currents than that grown by the thermal ALD with H_2O.

To further understand and optimize the ALD processes, we have used in situ Auger electron spectroscopy (AES) and high-resolution scanning Auger microscope (SAM) of a NanoSAM system, which is vacuum connected with an ALD chamber, to investigate the surface chemical compositions and distributions in the interface between the ALD Al_2O_3 and HfO_2 films and Si, Au and Ti substrate surfaces without exposing the ALD films to air. We have found (a) for the Al_2O_3 films grown with H_2O, the AES spectra show significant peaks of Al and O, but slight peak of C, which means the Al_2O_3 film deposited on Si, Au and Ti surfaces, but some C impurities remained unreacted in the film; (b) for the HfO_2 films grown with H_2O, the AES spectra show significant peaks of C and O, but very slight peak of Hf, which suggests that HfO_2 film hardly deposited on Si, Au and Ti surfaces, but many C impurities remained unreacted in the film; (c) for both Al_2O_3 and HfO_2 films grown with O_2-plasma, the AES spectra show significant peaks of Al and O, and Hf and O, respectively, but no peak of C is observed within the detecting limit of the NanoSAM. This indicates the Al_2O_3 and HfO_2 films deposited on Si, Au and Ti surfaces, high purity and free of carbon contamination from unreacted ligands when deposited at the optimized PEALD processes conditions.

The AES investigations of Al_2O_3 and HfO_2 films are well in agreement with the studies on their electrical properties, and again confirm the superior qualities of the PEALD Al_2O_3 and HfO_2 over the thermal ALD Al_2O_3 and HfO_2.

ALD Fundamentals
Room 116-118 - Session AF1-TuM
Precursor and Process II

Moderators: Mikko Ritala, University of Helsinki, Wonyong Koh, UP Chemical Co., Ltd.

8:00am **AF1-TuM-1 Atomic Layer Deposition of Yttrium Oxide from Bis(Methylcyclopentadienyl) (MethylPentyl Pyrazolato) Yttrium (III)***, Jun Feng, G Liu, M Fang, C Dezelah, J Woodruff, R Kanjolia,* EMD Performance Materials

Yttrium Oxide (Y_2O_3) is a promising dielectric material due to its relatively wide band gap (~5.5 eV), high permittivity (>10), and high thermal stability. As semiconductor fabrication processes move toward high-aspect-ratio structures, highly conformal deposition methods for Y_2O_3 are required. Herein, we report the atomic layer deposition (ALD) of Y_2O_3 thin films based on a newly developed liquid precursor, Bis(Methylcyclopentadienyl) (MethylPentyl Pyrazolato) Yttrium (III), with ozone or water as co-reactants. The ozone process was tested in the range of 150 - 250°C. The best uniformity and lowest thermal decomposition are achieved at 180 - 225°C substrate temperature window, where the saturated growth rate is ~0.5 Å/cycle and refractive index is 1.69. Using H_2O as the co-reactant tested in the range of 125 - 250°C, the optimum growth window is 135 - 180°C, with a growth rate of 0.5 - 0.6 Å/cycle and refractive index of 1.73. However, due to the reactivity between Y_2O_3 and water to form hydroxides, higher purging gas flow and extra-long purging time are required to obtain dense Y_2O_3 films. For the films deposited under different conditions, we performed XPS study for compositional information, as well as AFM study for surface morphology and roughness. Our Y_2O_3 ALD processes offer the material fundamentals to enable future high-performance electronic devices, especially those with three-dimensional frameworks that require dielectric coatings in high-aspect-ratio structures.

8:15am **AF1-TuM-2 Low-temperature Thermal ALD of SiO_2 – Increasing the Possibilities***, M Mäntymäki, J Kalliomäki, T Sarnet,* Picosun Oy*; T Pilvi,* Picosun Oy, Finland*; Q Demarly,* Air Liquide Electronics*; N Blasco,* Air Liquide Advanced Materials*; **Juhana Kostamo**,* Picosun Oy, Finland

Silicon dioxide has great chemical and electrical properties that have made it the sought-after solution in many applications. In addition to the classic microelectronics applications due to its dielectric properties, SiO_2 can also be used to tailor the mechanical properties of films or prevent gas diffusion to protect various materials.

In ALD, SiO_2 has been made by many different processes. The main issues with most of the chemistries, such as the chlorides or chlorosilanes has been the relatively high deposition temperatures (>300°C). Low deposition temperatures are important for both sensitive substrates and to prevent interlayer diffusion at interfaces. In addition, chloride precursors can create particles and chloride impurities in the films. These are unacceptable in many applications. Therefore, the amine precursors have become more popular.

In general, low deposition temperatures have been achieved with the assistance of plasma processing [1]. This is not advantageous, as thermal processing would enable throughputs that are an order of magnitude larger. Moreover, plasma processing gives limitations to aspect ratios of the substrates, as radical lifetimes are limited.

Furthermore, achieving industrially feasible growth rates at low temperatures with thermal processes has been a challenge. For example, with a commonly used process such as bis(diethylamino)silane and ozone, the growth rate at 100°C is only < 0.1Å per cycle [2].

We present a chemistry for reliably depositing SiO_2 at temperatures below 100°C with growth rates in excess of 1Å per cycle. At 100°C, the growth rate has been shown to be 1.4Å per cycle (Figure 1).

The experiments were made with a PICOSUN™ R-200 Advanced hot-wall ALD system, equipped with a Picohot300™ source for low vapor pressure precursors. 200mm Si wafers with native oxide layers were used as substrates. Properties such as growth rates, morphology, crystallinity, refractive index, composition, breakdown field strength and leakage current were studied to evaluate the process and the resulting thin films.

Figure 1: SiO_2 thickness series at 100°C. Nucleation delay of 21 cycles. Refractive index fixed at 1.457.

[1] Won et al., *IEEE Electron Device Lett.***31** 2010

[2] Hirvikorpi et al., *Appl. Surf. Sci.***257** 2010

8:30am **AF1-TuM-3 Non-pyrophoric Aluminum Precursor for Thermal Atomic Layer Deposition of Al_2O_3 Thin Films***, **Jungwun Hwang**, K Mun, J Seok, J Park,* Hansol Chemical, Republic of Korea

Al_2O_3 thin films are used for encapsulation layers of displays, passivation layers in solar cells, and gate dielectrics of microelectronics device such as dynamic random access memory (DRAM) and metal-oxide-semiconductor field-effect transistor (MOSFET). Trimethylaluminum (TMA) is a conventional precursor for atomic layer deposition (ALD) of Al_2O_3 because of its excellent step coverage and thickness control.

However, pyrophoric nature of TMA causes safety and handling issues, which has led to active research concerning an alternative to TMA.

In this research, a non-pyrophoric aluminum precursor was designed and characterized in thermal ALD of Al_2O_3 thin films as follows. First, evaporation of the new precursor was found to occur in a single step with low residue (< 1%) at 300°C. Second, comparisons of ALD of the Al_2O_3 thin films from the new precursor and TMA were made using H_2O or O_3 as an oxidant. Self-limiting reaction, growth rates, and growth linearity were investigated. Wide ALD windows of the precursor ranging from 130 to 320°C and from 200 to 300°C were shown using H_2O and O_3, respectively. Finally, properties of the Al_2O_3 films from both the new precursor and TMA were analyzed via XPS, XRR, and TEM. The analysis results confirmed stoichiometric composition of the Al_2O_3 thin films with no appreciable carbon incorporation as well as comparable density and excellent step coverage from both the new precursor and TMA.

8:45am **AF1-TuM-4 Study on ALD Carbide Chemistry Approach for Rhenium***, **Jani Hämäläinen**, K Mizohata, K Meinander, P King, M Heikkilä, L Khriachtchev, J Räisänen, M Ritala, M Leskelä,* University of Helsinki, Finland

Rhenium is both a noble metal and a refractory metal. Noble metals have substantial resistance to corrosion and oxidation, and thus are known for their inertness. On the other hand, refractory metals are typified by extremely high melt temperatures and high wear resistance. Rhenium is well known for its reluctance to form carbides, and therefore high pressures and high temperatures are distinctively required for synthesis of stoichiometric rhenium carbides. With that in mind we here examine such ALD chemistry that with other metals typically has resulted in carbide like films.

ALD of metal carbides has not been extensively studied and thus the selection of carbide materials and processes is quite limited. One of the most widely used approaches is to combine a metal halide with trimethyl aluminum (TMA) as recently exemplified by Blakeney and Winter [1]. In the same way, we use in our study $ReCl_5$, which has already been reported for ReS_2, ReN_x, and Re [2, 3], and TMA as a carbon source to deposit thin films at temperatures up to 300°C. The films were successfully grown on 5 x 5 cm^2 native oxide covered silicon (100) substrates in an ASM Microchemistry F-120 ST ALD reactor. The deposited films consisted of up to 70 at.% of carbon while the carbon to metal ratios were up to 4.3 as analyzed by TOF-ERDA. These values are among the highest carbon contents ever reported for thermal ALD. TOF-ERDA, XPS, Raman, EDX, and XRD techniques are used to examine the phase content and composition of these carbon-rich films.

[1] K. J. Blakeney and C. H. Winter, *J. Vac. Sci. Technol. A* 36 (**2018**) 01A104.

[2] 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] J. Hämäläinen, M. Mattinen, M. Vehkamäki, K. Mizohata, K. Meinander, J. Räisänen, M. Ritala, and M. Leskelä, ALD 2017, Denver, USA, talk.

9:00am **AF1-TuM-5 Development of Advanced Precursors for Deposition of Cobalt Films***, A Cooper, **Sergei Ivanov**,* Versum Materials*; S Lee, M Kim,* Versum Materials Korea, Republic of Korea*; A Derecskei-Kovacs,* Versum Materials

Copper encapsulation with thin cobalt films has been shown to greatly improve electromigration performance of Cu interconnects[1]. Further shrinkage of electronic devices brings new challenges for more selective deposition of Co films and more controlled atomic layer deposition (ALD) of thin Co films. One of the most common precursors used for deposition of pure cobalt films, tert-butylacetylene dicobalt hexacarbonyl (CCTBA), suffers from low thermal stability and low vapor pressure. Low-temperature thermal ALD of cobalt oxide films was demonstrated using CCTBA at 68°C but above 80°C saturation is limited by thermal

decomposition of CCTBA[2]. Relatively pure cobalt films can also be deposited at 150-170ºC by thermal CVD, but further increase in deposition temperature results in carbon contamination due to precursor thermal decomposition. The goal of this study was to identify a more thermally stable cobalt precursor for deposition of pure cobalt films with improved step coverage on patterned substrates.

In this study, Density Functional Theory (DFT) at the BLYP/DNP level was employed to calculate ligand dissociation energies from a series of cobalt acetylene complexes with various substituents on the acetylene ligand. The ligand dissociation energy in general decreased with an increase of the steric bulk of the acetylene ligand. Significant differences in thermal stability and carbon content in the cobalt films were observed depending on the type of substituent on the acetylene ligand. Liquid precursor, CCTNBA, was identified and showed improved thermal stability compare to CCTBA based on DSC and TGA analyses. Thermal CCVD and ALD processes were studied on various substrates. Step coverage of >80 % was demonstrated on patterned substrates. The effect of process conditions on step coverage and cobalt films properties will be presented.

1. Emiko Nakazawa, *et al.,* Advanced Metallization Conference (AMC) 2008, p.19-23, Materials Research Society (2009).

2. Byeol Han, et al., Electrochemical and Solid State Letters, 2012, 15 (2), D14-D1

9:15am **AF1-TuM-6 Diamine Adduct of Cobalt(II) Chloride for ALD of Stoichiometric Cobalt(II) Oxide and Reduction Thereof to Cobalt Metal Thin Films***, **Katja Väyrynen**, T Hatanpää, M Mattinen, M Heikkilä, K Mizohata, K Meinander, J Räisänen, M Ritala, M Leskelä,* University of Helsinki, Finland

Thin films of cobalt and its compounds can be utilized in a myriad of applications ranging from microelectronics to emerging energy technologies as well as catalysis and gas sensing [1–3]. For these materials to be adapted in future applications, accurate deposition methods, such as ALD, are required. The development of ALD processes for Co, CoO_x, CoN_x, or $CoSi_2$ has, however, been hindered by the lack of suitable precursors. There is a pressing need for new cobalt precursors that are volatile and thermally stable yet easy to reduce or oxidize depending on the desired material. The precursors should also be inexpensive and easy to synthesize to be applicable on an industrial scale.

In this work, we present a promising new precursor for the ALD of cobalt-based materials. $CoCl_2$(TMEDA) (TMEDA = N,N,N',N'-tetramethylethylenediamine) is a diamine adduct of cobalt(II) chloride that is extremely easy to synthesize with a practically quantitative yield, and it exhibits the characteristics of an ideal ALD precursor, also from the industry point of view. Furthermore, by changing the ligands, the same approach can be extended to other transition metals, such as nickel, as well.

Herein, we also describe a full ALD study of cobalt(II) oxide thin films deposited using $CoCl_2$(TMEDA) and water at 225–300°C. A saturated growth rate of 0.38 Å/cycle was measured at 275°C. $CoCl_2$(TMEDA) is reactive towards water, whereas most other Co precursors require ligand combustion by ozone or oxygen plasma that inevitably results in the formation of Co_3O_4 instead of CoO [4]. The films deposited using $CoCl_2$(TMEDA) were highly crystalline with a mixture of both hexagonal and cubic phases of CoO. The hexagonal phase is specific to nanomaterials only and is not seen in bulk CoO [5]. A 50 nm film deposited at 275°C exhibited 1:1 Co:O stoichiometry and very low impurity levels below 1.0 at.%.

$CoCl_2$(TMEDA) is a potential candidate also for the ALD of Co metal, provided that it is combined with a suitable reducing agent. In this work, Co metal films were prepared indirectly via reduction of the deposited CoO films. The reduction studies were carried out at an exceptionally low temperature of 250°C in forming gas using TiN substrates. The Co content of the reduced films was as high as 95 at.%, with the rest being oxygen and hydrogen.

[1] M. Lapedus. Interconnect Challenges Grow. In *Semiconductor Engineering*, 2015; http://semiengineering.com/interconnectchallenges-grow-2/.

[2] Y. Shao-Horn et al., *Nat. Mater*. **2003**, *2*, 464.

[3] J. Gerken et al., *J. Am. Chem. Soc.* **2011**, *133*, 14431.

[4] J. Kim et al., *Chem. Mater.* **2017**, *29*, 5796.

[5] W. Seo et al., *J. Am. Chem. Soc.* **2005**, *127*, 6188.

9:30am **AF1-TuM-7 Development New Metal Precursors for Atomic Layer Deposition at KRICT***, G Lee, S Han, E Jung, C Kim, B Park,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea*; J Han,* Seoul National University of Science and Technology, Republic of Korea*; **Taek-Mo Chung**,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea **INVITED**

We have deeply concentrated our passions to develop a wide variety of new metal precursors for atomic layer deposition (ALD) and chemical vapor deposition (CVD) for a few decades. To synthesize the desired metal precursors, we did our best efforts with the synthetic strategy for the design of organic ligands on the molecular level. From the research works, various new aminoalkoxide type organic ligands such as 1-(dimethylamino)-2-methyl-2-propanol (dmampH), 1-(dimethylamino)-2-methyl-2-butanol (dmambH), and 1-[2-(dimethylamino)ethyl](methyl)amino}-2-methylpropan-2-ol (demampH) have been prepared. With these organic ligands, a lot of novel precursors which exhibit high volatility and thermal stability and are suitable to be applied to thin films deposition by ALD have been successfully developed by the general synthetic methods. They are copper precursors for CuO and Cu_2O, nickel complexes for NiO, and strontium compounds for strontium titanium oxide (STO). Moreover, new metal precursors such as tin, indium, and gallium complexes have been recently developed for transparent conducting oxides (TCO) and applied to deposit their oxide thin films by ALD and CVD. In this talk, we will discuss development and application of metal precursors for ALD at KRICT.

ALD Fundamentals
Room 116-118 - Session AF2-TuM
Mechanism and Surface Science

Moderators: Simon D. Elliott, Schrödinger, Won Seok Yoo, Samsung Electronics

10:45am **AF2-TuM-12 Surface Chemistry during Atomic Layer Deposition of Nickel Sulfide***, **Ran Zhao**,* Peking University, China

Atomic layer deposition (ALD) of metal sulfides has been recently developing very rapidly, and many new metal-sulfide ALD processes have been reported over the past several years. However, the surface chemistry in many sulfide processes remains still yet to be investigated. Our group recently developed a new ALD process of nickel sulfide (NiS) using bis(*N,N'*-di-*tert*-butylacetamidinato)nickel(II) ($Ni(amd)_2$) as the nickel precursor and H_2S gas as the sulfur source (*Chem. Mater.***2016**, *28*, 1155). This process was found to follow a typical layer-by-layer ALD growth mode and was able to produce smooth, pure, and conformal NiS films. However, the film growth rate was relatively low (~0.015 nm/cycle), and therefore the associated surface chemistry deserves further investigation.

In this presentation, we will show our recent mechanism study on the surface chemistry of the ALD of NiS from $Ni(amd)_2$ and H_2S, using combined in-situ techniques of X-ray photoelectron spectroscopy (XPS), low-energy ion scattering (LEIS), quartz crystal microbalance (QCM), and quadrupole mass spectrometry (QMS). The surface chemistry was found to deviate from the conventional ligand-exchange scheme, as the amidinate surface moiety from $Ni(amd)_2$ was not released during the H_2S half-cycle. Further analysis with control experiments revealed that a non-volatile acid-base complex between the acidic surface sulfhydryl and the basic amidine was formed on surface during ALD. Since the precursors used herein are fairly representative for ALD of metal sulfides, the findings should be of important reference for many other sulfide ALD processes.

11:00am **AF2-TuM-13 Exchange Reactions during Atomic Layer Deposition: ZnO Conversion to Al_2O_3 by Trimethylaluminum***, T Myers, A Cano, J Clancey, D Lancaster, **Steven M. George**,* University of Colorado - Boulder

Atomic layer deposition (ALD) is typically described by the self-limiting reaction of precursors with surface species that leads to controlled thin film growth. Missing from this picture is the possibility that the precursors can also undergo exchange reactions and convert the surface of the initial substrate to a new material. These exchange reactions are expected if the conversion produces a more thermodynamically favorable reaction product. These exchange reactions may be common during ALD nucleation.

In this study, the exchange between Zn and Al is explored during the initial reaction of trimethylaluminum (TMA) on ZnO films during Al_2O_3 ALD at temperatures from 100-225°C. The exchange is evident from a variety of experimental measurements. Fourier transform infrared (FTIR) investigations detect absorbance changes consistent with ZnO loss and

Al_2O_3 gain after the TMA reaction on ZnO ALD films. Quadrupole mass spectrometry (QMS) measurements also observe $Zn(CH_3)_2$ reaction products as expected from the conversion reaction: $3ZnO + 2Al(CH_3)_3 \rightarrow Al_2O_3 + 3Zn(CH_3)_2$. In addition, studies of the effect of TMA exposures on ZnO nanoparticles with a diameter of ~10 nm measured the conversion of ZnO to Al_2O_3. The conversion produces a large mass loss that is consistent with the formation of an Al_2O_3 surface layer. The ZnO to Al_2O_3 conversion is also self-limiting as a function of TMA exposure.

X-ray photoelectron spectroscopy (XPS) and X-ray reflectivity (XRR) investigations are also consistent with the conversion of the surface of ZnO ALD films to Al_2O_3 after the initial TMA exposure. The XPS and XRR measurements both yield an Al_2O_3 surface layer with a thickness of ~1.0 nm on the ZnO ALD film. In addition, quartz crystal microbalance (QCM) measurements detect a substantial conversion of ZnO to Al_2O_3 after the initial TMA exposure during Al_2O_3 ALD. The QCM studies reveal that the mass losses are much more pronounced for thin ZnO films compared with thick ZnO films. In addition, the mass losses are more for ZnO surfaces terminated with $Zn\text{-}CH_3CH_3$ species compared with Zn-OH species.

These studies of the exchange between Zn and Al during the initial reaction of TMA on ZnO illustrate that ALD precursors can convert the surface of the initial substrate to a new material. These exchange reactions must be considered when analyzing ALD nucleation.

11:15am **AF2-TuM-14 Elucidation of the Mechanisms of Nickel (II) and Iron (III) Oxide Films Grown with Ozone by Atomic Layer Deposition***, **Joel Schneider**, J Baker, C MacIsaac, S Bent,* Stanford University

Atomic layer deposition (ALD) offers the capability of depositing materials in conformal films, roughly one atomic layer at a time in a controlled fashion. This ability, however, is highly dependent on the self-limiting nature of the constituent surface reactions. With the development of more sophisticated ALD processes such as ternary and quaternary materials that seek to finely tune materials properties, there is an increasing need to understand the mechanisms by which these materials grow. In this study, nickel (II) and iron (III) oxide thin films, two materials of interest in catalysis and microelectronics, were grown by ALD. Despite the prevalence of both processes in the literature, few studies examine their self-limiting behavior and growth mechanism. Here, the mechanisms of ALD were investigated using a combination of characterization techniques.

Nickel oxide and iron oxide thin films were grown from nickelocene and ozone and t-butyl ferrocene and ozone respectively, and films were characterized using variable angle spectroscopic ellipsometry,both *ex situ* angle-resolved and *in vacuo* x-ray photoelectron spectroscopies, x-ray reflectivity, and atomic force microscopy. It was found that significantly higher precursor doses than generally used in literature were required to reach saturation, resulting in higher saturation growth rates than are typical for ideal ALD; moreover, in the deposited films, the near-surface region was observed to have a different density than the bulk. This near-surface region was revealed to contain an accumulation of super-stoichiometric oxygen, and its thickness and oxygen content were found to correlate strongly with the ozone-to-precursor exposure ratio. Results of these studies suggest that oxygen is taken up into the film from ozone and then diffuses out again to react during subsequent metal precursor pulses.

The morphology of the films was also probed via synchrotron-based grazing incidence wide angle x-ray scattering and by scanning electron microscopy. It was found that the incorporation of surface oxygen correlates with degree of texturing in the films, but higher oxygen incorporation disrupts the film crystallinity entirely and mechanically stresses the film. The studies show that both the nickel (II) and iron (III) oxide processes exhibit significant non-idealities in ALD involving oxygen, and that these behaviors lead to changes in the structure and morphology of the film. This understanding illustrates how the growth and morphological properties of these films can be tuned with ozone exposure, and it has implications for both binary ALD and mixed ALD processes.

11:30am **AF2-TuM-15 Reaction Mechanisms of the Atomic Layer Deposition of Indium Oxide Thin Films Using Ethylcyclopentadienyl Indium***, **Fumikazu Mizutani**, S Higashi,* Kojundo Chemical Laboratory Co.,Ltd., Japan*; M Inoue, T Nabatame,* National Institute for Materials Science, Japan

Previously, we reported the development of a new liquid precursor, ethylcyclopentadienyl indium (EtCpIn), for atomic layer deposition (ALD) of high purity indium oxide films, and demonstrated the deposition of high purity indium oxide films using water and plasma oxygen as oxidizing reactants [1]. In this work, reaction mechanisms of the ALD using the EtCpIn were investigated.

As the EtCpIn molecules have the half-sandwich structure, it is considered that the EtCpIn adsorb to substrate by coordinate bonding between indium of EtCpIn and the surface oxygen. Therefore Si wafers with surface oxide films were used to settle the nucleation problem. To deposit high purity films, water and plasma oxygen were exposed in order as oxidizing reactants in the ALD cycles (WpO). For comparative investigation, other oxidizing reactants, water followed by oxygen (WO), plasma oxygen followed by water (pOW), only plasma oxygen (pO), only oxygen (O), and only water (W), were used instead of WpO.

Varying EtCpIn pulse time, thermal stability of EtCpIn was determined. Constant as the growth rates were at 150 degree C and at 200 degree C, the EtCpIn showed decomposition behavior at 250 degree C. Therefore, substrate temperature of 200 degree C was used for this ALD reaction mechanism study, and self-limited reactions were observed for water pulse time and plasma oxygen pulse time of WpO process at 200 degree C.

Linear growth with no nucleation delay was observed for WpO process, and the growth rate was about 0.09 nm/cycle. Since nucleation delay was not observed for all other processes (WO, pOW, pO, O, and W), it is probable that EtCpIn well adsorbs onto surface oxygen. For WO process, linear growth was also observed, and the growth rate was about 0.11 nm/cycle, significantly larger than that of WpO process. These results support the prospected reactions at oxidation step in WpO process; substitution of hydroxyl groups for ethylcyclopentadienyl ligands by water and subsequent sufficient surface oxidation by plasma oxygen. In WO process, the oxygen without plasma activation does not oxidize surface hydroxyl groups, and the remaining hydroxyl groups cause additional adsorption at the EtCpIn adsorbing step. The additional adsorption increases the growth rate of WO process. For the other processes (pOW, pO, O, and W), the growth rates were markedly small due to incomplete reactions in oxidation step.

Reference

[1] F. Mizutani, S. Higashi, and T. Nabatame, “High purity indium oxide films prepared by modified ALD using liquid ethylcyclopentadienyl indium”, 17th International Conference on Atomic Layer Deposition (2017)

11:45am **AF2-TuM-16 Reaction Mechanisms of Halogenated Silanes on N-rich Surfaces during Atomic Layer Deposition of Silicon Nitride***, **Gregory Hartmann**,* University of Texas at Austin*; P Ventzek,* Tokyo Electron America*; T Iwao, K Ishibashi,* Tokyo Electron Technology Solutions Ltd.*; G Hwang,* University of Texas at Austin

Atomic layer deposition (ALD) has recently received increasing attention for the growth of high-conformity silicon nitride (SiN) thin films. In particular, plasma enhanced ALD (PEALD) allows SiN deposition at substantially lower temperatures (< 400 °C) with better film properties, compared to thermal ALD. These advantages make PEALD more attractive for ultra large scale integrated circuit device fabrication where the growth of aspect ratio independent and high-quality conformal thin dielectric films is tremendously important. The PEALD of SiN films involves a two-step cycle: (1) adsorption and decomposition of silicon-containing precursors and (2) nitridation of the Si-rich surface by active N species emanating from the plasma. Halogenated silanes such as hexachlorodisilane, bis(tertiary-butyl-amino)- silane, and dicholorosilane (DCS, SiH_2Cl_2) have been utilized as Si precursors. Despite previous studies, the underlying reaction mechanisms of these Si precursors with a N-rich SiN surface during PEALD remain uncertain. Parameters controlling the rate of growth and uniformity have been demonstrated experimentally, but without knowledge of the reaction mechanisms, direct contributions of specific process conditions cannot be explained. Using first-principles density functional theory (DFT) calculations combined with experimental characterization, we have examined and identified a novel mechanism for the adsorption and decomposition of DCS on a N-rich SiN surface. Our study predicts that the DCS adsorption and dissociation can occur by overcoming a moderate barrier (≈0.3 eV), far lower than the prohibitively large barriers predicted for previously proposed mechanisms. Through a detailed electronic structure analysis of the reaction intermediates, we have also elucidated the principles underlying the reaction mechanism, notably the hypervalent nature of Si which permits the facile reaction of molecularly adsorbed DCS with a primary or secondary amine functional group on the surface, followed by dissociation releasing protons and Cl anions with subsequent HCl formation. We have examined the same mechanism utilizing alternative precursors and the predicted trends are corroborated with the important properties of the system. Understanding these principles allows us to develop guidelines for processing conditions, such as the importance of maintaining the proper surface composition to facilitate Si precursor adsorption and dissociation. Our study provides insight into the SiN ALD

process via chlorosilanes and guidelines to control the deposition for high-quality SiN films and provides a framework for future theoretical studies of surface reactions during ALD.

ALD Fundamentals
Room 116-118 - Session AF1-TuA
Characterization

Moderators: Sean Barry, Carleton University, Canada, HyeongTag Jeon, Hanyang University, Korea

1:30pm **AF1-TuA-1 Studying Metal ALD Processes through X-ray Based in situ Characterization***, J Dendooven,* Ghent University, Belgium*; E Solano,* ALBA Synchrotron Light Source, Spain*; R Ramachandran, M Minjauw,* Ghent University, Belgium*; G Portale,* University of Groningen, Netherlands*; D Hermida-Merino,* ESRF, France*; A Coati,* SOLEIL, France*; **Christophe Detavernier**,* Ghent University, Belgium **INVITED**

Initial nucleation is particularly important during metal ALD. Using three different case studies, we aim to demonstrate that x-ray based characterization techniques such as x-ray fluorescence (XRF), grazing incidence x-ray scattering (GISAXS) and x-ray diffraction (XRD) can offer unique insights in metal ALD processes, offering approaches towards the conformal deposition of metal nanoparticles with carefully controlled loading, size and composition, as required for e.g. applications in catalysis and plasmonics.

A first case study concerns Ag ALD. We recently reported that combining the Ag(fod)(PEt_3) precursor with NH_3 plasma results in a six-fold increase of the steady growth rate (0.24 ± 0.03 nm/cycle) when compared to H_2-plasma as reactant (0.04 ± 0.02 nm/cycle). The film morphology was investigated by electron microscopy and GISAXS, and it was found that films grown with the NH_3-plasma process exhibit a much higher particle areal density and smaller particle sizes on oxide substrates compared to those deposited using the H_2-plasma process (Chem. Mater. 29, 7114 (2017)).

A second case that will be discussed concerns initial nucleation during Pt ALD. The Me_3(MeCp)Pt precursor was combined with different reactants (O_2, O_2 plasma, O_3 and N_2 plasma), and in situ XRF and GISAXS measurements provided detailed information about the evolution of Pt loading, average particle dimensions, and mean center-to-center particle distance during the initial stages of ALD, revealing that the choice of reactant had a significant impact on the nucleation and growth of the Pt nanoparticles. In the case of oxidizing reactants, there was a clear impact of the mobility of Pt surface species on the evolution of island morphology. The particle areal density could be controlled by tailoring the number of ALD cycles using oxygen as reactant, while subsequent growth using the same Pt precursor in combination with nitrogen plasma as reactant allowed for tuning of the particle size at the atomic level (Nat. Comm. 8, 1074 (2017)).

A third case concerns a recently reported ALD-based synthesis of bimetallic Pt-In nanoparticles. First, a Pt/In_2O_3 bilayer is deposited by ALD, where the thickness control inherent to ALD enables an accurate control of the Pt/In composition ratio. After ALD, annealing in H_2 ambient results in a reduction of the In_2O_3 and the controlled agglomeration of the bilayer structure into a film of bimetallic nanoparticles. In situ XRD and GISAXS were used to study the annealing process, and illustrate the accurate phase and size control that is offered by this two-step approach (ACS Nano 10, 8770 (2016)).

2:00pm **AF1-TuA-3 Stresses in ALD Films: Aiming for Zero Stress Thin Films***, R Ritasalo,* Picosun Oy, Finland*; O Ylivaara,* VTT Technical Research Centre of Finland, Finland*; **Tero Pilvi**, T Suni,* Picosun Oy, Finland

When grown films by atomic layer deposition (ALD) both intrinsic and thermal stresses are formed into the film; latter due to the mismatch in the thermal expansion coefficient of the substrate and the grown film. Films under high residual stress may cause problems for further processing, and for device performance and reliability. High residual stress can induce film delamination or buckling; bend released structures or the materials where the films are attached. Especially in microelectromechanical system (MEMS) manufacturing, zero or well-controlled residual stress is desired, as the stress effect is more prominent on released structures. Here, the residual stress measured from most common metal oxides deposited by thermal ALD processes on silicon substrates are presented. The thermal processes have an advantage that those can be scaled up to batch processing to achieve through-put and cost efficiency required for volume production. By varying the process parameters (e.g. temperature, chemicals) we aim for zero stress films or film stacks as well as for comprehensive stress data set to help for example MEMS designers and process integrators choosing proper thin film material, and ALD process chemistry and process conditions.

All films were grown in Picosun™ R-200 advanced reactors using thermal ALD processes. Deposited materials were HfO_2, TiO_2, SiO_2, Al_2O_3 and Ta_2O_5 and combinations of these. The ALD temperature was varied between 150°C and 300°C. The substrates used were 150 mm diameter double side polished silicon wafers, which have been pre-measured for stresses before the ALD. For stress measurement we used TOHO FLX-2320-S wafer curvature measurement tool and the measurements were carried out at room temperature. Deposited film thicknesses were measured with Semilab SE-2000 ellipsometer.

Residual stress data from most common metal oxides are presented. For some of the films there is also comparison for the same film material made with different precursors. In Figure 1 the residual stress data for the HfO_2 film grown at varying temperature is presented. The stress changes from compressive to tensile as the ALD temperature was increased from 150°C to 200°C.

Acknowledgements: This work has been done in the ECSEL Joint Undertaking project InForMed (An integrated pilot line for micro-fabricated medical devices) coordinated by Philips Electronics Netherlands BV.

2:15pm **AF1-TuA-4 High-throughput Screening of Atomic Arrangements of Surface and Interfacial Structures of ALD-deposited Thin Films***, **Orlando Trejo**, N Dasgupta,* University of Michigan

Atomically-precise engineering of surfaces and interfaces is critical for the development of PV technology. To address such atomic-scale engineering challenges, it is necessary to exploit advances in atomic-scale synthesis and characterization techniques by leveraging advances in corresponding theoretical understanding, modeling algorithms, and computational performance. However, there is a lack of software and modeling platforms to enable user-friendly and systematic investigation of surface and interfacial structure/disorder. Therefore, in this work we are developing a computational procedure for high-throughput screening of atomic arrangements of surface and interfacial structures.

Atomic structures of interfaces are typically a few Angstroms thick, not well-defined, multi-phase, non- periodic, and have intermixing of chemical species. Techniques like X-ray absorption near edge structure (XANES) and electron energy less spectroscopy (EELS) are promising to characterize interfacial structure as they capture element-specific geometric and electronic information [1]. However, identifying viable atomic configurations to simulate XANES spectra with density functional theory (DFT) is challenging due to computational time limitations. In my previous work [2,3], no more than 40 atomic arrangements were explored due to computational time limitations.

A statistical screening method for empirical fitting of experimental XANES spectra with simulated spectra is performed by a regression on critical geometric descriptors (e.g. space groups, unit cell parameters, and fractional coordinates). This process narrows down the range of atomic arrangements that produce simulated XANES spectra that resemble the experimental spectra. To determine the fit quality, the coefficient of determination (R2) is calculated between normalized experimental and simulated spectra over a defined X-ray energy range. The atomic arrangements yielding the best-matched XANES spectra are ran in DFT packages in order to determine their relative energetic stability and likelihood of representing the actual surface or interfacial structure.

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2:30pm **AF1-TuA-5 Application of Low Energy Ion Scattering for Characterization of Modern ALD Films of Industrial Relevance***, **Philipp Brüner**, T Grehl,* ION-TOF GmbH, Germany*; G Saheli, Y Uritsky, Y Xu, Y Lei, Y Yang, W Tang,* Applied Materials

ALD has become an essential part of the semiconductor manufacturing process. More and more materials are deposited using this technique, and its application will become even more relevant in the future. It is therefore of high importance to also expand the means of characterization of the films during and after growth, supporting both process development and quality control.

One technique that is well suited for this purpose is Low Energy Ion Scattering (LEIS). Noble gas ions of a few keV are scattered back from the surface; by measuring the energy spectrum of these ions, the composition of the outer atomic layer is determined in a quantitative way. Even more, LEIS determines information about the depth distribution of the elements over the first few nm of the film. In this way, the film can be monitored from nucleation to film closure and beyond. While the surface coverage is measured directly, information of the thickness distribution can be deducted from the tails in the spectrum. The combination of surface coverage and thickness distribution allows determining the growth mode. The minimal continuous thickness can be identified either by looking for the film reaching a coverage of 100%, or by the substrate signal disappearing. Depending on the masses of the elements involved, one of the two approaches is more sensitive. Also diffusion and surface segregation can be studied, and contaminations monitoring is possible.

Due to the ultimate surface sensitivity, the focus of LEIS studies is usually the nucleation phase, from the first cycle to formation of a closed film. In this presentation, a range of samples systems are studied to demonstrate the application of LEIS in the industrial R&D context. These examples include W on SiO_2 substrate for contact application with a thickness range of 0 – 1.5 nm. These films were grown under two different conditions and the effect of these conditions is shown. Another set of samples – again under two different growth conditions – includes 0.2 – 1.7 nm TaN on 1.5 nm TiN for barrier and work function applications. Time permitting, one or two other examples will be shown to illustrate the range of information that can be deducted from the LEIS results.

2:45pm **AF1-TuA-6 Characteristic Evaluation of ZrO_2 Thin Films by PEALD to Semiconductor and Display using Cp-Zr Precursor***, **Sang-Yong Jeon**, G Park, S Lee, W Chae, S Yim, J Park, S Lee, M Kim,* DNF Co. Ltd, Republic of Korea

ZrO_2 has been widely used for high-k material and studied in various fields such as hardmask, thin film transistor (TFT), and encapsulation layer of Organic light-emitting diodes (OLEDs) due to its low dry etch characteristics and low moisture permeability.

In this study, we used $CpZr(DMA)_3$ as a precursor to evaluate characteristics of ZrO_2 by PEALD method and confirmed high applicability to high-k, hardmask, encapsulation, and TFT due to its electrical characteristics, dry etch rate, and WVTR characteristics.

ZrO_2 grown on Si substrate showed ALD window up to 280℃, which is relatively high temperature as shown in Fig. 1, and self-limited reaction was observed in linearity evaluation as shown in Fig. 2. The deposition rate was 29Å/min, which is relatively fast. The XPS results showed that the films were free of N and, C, and pure films with an O/Zr ratio of about 1.9. The dielectric constant and leakage current density of the ZrO_2 thin films were about 23 and 5E-8A/cm^2, respectively. In addition, it was confirmed to be HT-ACL of less than 40% of that of HT-ACL in a dry etch atmosphere based on C4F8 gas.

The WVTR of ZrO_2 deposited on PEN film at low temperature (<100℃) for OLED application was 10 times better than SiO_2 of the same thickness as shown in Fig. 3.

As can be seen from the above results, it was confirmed that the ZrO_2 thin film deposited with PEALD can be applied to various areas such as high-k, hardmask, TFT and encapsulation.

3:00pm **AF1-TuA-7 Hybrid Electronically Tailorable Dielectric Thin Films and Substrate Effects on Electrical and Chemical Properties of ALD Al_2O_3***, **Jessica Kopatz**,* Pennsylvania State University*; J Daubert, W Xie,* North Carolina State University*; A Meddeb, Z Ounaies, M Lanagan,* Pennsylvania State University*; G Parsons,* North Carolina State University

Our study is focused on the fundamental understanding of electronic transport and reliability of dielectric interfaces resulting from both MLD and ALD-grown thin films on two technologically important substrates: silicon and polymers. Based upon the deposition sequence and deposition time, the hybrid film possesses a range of properties incorporating both inorganic and organic natures. The organic alucone is grown via ethylene glycol and trimethylaluminum (TMA) precursors, while the use of water and TMA enables the growth of Al_2O_3. By capping 80 nm of MLD alucone with 20 nm ALD Al_2O_3, the permittivity was found to exceed the permittivity of Al_2O_3 itself, while the low loss remained in the same order of magnitude. This was unexpected because organic materials generally have a lower polarizability compared to inorganic metal oxides, thus causing lower permittivity values. The focus was then directed towards investigating the capacitive behavior and the nature of charge transport at the substrate-ALD interface by depositing Al_2O_3 onto different types of substrates. Herein, we examine the effect of substrate interface on the electrical and chemical properties of atomic layer deposited 100 nm Al_2O_3 thin films at deposition temperatures ranging from 100-300°C. Our substrates included platinized silicon (1500 Å) and low-resistivity (0.001-0.005 Ω*cm) p-type and n-type silicon. Electrical measurements consisted of utilizing current-voltage sweeps, dielectric spectroscopy, and capacitance-voltage sweeps. The use of platinized silicon was found to have a significant improvement on the dielectric permittivity of the deposited Al_2O_3 compared to the highly doped silicon substrates with values of 9 as opposed to 7.5, respectively. Capacitance-voltage measurements will help determine trapped states present within the highly doped silicon substrates. Chemical measurements regarding the refractive index of the deposited films were obtained using a Woollam Ellipsometer and Cauchy model. According to Ellipsometry, the refractive index of all Al_2O_3 films deposited at 300 °C was 1.66. This similarity demonstrates the difference in permittivity values must result from the interfacial reactions and not from film quality. At 300°C, the growth rate of 0.80 Å/cycle was calculated. Atomic force microscopy images of the Al_2O_3 films will offer insight on the relationship between surface roughness, deposited thickness, and deposition temperature.

3:15pm **AF1-TuA-8 Atomic Layer Deposition of Pyrite FeS_2, CoS_2, and NiS_2***, **Xinwei Wang**,* Peking University, China

The pyrite-type transition-metal disulfides (MS_2, M = Fe, Co, Ni) form a series of compounds that are highly interesting in many aspects. These compounds share the same cubic pyrite crystal structure but differ in the progressive increase of an anti-bonding *d* electron in the conduction band, and as a result, the metal pyrites exhibit very diverse and intriguing electrical magnetic properties from diamagnetic semiconductive to itinerant-electron ferromagnetic and to antiferromagnetic semiconductive. This diversity of the material properties has not only offered a model system platform for fundamental science studies but also enabled tremendous engineering possibilities for practical applications, such as solar cells, lithium/sodium-ion batteries, and electrocatalytic hydrogen evolution, oxygen evolution, and oxygen reduction.

In this presentation, we will show our latest progress on the development of atomic layer deposition processes for the metal pyrites of FeS_2, CoS_2, and NiS_2 (*Angew. Chem.Int. Ed.* 2018, doi:10.1002/anie.201803092). We use the metal amidinate compounds as the precursors for the metals and H_2S plasma as the sulfur source, and we will show that the deposition processes for FeS_2, CoS_2, and NiS_2 all follow ideal layer-by-layer ALD growth behavior over a wide temperature range to produce fairly pure, smooth, pyrite-structure metal disulfide films. We will further show that the ALD FeS_2, CoS_2, and NiS_2 films can be conformally deposited into deep narrow trenches with aspect ratios as high as 10:1, which thereby highlights the broad and promising applicability of these ALD processes for conformal film coatings on complex high-aspect-ratio 3D architectures in general.

ALD Fundamentals
Room 116-118 - Session AF2-TuA
High Aspect Ratio

Moderators: Scott Clendenning, Intel Corporation, Han-Bo-Ram Lee, Incheon National University

4:00pm **AF2-TuA-11 Modeling the Infiltration Kinetics of Porous, High Surface Area Materials in ALD: Effective Diffusivities, Saturation Times, and Densification**, ***Angel Yanguas-Gil****, J Elam,* Argonne National Laboratory

Understanding the infiltration dynamics in high surface area materials is crucial to evaluate the scale up of ALD processes involving the functionalization or densification of these materials. One of the challenges in ALD is that, due to the time dependent nature of the chemistry, modelling infiltration involves three very different timescales: the timescale of the transport of individual species inside high surface area materials, the surface kinetics, and the evolution of the internal porosity with the number of cycles.

In this work we apply an approach that we have recently developed to model ALD infiltration on disordered porous materials. Based on the treatment of the reactive transport of ALD precursors and other gas phase species as a Markov chain, the model allows us to obtain local sticking probabilities in a very efficient manner. Our simulation consists of two steps: we first generate random structures through the simulation of a particle sedimentation process, with various degrees of freedom to allow for the formation of materials with different porosity and pore size distribution, as well as their inverse structures. We then use these substrates as a starting point to model both the reactive transport of gas phase species within the porous material, and the evolution of the densification process as the ALD coatings grow to fill the pores.

Finally, we also model the impact of ALD processes on the electronic properties of the resulting scaffolds: using the simulated, coated structures as a starting point, we have modeled the carrier transport efficiency of a hypothetical nanostructured electrode under two assumptions: one in which charge transport is enhanced via ALD infiltration, and a second in which the simulated coating acts as a passivation layer reducing recombination.

4:15pm **AF2-TuA-12 Thin Film Conformality Analysis, Reliability and Modeling using All-silicon Lateral High Aspect Ratio Structures**, ***Oili Ylivaara****, M Ylilammi, V Korpelainen,* VTT Technical Research Centre of Finland, Finland*; R Puurunen,* Aalto University, Finland

Device downscaling in semiconductor and microelectromechanical device industry brings new challenges from the process perspective as increased three-dimensionality sets demands towards higher aspect ratio structures which have to be filled conformably. Atomic layer deposition (ALD), based on the use of repeated, self-terminating reactions of typically at least two compatible reactants on a solid substrate, is a promising technique especially from the conformality point of view. Traditionally thin film conformality has been analysed with cross sectional specimens. Our approach is to turn the analysis to horizontal plane with all-silicon lateral high aspect ratio structures (LHAR) and reflectometry line-scans.

This work continues on earlier work on conformality analysis [1–6]. The LHAR structures consist of a lateral gap of typically 500 nm in height while the gap length varies from 1 to 5000 µm, giving aspect ratios of 2:1 to 10 000:1. LHAR chips were coated with ALD Al_2O_3 and TiO_2 films, the effects of pulse and purge times were inspected from conformality point of view, and the measurement reliability was characterized with atomic force microscopy and QuickVision optical coordinate measuring tool. Diffusion model [6] was used to study the propagation of the ALD growth in the narrow channel. According to reflectometry measurements longer pulse time increased the penetration depth of the film to the narrow channel. The diffusion model was well in agreement with the experimental results. Measurement reliability and uncertainty components of the measurement were studied systematically. Therefore realistic uncertainty estimates can be given for the results. The LHAR structures presented here with thin film analysis and theoretical diffusion model accelerate the process up-scaling from small to large industrial scale.

Acknowledgements: Funding for this work comes from Academy of Finland's Finnish Centre of Excellence in Atomic Layer Deposition and Tekes PillarHall project.

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4:30pm **AF2-TuA-13 High Step Coverage Properties of New Zr Precursors with High Thermal Stability for High-k**, ***Haeng-Don Lim****, S Jeon, J Cho, W Chae, J Park, S Yim, S Lee, M Kim,* DNF Co. Ltd, Republic of Korea

New Zr precursors have been developed using a tri-amine structure with enhanced thermal stability. Currently precursors of Cyclopentadienyl structure (Cp-Zr), which have high thermal stability, are used as precursors of ZrO_2 thin films. We synthesize Zr precursors of tri-amine structure (ZTA-01) with further improved thermal stability, and analyze characteristics according to structure difference with Cp structure.

The ALD window of ZTA-01 is 220 to 320℃ (Fig. 1(b)). Compared with Cp-Zr, the high-temperature stability of ZTA-01 was found to be about 20℃ higher. As a result of XRD analysis, distinct tetragonal peaks of ZrO_2 were clearly observed at 310℃ (Fig. 2). The stoichiometric ratio of O / Zr was found to be close to ideal ZrO_2 (O / Zr = 2.00) with ZTA-01 of 1.96 by XPS at 310℃. Impurities C and N were not detected.

The hole structure pattern of aspect ratio 60-65: 1 is used and the step coverage characteristics are analyzed at the ALD window temperature of 290 ~ 330℃ of ZTA-01. (Fig. 3) The step coverage is 97% at wafer temperature 290℃, 98% at 300℃, 99% at 310℃, 97% at 320℃, and 94% at 330℃. The ZTA-01 step coverage in the ALD window is more than 97 to 99%, which is evidence of the high thermal stability of ZTA-01 and the ideal self-limited reaction. Under the same conditions, the step coverage characteristic of the ZrO_2 thin film using Cp-Zr is 90% (Fig. 4(a)). This experiment shows that the Zr precursors of the tri-amine series are improved by at least 8% in the step coverage characteristics when compared with the Zr precursors of the cyclopentadienyl structure. Similar to the step coverage characteristic of ZrO_2 single layer using ZTA-01, the step coverage characteristic is 99% even in ZAZ laminated structure for reducing the leakage current (Fig. 4(b)).

This result shows that the inter-molecular stability and the intra-molecular stability of the Tri-amine structure are all high, so that it is not subjected to thermal decomposition to the bottom of the high aspect ratio and shows step coverage of 99% through a self-limited reaction.

4:45pm **AF2-TuA-14 Atomic Layer Deposition: Tailoring High Aspect Ratio TiO_2 Nanostructures**, ***Raul Zazpe****, H Sopha, J Prikryl, M Krbal, J Macak,* University of Pardubice, Czech Republic

The ongoing advances in the fabrication techniques over the last decades have allowed the shrinking of the devices to nanoscale dimensions, yielding a new generation of promising nanostructures as nanowires, nanorods or nanotubes. Among such nanostructures, anodic self-organized 1D TiO_2 nanotube layers have received significant scientific and technological interest, motivated by the semiconductive nature of the TiO_2, unique tubular architecture, chemical and mechanical stability, unidirectional electron transport through nanotube walls, biocompatibility, as well as simple and low cost fabrication process.[1,2]

An encouraging further step lies on the fabrication of TiO_2 nanotubular composite structures with new functionalities by the deposition of secondary materials. However, the shrinking to nanoscale dimensions brings the challenge of attaining conformal, homogeneous and continuous secondary material coatings. Conventional thin film deposition methods result inefficient and display serious limitations for the secondary material coating of high aspect-ratio nanostructures.[3] To date, atomic layer deposition (ALD) is the only deposition method capable to deposit continuous and conformal layers into high aspect-ratio nanostructures with an unprecedented sub-nanometer thickness control.[4] Thus, TiO_2 nanotubular composite structures have been produced via ALD by the deposition of ultrathin films of materials as TiO_2,[5] Al_2O_3,[6] ZnO,[7,8] or CdS,[9] or homogeneous decoration with noble metal nanoparticles.[10] The composite nanostructures display synergetic effects resulting in enhanced performance in a wide range of applications, such as photocatalytic,[5] sensing,[8] solar cell,[9] catalytic,[11] and battery.[12]

The presentation will focus on fabrication and experimental details, and recent photocatalytic,[5] sensing,[8] solar cell,[9] catalytic,[10] and battery[11] reports will be presented and discussed.

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5:00pm **AF2-TuA-15 Mechanisms Limiting Conformality in Thermal and Plasma-assisted ALD Investigated by Lateral High Aspect Ratio Structures***,*

Karsten Arts*, V Vandalon,* Eindhoven University of Technology, Netherlands*; F Gao, M Utriainen,* VTT Technical Research Centre of Finland, Finland*; R Puurunen,* Aalto University, Finland*; E Kessels, H Knoops,* Eindhoven University of Technology, Netherlands

This work investigates the processes governing conformality achieved by ALD, using Lateral High Aspect Ratio (LHAR) test structures supplied by VTT.[1] We show that these structures are well suitable for investigating the underlying ALD chemistry, as the shape of the thickness profile and the penetration depth are indicative for the growth regime and provide insight into parameters such as sticking probabilities.

In the new PillarHall™ LHAR3 structures the reacting species diffuse underneath a removable membrane which is supported by pillars giving a 500 nm spacing. This configuration offers new possibilities compared to traditional vertical structures. Among others, top-view diagnostics can be applied to straightforwardly determine the thickness profile and material properties. A range of diagnostics is validated in this work for this top-view analysis. Moreover, the structure has features with aspect ratios up to 10000. Therefore a non-fully saturated profile is acquired for even the most conformal processes, which provides information on the limiting mechanisms.

Two cases are discussed to exemplify these possibilities. Firstly, in the case of thermal ALD of Al_2O_3 using TMA and water it is known from recent work that at low temperatures the growth is limited by the reduced reactivity of H_2O towards $–CH_3$ groups.[2] We examine how this reactivity affects the conformality, by measuring and simulating Al_2O_3 thickness profiles for different substrate temperatures. For example, at 200°C table temperature a sloping profile is observed with a half-thickness-penetration-depth (HTPD) of ~400 µm (AR=800). This profile seems to be consistent with the low sticking probability of water at these temperatures ($s \sim 3 \cdot 10^{-5}$).[2] That is, from Monte Carlo simulations a growth regime in between reaction-limited and diffusion-limited growth is expected for this sticking probability and penetration depth, yielding such a sloping profile.

Secondly, in the case of plasma-assisted ALD of Al_2O_3 recombination-limited growth is observed, as the HTPD is reduced to ~30 µm (AR=60) through recombination of the reactive O radicals. As even these short profiles can be resolved using top-view diagnostics, the LHAR3 structures can be employed to investigate recombination probabilities in plasma-assisted ALD as well. On the basis of the aforementioned studies, these and other insights into ALD chemistry relevant to conformal growth will be provided.

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5:15pm **AF2-TuA-16 Multilayers on Reinforcement Fiber Fabrics with ALD***,*

Pauline Dill*, F Pachel, M Scharf, W Goedel,* Chemnitz University of Technology, Germany

Carbon fiber fabrics, with a size of 30x8 cm, were coated smooth in a homebuilt reactor with combinations of three different ALD-layers. We used inorganic ALD coating (Al_2O_3, TiO_2, $Ti_3(PO_4)_4$) as well as an organic-inorganic TiO_2/furfuryl alcohol coating.[1] The coatings were combined in such a way that stacks of inorganic/organic-inorganic/inorganic were produced. The layer thickness and the homogeneity of each layer and the combination of the three layers were investigated with scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). The elemental analysis of the coating was investigated with energy-dispersive X-ray spectroscopy (EDXS). The coated fabrics will be embedded in a ceramic matrix to give a fiber reinforced ceramic, in which the coating should provide oxidation protection for carbon fibers and also the coating may be helpful for crack deflection in the composite. Each of the coating in the combination has at least one task to protect the carbon fiber in the ceramic matrix composites. The first coating should protect the fiber from oxidation environment, the second one is needed for crack deflection and the top coating is needed to protect the remaining coated carbon fiber fabrics, when it will be sintered at high temperatur. For good crack deflection the three coatings should not stick too tight to each other, so that the fiber is able to move along the fiber axis. The delamination behavior of the coatings was also seen in SEM images.

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ALD Fundamentals
Room Premier Ballroom - Session AF-TuP
ALD Fundamentals Poster Session

AF-TuP-1 Kinetic Study on Atomic Layer Deposition of Zinc Oxide from Diethylzinc and Water*, **Sungjoon Kim**, Y Min,* Konkuk University, Republic of Korea

Zinc oxide is a semiconducting material used in various applications due to its easily tunable electrical conductivity and transparency. Atomic layer deposition (ALD) is a preferred method when depositing thin films of ZnO due to its ability to deposit conformal layers of material even on high aspect ratio substrates. Despite ALD's advantages, the mechanisms and reaction pathways regarding the deposition processes are still under investigation, even for the most widely operated processes. The complex nature of the deposition environment make accurate predictions difficult, and although calculative methods such as the density functional theory (DFT) offer some insight to the reaction kinetics, their usefulness is somewhat limited in real applications. In this study, we propose a mechanism for diethylzinc adsorption on ZnO film which incorporates a molecular adsorption equilibria before the precursor molecule irreversibly adsorbs on the surface. The saturation curves at various deposition temperatures and precursor exposure times were analyzed to evaluate the effect of temperature on the rate of adsorption reaction. Reaction parameters such as the effective activation energy and the steric hindrance factor were extracted from the proposed model. The effective activation energy of the adsorption of diethylzinc on ZnO film was around 0.14 eV, and the decrease in growth-per-cycle may be attributed to the shift in adsorption/desorption equilibria at high temperatures. The effect of de-hydroxylation of the film's surface was found to be insignificant in the temperature range of this work.

AF-TuP-2 Effects of Organic Doped on the Performance and Stability of ALD Grown ZnO Thin Film Transistor*, **Hongbum Kim**, S Yu, M Sung,* Hanyang University, Republic of Korea

We fabricate zinc oxide thin-film transistors (TFTs) using 4-mercaptophenol (4MP) doped atomic layer deposition (ALD) grown ZnO that results in highly stable and high performance. The 4MP concentration in ZnO films were varied from 1.7% to 5.6% by controlling Zn:4MP pulses. The n-type carrier concentrations in ZnO thin films were controlled from $1.017\times10^{20}/cm^3$ to $2.903\times10^{14}/cm^3$ with appropriate amount of 4MP doping. The 4.8% 4MP doped ZnO TFT revealed good device mobility performance of 8.4 cm^2/Vs and the on/off current ratio of 10^6. Such 4MP doped ZnO TFTs exhibited relatively good stability (ΔV_{TH} : 0.4 V) under positive bias-temperature stress while the TFTs with only ZnO showed a 4.3 ΔV_{TH} shift, respectively.

AF-TuP-3 Investigation of Annealing Effects on Structural and Compositional Properties of AlN Films Deposited by Atomic Layer Deposition*, **Jun Chen**, F Zhang, X Liu, G Yan, Z Shen, Z Wen, L Wang, W Zhao, G Sun, Y Zeng,* Institute of Semiconductors, Chinese Academy of Sciences, China

We have investigated and compared the influence of annealing temperature on properties of AlN thin films grown on Si (100) substrates by atomic layer deposition using trimethylaluminum and ammonia as precursors at 400℃. Those as-deposited films were annealed by rapid thermal annealing at 700℃, 800℃, 900℃ and 1000℃ for 1 min in N_2 atmosphere, respectively. The thickness, refractive index, and surface morphology and composition of AlN films were measured by spectroscopic ellipsometer, scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS).

As the annealing temperature increased, the thickness of AlN thin films decreased because annealing temperature increased the density of the AlN film, as shown in Figure 1. This result was in good agreement with the surface morphology measured by SEM, as shown in Figure 2. We observed that there were obvious grains on the surface of the as deposited AlN films, which indicates that nucleation and island growth were simultaneous. With the increase of annealing temperature, the grain size of AlN thin films gradually became smaller. The possible reason is that the annealing temperature increased the kinetic energy of atoms and then the films tended to form the stable structure and became denser.

Moreover, the refractive index increased with the increase of the annealing temperature,as shown in Figure 3, which is probably due to the changes of the components in the films. In the as-deposited films, the value of refractive index was small because of the high content of AlON contained, as shown in Figure 4(a). As the annealing temperature increased, Al-O-N bond decreased and more Al-N bond increased in the films, as shown in Figure 4(b) and Figure 4©. Since the refractive index of AlN is higher than AlON[1], the increase of AlN in the films resulted in an increase of the refractive index.

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AF-TuP-4 PE-ALD Growth of GaN on Various Substrates and their Device Applications*, **Xinhe Zheng**, Y He, M Li, S Liu, Y Song, H Wei, M Peng, P Qiu, Y An,* University of Science and Technology Beijing, China

Gallium nitride (GaN) based films and devices on various substrate or templates can produce different potential in electronic and/or optoelectronic applications. The device systems include high-frequency hot electron transistors (HETs) relying on the vertical transport of a controlled source of hot-electrons implementing two-dimensional (2D) materials, such as graphene and Molybdenum disulfide (MoS_2), etc., in the base region to form GaN/2D materials heterojunction systems on silicon and thin-film transistors (TFTs) on flexible substrates. To reap this benefit, one of great challenges is to grow high-quality GaN films on various templates at reasonably-high deposition temperature, but no damage of templates or flexible substrates is allowed. This challenge implies that the overall thermal budget of the device processing should be as low as possible, especially in the case of GaN deposition. The two device systems share the same requirements from endurable temperature processing of templates and/or flexible substrates and reasonably-high deposition temperature for high crystalline quality and realization of good performing device.

Therefore, the trade-off of temperature choices on various templates or substrates will play a critical role in the ALD processing. In this presentation, we report some detailed growth results of GaN films on graphene, MoS_2 templates and flexible KAPTON substrates at lower and higher temperatures, respectively. It is found that during the ALD window, all GaN films show a polycrystalline with wurtzite structure and have a tendency to form preferential crystallization with increasing of the thickness. While the window temperature increases, the crystalline quality and GaN density are intriguingly enhanced. For the case of GaN films over templates onto SiO_2/Si substrates, a very sharp interface between them is observed. While in the case of KAPTON substrates, transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) measurements reveal a back diffusion of GaN into the KAPTON. Possible reasons behind these intriguing observations are in detail discussed in the presentation.

AF-TuP-5 Novel Tin Precursors for Atomic Layer Deposition of Tin Oxide Thin Films*, **Seong Ho Han**, T Chung,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea*; S Son,* Sungkyunkwan University (SKKU), Republic of Korea*; B Park, C Kim,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea

In the past decade, oxide semiconductor materials have attracted great attention for various applications in thin film transistors (TFTs), gas sensors, lithium batteries, and solar cells. Especially, tin(II) monoxide (SnO) which is a p-type material, has attracted material because of wide optical band gap energy (2.7~3.0 eV), which highlights the possibility of completely transparent electronic devices. Moreover SnO based TFT recently showed the record field effect mobility of ~6.75 $cm^2/V\cdot s$ and Hall mobility of ~18.71 $cm^2/V\cdot s$. On the other hand, tin(IV) dioxide (SnO_2) is an n-type material, which has also wide band gap energy (~3.6 eV) with excellent optical, electrical, and chemical properties. SnO_2 is transparent under visible light and the resistivity of SnO_2 films can vary at wide range. Doped SnO_2 films can be applied as transparent conducting electrodes. Generally, chemical vapor deposition (CVD) or atomic layer deposition (ALD) are required for uniform and conformal thin film growth. Moreover, SnO or SnO_2 can be deposited selectively by the oxidation state control with Sn(II) precursors and oxygen source. In the cases of ALD, various Sn precursor/reactant combinations have been studied to grow SnO or SnO_2 films, and many cases resulted in n-type SnO_2 films.

In pursuit of novel tin(II) precursors for thin film applications, we have synthesized new tin complexes using tin(II) chloride as starting material. The resulted complexes were characterized by various analysis equipments such as nuclear magnetic resonance (NMR), elemental analyses (EA), thermogravimetric analysis (TGA), and single crystal X-ray diffraction.

AF-TuP-6 Preparation of Transition Metal Molybdenum Precursors and MoS_2 Thin Films Growth by Atomic Layer Deposition (ALD), ***Sunyoung Shin**, J Kim, B Park, C Kim, T Chung,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea

Molybdenum disulfide (MoS_2) has in recent years become one of the most intensely studied subjects in materials chemistry and materials science, because MoS_2 is a layered semiconductor with a thickness-dependent optical band gap in the range of 1.2–1.8 eV. 2D MoS_2 has been utilized for battery, gas, and biosensor applications, and extensively for catalytic hydro-desulfurization and hydrogen evolution processes. Precursor used in the ALD requires volatility, stability, and low deposition temperature. Precursors using a heteroleptic ligands with different reactivity have advantage of selective reaction of the heteroleptic ligands on substrate during ALD process. In this study, we have synthesized new heteroleptic molybdenum precursors with aminoalkoxides which have been widely used for the development of precursor because of their chelating effects by increasing the coordination number of the metal, and advantages to synthesize a single precursor. A newly synthesized Mo(IV) precursors will be adopted for MoS_2 thin films by ALD.

AF-TuP-7 Synthesis and Characterization of Molybdenum Precursors Containing Aminoalkoxide and Aminothiolate Ligands for MoS_2 Thin Films by Atomic Layer Deposition, ***Jahee Kim**, S Shin, B Park, C Kim, T Chung,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea

Transition metal dichalcogenides (TMDCs), MX_2 (M = Mo, W; X = S, Se, Te), have been widely studied for various applications such as future electronic materials and various catalysts due to their interesting properties of two-dimensional layered structure. The unique structure of TMDCs is attracting attention as a next generation flexible devices. Among them, molybdenum disulfide is most interesting because MoS_2 has a band gap of 1.2-1.8 eV and excellent optical and mechanical properties. It can be applied to wide variety of applications to such as semiconductor devices, batteries, supercapacitors, optoelectronics, hydro cracking and hydrodesulfurization catalysts.

In order to produce uniform and high-quality MoS_2 thin films by atomic layer deposition, it is essential to develop reactive molybdenum precursors without producing harmful or corrosive by-products.

In this study, we synthesized molybdenum precursors containing aminoalkoxide and aminothiolate ligands to fabricate MoS_2 thin films. Newly synthesized molybdenum complexes were characterized by elemental analysis (EA), FT-IR, ^{1}H NMR and Mass, and the crystal structure was analyzed by single crystal X-ray analysis. The thermal stability and volatility were confirmed by thermogravimetric analysis (TGA).

AF-TuP-8 Synthesis of Manganese Nitride Precursors, ***Sunju Lee**, B Park, T Jung, C Kim,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea

Cu diffusion barrier materials are important to prevent Cu diffusing onto substrate. Among a variety of Cu diffusion barrier materials, TaN has high resistance against Cu migration, robust mechanical properties, and high chemical stability. For the Cu diffusion barrier, TaN film has thickness of more than 10 Å includes a TaN layer above Ta layer. However, for smaller nodes (less than 32 nm), a thinner TaN thin film (5 nm) is required. TaN thin film with the thickness is non-continuous, resulting in larger wiring resistance and lower copper barrier properties. Therefore, manganese nitride thin film can be presented as one of the most promising material in back-end of line copper wiring of next-generation devices.

Precursors for manganese nitride thin film are Mn(amidinate)2, Mn(guanidinate)2, Mn(β-diketiminate)2, etc. However, the precursors have some issue such as volatility, thermal stability, and reactivity to use in the ALD method. Therefore, development of new manganese precursor is required. Recent in precursor chemistry are developments of heteroleptic precursor bonded to different types ligands. The heteroleptic precursors can have a distinct advantage of having a different dissociation pattern for each ligand.

Herein, we report the synthesis of new heteroleptic manganese precursors for thin films containing manganese. Also, the precursors were fully characterized by IR, thermogravimetric analyses (TGA), microanalyses, and structural analysis through X-ray single crystallography.

AF-TuP-9 Atomic Layer Deposition of HfO_2 Thin Film using a Novel Linked Cyclopentadienyl-amido Hf Precursor, *J Park,* ***Min Hyuk Nim**, M Park, K Moon, J Park, K Lim, J Seok,* Hansol Chemical, Republic of Korea

Hafnium oxide (HfO_2) is presently considered as one of the most promising candidates for alternative gate oxide insulating layers in CMOS (complementary metal oxide semiconductor) devices because of its thermal stability, high permittivity, and relatively large bandgap. Other possible applications for HfO_2 thin film include DRAM (dynamic random access memory) capacitors and optical coatings. In this study, we introduce a novel linked cyclopentadienyl-amido Hf precursor, CMENHa. Also, we compared the properties of the HfO_2 thin film of CMENHa to those of CpHf(NMe2)3 grown by atomic layer deposition (ALD).

The physical characteristics of CMENHa, CpHf(NMe2)3 and Hf(NEtMe)4 were investigated by NMR and viscometer. It was notable that the viscosity of CMENHa was similar to CpZr(NMe2)3. The thermal stability of CMENHa was also investigated by thermogravimetric analysis (TGA). The amount of residue was about 0.6% for CMENHa, which had a less residue compared to CpHf(NMe2)3 (2.5%) and Hf(NEtMe)4 (3.2%). The ALD characteristics of CMENHa compare to CpHf(NMe2)3 will be discussed in the conference. Based on suitable viscosity and good thermal stability, the CMENHa is expected to be promising precursor for insulating layer in gate oxide and DRAM capacitors.

Figure 1. (a) Thermogravimetric analysis of Hf precursors, (b) Physical characteristics of Hf precursors

AF-TuP-10 Al_2O_3 Thin Film Fabrication by UV-assisted Atomic Layer Deposition, ***Gyu Sang Yi**, M Sung,* Hanyang University, Republic of Korea

We have deposition Al_2O_3 thin films at room temperature by UV light enhanced atomic layer deposition on poly(ethylene terephthalate) (PET) substrates. We have used trimethylaluminum (TMA) for metal source and H_2O for oxygen source as precursors during UV irradiation. The atomic layer deposition can be done with pulsing of the precursor gases onto the substrate surface followed by chemisorption of the precursors onto surface. In general cases, the surface reactions of the atomic layer deposition are not conducted at low temperature.

In this experiment, by using UV radiation ,the reactions were self-limiting surface reaction and complementary enough to yield uniform and conformal Al_2O_3 thin films at low temperature. The UV light was very efficient to get the high quality Al2O3 thin films without any defect on polymer substrate. The thickness, density, morphology and electrical property of the Al2O3 thin films were measured by AFM, XRR, ellipsometry, and C-V measurement

AF-TuP-11 Fabrication and Characterization of Organic-Inorganic Hybrid Thin Films, ***Thu Huong Chu**, M Sung,* Hanyang University, Republic of Korea

Nowadays, the next generation electronic devices require new materials that have great properties. One way to fabricate new materials is the hybridization of existing materials having different properties. The hybrid materials mixed by organic and inorganic components are expected to have combined properties both of inorganic parts, such as stability and high electrical or optical performance and organic parts, such as flexibility and functionality. Furthermore, the hybrid materials are expected to have synergic effects which are not shown in just one component.

In this report, we fabricated new types of organic-inorganic hybrid thin films by molecular layer deposition. The hybrid thin films were made by sequential surface reactions of metal alkyls and bifunctional monomers. Diethyl zinc and 2,4-hexadiyne -1,6-diol are used as an inorganic precursor and an organic precursor, respectively, in order to fabricate poly(zinc diacetylene). Some methods are used to characterize the microstructure and compositions of the hybrid films such as Raman, XPS and TEM analysis. And, the electric and optical properties were analyzed by a TFT fabrication and photoluminescence spectroscopy, respectively. The high performance of TFTs, on/off ratio of over 107 and saturation electron mobility of over 10 $cm^2/V\cdot s$, and the low-temperature process indicate the possible use of the hybrid films to flexible devices.

AF-TuP-12 Low Temperature Atomic Layer Deposition of Yttrium Oxide using Plasma Excited Humidified Argon, ***Kentaro Saito**, K Tokoro, K Kanomata, M Miura, B Ahmmad, S Kubota, F Hirose,* Yamagata University, Japan

Yttria (Y_2O_3) is attracting much attention since this material has an excellent corrosion resistance. In the conventional technologies, Y_2O_3 films were deposited by thermal atomic layer deposition with temperatures exceeding 250˚C, where the high temperature process is the biggest obstacle for the organic electronics applications. We newly developed an atomic layer deposition (ALD) of Y_2O_3 using tris(butylcyclopentadiyl)yttrium ($(BuCp)_3Y$) and plasma excited humidified argon and succeeded in Y_2O_3 film formation at 150˚C and room temperature (RT).

In the experiments, we used a double-sided polished p-type Si (100) substrate with a resistivity of 10 Ωcm as a sample. The sample size was 10 ×

45 mm^2. To confirm the Y_2O_3 formation, we carried out an atomic ratio analysis of Y_2O_3 film by X-ray photoelectron spectroscopy (XPS). The XPS shows the Y3d peak of the film when the ALD was performed with 60 cycles with a precursor exposures of 200000 L and an oxidation time of 10 min at 150˚C or RT. These were close to the full oxidized peak position. It is considered that Y_2O_3 was grown at both 150˚C and RT. To determine the growth per cycle of the Y_2O_3 film, the film thicknesses were measured by spectroscopic ellipsometry. The growth per cycle of Y_2O_3 at 150˚C and RT are recorded 0.06 nm/cycle and 0.6 nm/cycle, respectively. The growth per cycle at RT is 10 times larger than that of 150˚C. We consider this is advantageous for the application of Y_2O_3 film as anticorrosion films.

AF-TuP-13 Fabrication of Zeolite Thin Films by Room-temperature Atomic Layer Deposition, ***Yoshiharu Mori**, Y Noguchi, K Kanomata, M Miura, B Ahmmad, S Kubota, F Hirose,* Yamagata University, Japan

In recent years, zeolite thin films are applied in various fileds such as ion absorbers. The zeolite films were deposited by hydrothermal synthesis although it requires high temperature processes. In addition, it is difficult to control the film thickness in nanometer scale. We newly developed room temperature ALD of zeolite using tris [dimethylamino] silane (TDMAS), trimethylaluminum (TMA) and plasma-excited humidified Ar. We demonstrate the adsorption ability of Na and K cations. We show the results of the Na adsorption test. It is confirmed that the adsorption ability of the zeolite thin film was larger than pure SiO_2 or Al_2O_3 . We also demonstrate the ion exchange properties using zeolite thin film formed by this method. The ion exchange rate from Na to K is recorded as 62 % at room temperature for 30 minutes.

AF-TuP-14 Atomic Layer Deposition of Cuprous Oxide Thin Films using bis(1-dimethylamino-2-methyl-2-butoxy)Copper Precursor, ***Seungmin Yeo**,* Korea Research Institute of Chemical Technology(KRICT), Republic of Korea*; J Han,* Seoul National University of Science and Technology, Republic of Korea*; B Park, C Kim, T Chung,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea

Copper oxide is very attractive material due to its many advantages of non-toxicity, earth-abundance, low cost and direct band gap. Specifically, cuprous oxide (Cu_2O) is known to have band gap of 2.1 ~ 2.6 eV, carrier concentration of ~ 10^{16} cm^{-3}, hole mobilities of ~ 100 cm^2/Vs at room temperature. Owing to these properties, Cu_2O thin films have been investigated for various applications such as gas sensor, photodiode, anode materials in batteries, thin film transistors (TFTs), solar cells and photo-catalysts.

In this study, Cu_2O thin films were grown by atomic layer deposition (ALD) using bis(1-dimethylamino-2-methyl-2-butoxy)copper ($C_{14}H_{32}N_2O_2Cu$) and H_2O vapor as precursor and reactant, respectively. Several *ex-situ* characterizations such as X-ray diffractometry (XRD), X-ray photoelectron spectroscopy (XPS), and X-ray fluorescence (XRF) were performed in detail to investigate the properties of Cu_2O films on SiO_2/Si substrate. All the analysis results clearly showed that polycrystalline with cubic structure and pure with negligible C impurity Cu_2O thin films were successfully achieved using $Cu(dmamb)_2/H_2O$ chemistry. It was also observed that self-limiting film growth with the growth rate of 0.04 nm/cycle was observed with varying the precursor and reactant pulsing time. The XRD results of the ALD Cu_2O film showed specific six peaks corresponding to the cubic Cu_2O structure. The XPS analysis strongly supports that the films deposited with the optimal conditions in this study mostly consist of the Cu_2O phase, which is well matched with XRD results. From the Tauc plot, estimated band gap of ALD-Cu_2O film was ~ 2.3 eV. We believe that ALD Cu-$_2$O films can be applied to various devices including TFTs, catalyst, anode material in batteries, etc.

AF-TuP-15 Recent Development of Group 4 Transition Metal Precursors for ALD, ***Ga Yeon Lee**, C Kim, B Park, T Chung,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea

In the case of dynamic random access memory (DRAM), capacitor dielectrics have required new dielectric materials with a higher k-value than that of traditional SiO_2. HfO_2 and ZrO_2 have been extensively investigated as the gate dielectric oxide or the capacitor dielectrics.

A series of novel group 4 transition metal complexes containing amino-alkoxy as stabilizing ligands, were synthesized for the deposition of metal dioxide. The new heteroleptic group 4 metal precursors have two amino ligands and alkoxide ligands containing nitrogen donor.

The synthesized compounds were characterized by FTIR and NMR spectroscopy as well as elemental and thermogravimetric (TG) analysis. The molecular structures of compounds were inspected by single crystal X-ray diffraction, displaying that they crystalized in the monoclinic space group P2(1)/n as monomer.

AF-TuP-16 SAOLs-Al_2O_3 Nanolaminated Thin Films with Ultrahigh Gas Barrier Performance using Molecular Layer Deposition and Atomic Layer Deposition, ***Jinseon Park**, M Sung,* Hanyang University, Republic of Korea

Organic light-emitting diodes (OLEDs) have emerged as a potent candidate for next-generation displays due to their multiple advantages. However, the life span of OLEDs are limited because of their sensitivity to moisture and air. So one of the major challenges in OLEDs industry is the development of protection film with extremely low moisture and oxygen permeabilities. For commercial applications, the water-vapor transmission rate (WVTR) of approximately 10^{-6} g m^{-2} day^{-1} is generally cited as the minimum requirement to assure adequate lifetime stability for most OLED devices. Herein, we presents a novel organic−inorganic nanolaminated thin films that combine self-assembled organic layers (SAOLs) with an inorganic Al_2O_3 layer through MLD and ALD, respectively. This SAOLs- Al_2O_3 thin film achieved a high degree of mechanical flexibility, excellent transmittance (> 95%), and an ultralow WVTR (2.99×10^{-7} g m^{-2} day^{-1}), which represents one of the lowest permeability levels ever achieved by thin film encapsulation. Furthermore, Modulation of the relative thickness ratio of the SAOLs and Al_2O_3 enabled control over the elastic modulus and stress in the films. On the basis of its outstanding barrier properties with high flexibility and transparency, the nanolaminated film was applied to a commercial OLEDs panel as a gas-diffusion barrier film. This demonstrated excellent encapsulation performance, leading to remarkably high durability of the panel in air.

AF-TuP-17 Remote Plasma Enhanced-atomic Layer Deposition of SiON Thin Films with a High Growth Rate (> 0.25 nm/cycle) using Novel Si Precursor, ***Dae Hyun Kim**, H Lee, H Jin,* Hanyang University, Republic of Korea*; H Lee, J Kim, M Yoo, T Kim, J Kim, M Lee, K Cho, J Lee, J Kim,* Dongjin Semichem, Republic of Korea*; T Park,* Hanyang University, Republic of Korea

Silicon oxide (SiO_2) and silicon nitride (Si_3N_4) thin films have been widely used in semiconductor industry as insulating and dielectric materials for electronic devices. Recently, atomic-layer-deposited (ALD) SiO_2 and Si_3N_4 films are used as a physical and electrical passivation layer such as a gate spacer in metal-insulator-semiconductor field-effect transistor and moisture protective layer in flat display panels, and hard mask layer in self-aligned double patterning process. For these processes, the requirements on materials properties and process conditions are quite stringent in common; high growth rate, low process temperature, high physical density, and high physical/chemical uniformity. Especially, low growth rate of ALD film is a critical drawback in view point of mass-production.

Meanwhile, in an era of 3-dimensional device integration the considerable part of direct plasma enhanced ALD (PEALD) processes would be replaced with remote PEALD processes, because physical and chemical non-uniformity become more critical as well as plasma damage on a substrate.

Therefore, in this work, we demonstrated a high growth rate over 0.25 nm/cycle of PEALD SiON films using new Si precursor and ICP-type remote plasma such as N_2 and NH_3 plasma. Furthermore, SiON films can be grown at the temperature lower than 100°C. The experimental results will be presented in detail.

AF-TuP-18 Automation of Reactivity Modelling in Thin Film Process Chemistry, *T Mustard, **H. Shaun Kwak**, L Jacobson, A Bochevarov,* Schrödinger, Inc.*; S Elliott,* Schrödinger, Inc., Ireland

Modern day modeling and simulation of reactive pathways for individual ALD processes often relies on quantum mechanical predictions of energetics of stationary points on the potential energy surface. The predicted free energies of equilibrium states provide direct insight into thermodynamics of the ALD process whereas the transition state barrier heights among them provide control over the kinetics. Finding the relative kinetics of competing reaction steps is particularly useful for understanding saturating reactions, thermal decomposition and selective-area ALD. Unlike computing the energetics of equilibrium stationary points, however, finding transition states of new reaction pathways for these complex chemistries has widely been acknowledged as labor-intensive, non-transparent, and even an art-like process owing to the extreme nonlinearity of the energy and configuration space. In this work we present a fully automated formalism based on density functional theory (DFT) calculations designed to find a transition state between equilibrium surface structures along key ALD reaction pathway. The new automated transition-state search algorithm, referred to as AutoTS[1], has already been presented with its

recent success in finding thousands of transition states and predicting reactivity in a wide variety of reactions in purely organic systems such as the Michael addition, Diels-Alder cycloaddition, and hydrogen abstraction. Here we extend our method to reactions relevant to ALD chemistry, particularly those involving semimetal and metal precursors. Examples are presented using a selection of Si and Al half-reactions, and validated against manually calculated and characterized results. The novel automated transition state search can be combined with such techniques as virtual screening and generation of novel precursor libraries, promising faster research and development of new ALD precursor chemistry with tunable processing parameters.

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AF-TuP-19 Development of High Speed Flow Metering on Pulsed Delivery Systems for ALD and ALE Applications.*, **Patrick Lowery**, T Hoke,* HORIBA*; H Nishizato,* HORIBA, Japan

Atomic layer processes, such as atomic layer deposition (ALD), atomic layer etch (ALE), and selective deposition/ etch processes are the becoming some of the predominant methods used to achieve new device geometry shrinks with smaller lithographic nodes. Current fluid delivery solutions used with these atomic layer processes are challenging due to very fast delivery time or pulsation intervals, and the chemical vapors used in ALD processes have to be delivered at elevated temperatures with highly volatile and reactive organometallic chemistries. In this study, we look at the development and implementation of new technologies into pulsation gas delivery systems for ALD/ALE applications. A high speed piezoelectric actuated valve solution allows for fast pulsation time control resolution of less than 10msec, can provide feedback enabled and settable waveform control, and will enable accurate precursor concentration, injection time control, and repeatability. This additional fast flow metering capabilities will allow for precise process calculations, and could greatly reduce precursor waste thru improved injection timing for purge steps, and reduction of excess precursor due to oversaturation of ALD chamber.

AF-TuP-20 Combined XPS-UPS Study of Conduction and Valence Band Offsets for Al_2O_3/HfO_2 High-*k* Dielectric Nanolaminates Grown on Single-crystal GaN and Ga_2O_3 by Atomic Layer Deposition*, **David J. Mandia**, B Kucukgok,* Argonne National Laboratory*; J Liu,* Northwestern University*; J Libera,* Argonne National Laboratory*; J Leach,* Kyma Technologies, Inc.*; A Yanguas-Gil, J Elam,* Argonne National Laboratory

The search for adequate binary metal oxide dielectric nanolaminates (NLs) to prevent degradation of power semiconductor devices is ongoing and involves the atomic layer deposition (ALD)-growth of a variety of binary metal oxide combinations. In the present work, we explore the ALD growth of amorphous (x)HfO_2/(y)Al_2O_3 NLs on Si (with native SiO_2 layer) substrates and then on both GaN and Ga_2O_3 single crystals. A variety of samples ranging from their homogeneous mixtures to HfO_2 or Al_2O_3-rich NLs are assessed before and after a thermal annealing by spectroscopic ellipsometry (SE), XAS techniques such as X-ray photoelectron spectroscopy (XPS) and X-ray absorption fine structure (EXAFS) measurements in order to elucidate the structural evolution of the NL at the GaN (or Ga_2O_3)-NL interface. By quantifying the HfO_2 incorporation throughout the Al_2O_3 layer and using the programmable nature of ALD to alternate layers of the HfO_2 and Al_2O_3 in an $(AB)_x$-$(CD)_y$ fashion, the influence of HfO_2 mobility within Al_2O_3 layer on the NL dielectric constant can be verified unequivocally. EXAFS is a powerful tool for determining the local coordination environment of the Hf at the GaN or Ga_2O_3(001)-HfO_2 interface and, at low super-cycle numbers (sub-nm scale), the ultimate stability of the NLs can be probed and optimized such that the bulk material properties are retained. Finally, via a modified Kraut's method,[1] Ultraviolet photoelectron spectroscopy (UPS) is used to obtain the valence band maximum of the GaN and Ga_2O_3 substrates and combined with the high-resolution XPS data for the Hf and Ga shallow core-level photoelectrons ejected from the thin HfO_2/Al_2O_3 overlayer in order to assess the conduction band offset (CBO) at the film-substrate heterojunction. Probing the insulator properties imparted by the high-k overlayer on the wide bandgap semiconductor surfaces of GaN and Ga_2O_3 is crucial in order to understand and prevent the degradation problem in Ga_2O_3/GaN-based power semiconductor devices. Moreover, photoluminscence (PL) studies of the coated and pristine samples will corroborate the effect of the bulk defect concentration on the conduction/valence band properties of the material.

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AF-TuP-21 Low Temperature Thermal ALD of Pt Films with Novel Precursor*, **Jacqueline Wrench**, Y Yang, W Tang, N Yoshida, P Ma,* Applied Materials*; T Enomoto, R Harada,* Tanaka, Japan

Platinum (Pt) has attracted considerable attention for applications in sensing, catalysis and nanoelectronics due to its excellent electric and catalytic properties.[1,2] For use in these applications, uniform, thin films on high aspect ratio structures are necessary making ALD an ideal technique for deposition. The conventional ALD process of Pt films using $MeCpPtMe_3$ and oxygen deposits at processing temperatures >250°C.[3] Lower temperature deposition requires plasma or O_3 to achieve which can cause severe damage to substrates.[4]

In this work, a novel precursor deposited Pt films at 130°C in an ALD process with H_2. The film demonstrated a clear preference for deposition on metallic substrates with a growth rate of 0.3Å/cyc on in situ TiN substrate (fig 1). The films are highly pure Pt(111) with <5% C content and an RMS roughness of 0.3 nm (fig 2). Step coverage on TiN substrates for 30Å Pt films of >95% was achieved making this a useful low temperature, non-destructive ALD procedure.

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AF-TuP-22 By-product HCl Influence on SiN ALD Process using Chlorine-containing Silicon Precursor*, **Hayato Murata**,* Taiyo Nippon Sanso Corporation, Japan*; N Tajima,* National Institute for Materials Science, Japan*; K Suzuki,* Taiyo Nippon Sanso Corporation, Japan

We found by-product HCl was an inhibitor on the thermal ALD process using chlorine-containing silicon precursor to form the high-quality silicon nitride (SiN) film.

Recently, high-quality SiN films formed below 400°C are required for next-generation semiconductor devices. We have studied the SiN ALD reaction mechanism using ammonia (NH_3) and dichlorosilane (DCS, SiH_2Cl_2) or hexachlorodisilane (HCDS, Si_2Cl_6), and found HCDS/NH_3 was better to form SiN films under lower deposition temperature than DCS/NH_3[1]. On the other hand, low-temperature deposition results in degradation of the SiN film quality in general. Therefore, we focused on HCl, by-product, effect to film quality.

We calculated activation energies (ΔEa) and enthalpies of formation (ΔHf) using quantum chemical calculation to discuss the HCl's reactivity to the nitrided surface structures which were formed by DCS/NH_3 or HCDS/NH_3. The calculation was performed by B3LYP density functional with cc-pVDZ basis set. Table 1 shows ΔEa and ΔHf calculated for chemisorption reactions. Firstly, for the case of HCDS/NH_3, ΔEa of HCDS chemisorption reaction to >NH surface structure was 57 kJ/mol. ΔEa of HCl reaction to the HCDS/NH_3 nitrided surface structure was 56 kJ/mol. So, we found ΔEa's are nearly equal in both reactions. On the other hand, according to the ΔHf values, the HCl reaction is exothermic and the HCDS chemisorption reaction is endothermic. We got similar results in DCS/NH_3. These results indicate the HCl reaction, dry etching of >N-Si bond, is faster than HCDS chemisorption. In addition, the by-product HCl of HCDS/NH_3 process might be generated more than that of DCS/NH_3 process, because HCDS has three times more Si-Cl bond than DCS. And we suppose that HCDS/NH_3 is susceptible to by-product HCl and form rough thin film easily.

From the above, we propose the necessity to develop HCDS/NH_3 process condition to minimize the influence of the by-product HCl.

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AF-TuP-23 Conformality Measurement Needs and Challenges: Survey among ALD professionals*, **Mikko Utriainen**, R Puurunen,* VTT Technical Research Centre of Finland, Finland

Conformality is a core value proposition of Atomic Layer Deposition (ALD) and related thin film processing methods. However, conformality is challenging to measure and quantify and standardized methods do not exist either.

This study focuses to identify specific needs and problems in the conformality measurements. The method was a survey and questionnaire. Responders were ALD or other thin film R&D and process engineering experts (N=45), representing academic (N=24) and industry (N=21) and geographically 55% Europe, 25% North America, 20% unknown.

All responders considered that it is important or very important to measure conformality, however, only 38% were satisfied with their present measurement methodology. The dominant method is SEM/TEM analysis from microscopic vertical trenches or other high aspect ratio structures. Only few uses alternative approaches (e.g. macroscopic lateral stacks or indirect methods) and those more frequently in academy than in industry. Some responders also state that they try to avoid conformality measurements.

Survey showed that the most important attribute was the reliability and accuracy (98% responded 4-5, in the range 1-5) followed by availability of test structures (87%). Lowest success in the present methodology was the speed of measurement (84% responded 1-3, in the range 1-5), followed by cost (71%) and availability of test structures (67%).

Responders also described their main challenges. Slow speed is due to tedious (cross-sectional) sample preparation, inaccurate dimensional analyses and multiple sample fractions. Test structures should be comparable to dimensions of real substrates, provide variable 3D dimensions and be available at low cost. Avoidance of breaking valuable wafers was also mentioned. Alternative self-made stacks have challenges e.g. in processing condition compatibility. Other accuracy challenges were low film thickness, inadequate resolution in SEM and missing surface area factor. Responses also pointed out the need of mapping the details on the trench wall/ 3D surface, like morphology, composition, evolution of the film and properties of the film.

Significant gap between high importance and low satisfaction of the current measurement approaches leads to conclude that there is a strong need among professionals to get improvements. In this respect, new innovations or joint activities in standardization can support the whole ALD community.

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AF-TuP-24 AlN Films Prepared by PEALD using Different Plasma Sources, *M Kot,* BTU Cottbus-Senftenberg, Germany*; F Naumann,* SENTECH Instruments GmbH, Germany*; S Garain, E Pożarowska, Z Rouissi,* BTU Cottbus-Senftenberg, Germany*; **Hassan Gargouri,*** SENTECH Instruments GmbH, Germany*; K Henkel, D Schmeißer,* BTU Cottbus-Senftenberg, Germany

Aluminum nitride (AlN) has remarkable properties such as wide band gap, low electrical conductivity, high dielectric constant, low thermal conductivity, and shows piezoelectric behavior. Thus, thin AlN films are promising for a broad range of applications in the field of (opto)electronics and sensors, to name a few.

We present a comparative study of thin AlN films grown by plasma-enhanced atomic layer deposition (PEALD) at 350°C on silicon 8" wafers in the SENTECH SI ALD LL system [1,2]. As precursor and co-reactant trimethylaluminium and ammonia were used, and either a capacitively coupled plasma (CCP) or a direct PTSA (planar triple spiral antenna) source was applied.

The films were characterized by ellipsometry, X-Ray diffraction, field emission scanning electron microscopy, atomic force microscopy, X-Ray photoelectron spectroscopy, and electrical measurements. The layer properties are discussed concerning the varied PEALD process parameters (plasma source, plasma power, plasma pulse duration).

In general, the films prepared with the usage of the direct PTSA plasma source posses higher refractive index and better homogeneity over the wafer in comparison to the process applying the CCP source. Furthermore, higher growth rates per cycle (GPC) in reduced total cycle durations were achieved by the PTSA process. Films with refractive index in the range of 2.07 and permittivity around 8 were realized with a GPC of 1.54 Å/cycle.

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AF-TuP-25 Feature-Scale Simulation of ALD: Steric Hindrance and Under-Exposure Effects, ***Paul Moroz,*** TEL Technology Center, America, LLC

Progress in the semiconductor industry allows ever shrinking feature dimensions, in some degree, due to application of such methods as Atomic Layer Deposition (ALD) and Atomic Layer Etching (ALE). Here we are concerned with the ALD processes, and would like to note that while the number of ALD experimental achievements and applications grow dramatically [1-2] since as far back in time as the 1960s – 1970s [3], the realistic simulation of ALD processing is well behind due to significant difficulties. Among major difficulties are the requirements to simulate evolution of relatively large features with the accuracy of a single monolayer, often in addition to very low sticking probabilities and the requirement of high gas pressures when incident fluxes are very large. Another difficulty for simulations comes from the fact that in most ALD cases the rate of deposition is so low that a single monolayer is deposited only after a few identical cycles. In spite of that, a number of semi-analytic models for ALD processes were reported (among recent see, for example [4-5]), However, to our knowledge, so far only simulations via the FPS3D code reported in [6-9], have the capability of modeling the temporal evolution of feature profiles during a general ALD processing. In current presentation, the results of ALD simulations are demonstrated in detail. The non-ideal effects of roughness, film composition change, and reduced step coverage along the surface might appear in conditions of time-exposure limitations and large aspect ratios. Those effects are simulated during profile evolution due to FPS3D. A special role which steric hindrance could play during ALD processes is demonstrated, and computational methods used for simulations are outlined.

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AF-TuP-26 Novel Tungsten ALD Precursors Supported By Chelating Nitrogen-Based Ligand Frameworks, ***Keith Huynh**, C Brown, J Dube,* Digital Specialty Chemicals, Canada*; T Knisley, J Anthis, M Saly,* Applied Materials

Tungsten-based thin-films have found widespread applications in advanced microelectronics devices. Gate contacts composed of tungsten metal or tungsten silicide have been reported, while tungsten nitride films are useful as a copper diffusion barrier layers due to their inherent high density. In addition to microelectronics, tungsten carbide thin-films are refractive materials that have high melting points, are chemical resistant with high hardness, which lend applications in aerospace as coatings and turbine components. Thin-films containing tungsten are achieved via deposition techniques such as chemical vapor deposition (CVD) or atomic layer deposition (ALD) where controlled growth of film thickness and conformality are achieved by process design and precursor development. The bench-marking precursor in CVD/ALD applications has been tungsten hexafluoride; yet in recent years, focus has been placed on developing fluoride-free organometallic tungsten precursors due to the release of toxic HF during CVD/ALD processes, and its propensity to induce unwanted etch in other surfaces. To this end, we have centered our attention in developing organometallic tungsten precursors based on a bis-*tert*-butylimido motif. This poster will focus on our developments in bis-*tert*-butylimido tungsten complexes supported by chelating nitrogen-based ligands and their effect in enhancing volatility and thermal stability. Initial findings reveal candidates that exhibit single-step weight losses and clean sublimations; which have the potential to displace current state-of-the-art for tungsten thin-film deposition.

AF-TuP-27 Growth of Titanium Nitride by PE-ALD: Effects of Intermittent Argon Plasma Exposure, *K Keskinbora, **Gül Dogan**, U Sanli,* Max Planck Institute for Intelligent Systems, Germany*; H Karl,* University of Augsburg, Germany*; G Schütz,* Max Planck Institute for Intelligent Systems, Germany

Titanium nitride (TiN) films have been heavily studied for many applications ranging from protective coatings to diffusion barriers and more recently to refractory plasmonics. Polycrystalline TiN thin films have been already produced *via* atomic layer deposition (ALD) which offers unique capabilities like deposition of highly conformal coatings over complex geometries, accurate thickness and composition control. However, highly textured films are more preferable in terms of improved optical and electrical properties. The adatoms during film growth need to have sufficient mobility in order to enhance crystalline quality. Due to that thin film growth is generally carried out at high temperatures. However, this gives rise to desorption of the deposited material in ALD processes. Alternatively, a plasma treatment can be applied to improve crystallinity at low substrate temperatures [1]. In a recent study by Shih *et. al.* low-temperature epitaxial growth of aluminum nitride (AlN) was demonstrated *via* ALD. In each ALD cycle, an additional *in-situ* plasma treatment was performed. They denoted this process step as “atomic layer annealing (ALA)” [2]. It was proposed that ALA treatment could enhance the adatom movement and migration at the surface, which is favorable for improved crystallization of the deposited films. In this study, we applied the ALA approach for the growth of TiN thin films with favorable chemical and electrical properties.

TiN thin films were deposited on sapphire (0001) substrates at 500°C by plasma-enhanced atomic layer deposition (PEALD) using $TiCl_4$ and N_2-H_2 plasma. TiN thin films were exposed to Ar plasma for 40 s after each ALD cycle to achieve a highly textured structure. The deposition rate was around 0.29 nm/cycle according to XRR analysis and the linear increase of thickness as a function of number of cycle was observed by *in-situ* spectroscopic ellipsometry (SE) confirming the ALD type growth. The structural analysis was carried out by X-ray Diffraction (XRD) technique. A low resistivity of 168 µohm.cm was achieved thanks to highly crystalline structure and a low chlorine content revealed by X-ray photoelectron spectroscopy (XPS). Further structural and chemical analysis results and their relation to the achieved properties will be discussed.

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AF-TuP-28 Plasma-assisted Atomic Layer Deposition of Phosphorus Oxide, ***Bodo Kalkofen**, B Ahmed, M Silinskas,* Otto von Guericke University, Germany*; S Beljakowa,* Friedrich-Alexander-Universität, Germany*; B Garke,* Otto-von-Guericke University, Germany*; M Lisker,* IHP, Germany*; E Burte,* Otto von Guericke University, Germany

Plasma-assisted atomic layer deposition (PALD) of thin films of phosphorus oxide on silicon substrates was carried out. The intention of our work is to precisely deposit a finite dopant source on the semiconductor material for creating ultra-shallow junctions close to the surface after subsequent rapid thermal annealing. Phosphorus oxide is known to be extremely sensitive to water vapor. Probably, this is the reason why no recent reports on ALD processes for this material were found in the literature.

The experiments were carried out in a commercial PALD reactor build by Sentech Instruments GmbH Berlin. Tris(dimethylamido)phosphine (TrisDMAP) was used as phosphorus precursor. Dosing was achieved by “vapor-draw” into a nitrogen carrier flow by fast acting valves. Oxygen radicals in the PALD processes were generated by a remote inductively coupled plasma source. Typical process parameters for the phosphorus oxide deposition were: TrisDMAP: 50°C source temperature, 10 ms pulse time, 5 s purge time; oxygen plasma: 50 W, 5 s pulse time, 2 s purge time. Growth per cycle of 0.1 to 0.16 nm was typically achieved. The ALD window for different process temperatures and saturation behavior was investigated by varying the relevant process parameters.

The phosphorus oxide films were, as expected, highly unstable in ambient air and needed to be stabilized for further ex-situ investigation by mixing them with stable oxides (e.g. antimony oxide) or by applying capping films of varying thickness. The films and film stacks were measured by spectroscopic ellipsometry and composition of the film stacks was analyzed in detail by x-ray photoelectron spectroscopy (XPS) and secondary-ion mass spectrometry (SIMS).

AF-TuP-29 Isotopic Tracing of Hydrogen and Oxygen Exchange Reactions in Al_2O_3 Thin Films, ***Sami Kinnunen**, K Arstila, T Sajavaara,* University of Jyväskylä, Finland

ALD thin films can be used as moisture and gas diffusion barriers [1]. In this work hydrogen and oxygen isotope exchange reactions accompanied by diffusion were studied in ALD Al_2O_3 thin films on silicon substrate. Films were deposited using trimethylaluminum and deuterated water, $^2H_2{}^{16}O$, and oxygen-18 enriched water, $^1H_2{}^{18}O$. Similar isotopic tracing has been used only in post-deposition treatments [2]. After deposition films were annealed at low temperatures in moist conditions in order to accelerate diffusion and isotope exchange reactions. For example deuterium incorporated in the films is exchanged to hydrogen even in room temperature and normal humidity conditions. In addition, post-deposition annealing was made in $^{16}O_2$-atmosphere. Elemental composition of the films was investigated before and after the post-deposition treatment using ToF-ERDA (Time-of-Flight Elastic Recoil Detection Analysis) measurements. ToF-ERDA can resolve different isotopes of an element and enables tracing of hydrogen and oxygen diffusion in the films. Morphology of the films was studied with HIM (Helium Ion Microscopy).

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AF-TuP-30 Plasma Source Diagnostics for Plasma Assisted Atomic Layer Deposition, ***David Boris**, V Wheeler,* U.S. Naval Research Laboratory*; V Anderson,* Kennesaw State University*; N Nepal,* U.S. Naval Research Laboratory*; S Rosenberg,* American Association of Engineering Education*; A Kozen,* The American Society for Engineering Education*; J Hite, S Walton, C Eddy, Jr.,* U.S. Naval Research Laboratory

Plasma assisted atomic layer deposition (PA-ALD) is a low temperature conformal layer-by-layer deposition technique that is based on a pair of self-terminating and self-limiting gas-surface half-reactions, in which at least one half-reaction involves species from a plasma. This approach generally offers the benefit of substantially reduced growth temperatures and greater flexibility in tailoring the gas phase chemistry to produce varying film characteristics. The flexibility and lower growth temperatures that plasmas provide come at the cost of a complex array of process variables that often require great care on the part of the user.

In response to this challenge, this work focuses on the use of plasma diagnostics to inform the choice of process conditions for PA-ALD systems. In this work we employ optical emission spectroscopy, vacuum ultra-violet emission spectroscopy and charged particle collectors to characterize the plasma source of a Fiji 200 (Veeco) PA-ALD tool. In particular, we assess the total ion flux reaching the substrate surface, the relative flux of VUV photons reaching the surface, and the relative fractions of atomic and molecular species generated in the plasma under a variety of pressures and gas input flow fractions. This work is relevant to the growth conditions for plasma enhanced atomic layer expitaxy of AlN, InN, TiO_2, and Ga_2O_3 films.

AF-TuP-31 How ALD has Changed: Analyzing Topic Evolution through Text Mining, ***Elsa Alvaro**,* Northwestern University*; A Yanguas-Gil,* Argonne National Laboratory

Using a combination of bibliometric, social network, and text analysis, we recently examined the rate of knowledge production as well as changes in authors, journals, and collaborators, in the field of atomic layer deposition [1]. As a result of this study, we compiled a dataset comprising more than 11,000 individual papers published between 1981 and 2015.

In this work, we analyze the content of the abstracts in our ALD dataset by using topic modelling and other text mining tools. The result provides information on the topics or hidden semantic themes present in our document collection; the study of the evolution of those topics over time can help further understand the history of ALD. In addition, we focus on extracting chemical compounds present in the abstracts as a way of identifying different precursors and ligands in the ALD literature.

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AF-TuP-32 Ruthenium Atomic Layer Deposition on Platinum using the ToRuS Precursor*, **Daniel Potrepka**,* U.S. Army Research Laboratory*; N Strnad,* University of Maryland*; G Rayner,* Kurt J. Lesker Company

The Ru precursor ToRuS was developed to provide for the growth of Ru thin films at substrate temperatures of 75-100°C. Preventing deleterious Ru film accumulation in a hot-wall reactor while providing sufficient ToRuS reactivity for the deposition of Ru onto the substrate is difficult due to the limitation imposed on the wall temperature by this low-temperature ToRuS ALD window which, in turn, limits the effectiveness of the purge following the ToRuS dose. In contrast, a Ru precursor with an ALD window of 100-150°C has been successfully used to deposit a Ru seed layer onto a metal contact for suitable Cu growth in FERAM and DRAM metal-contact processes [1].

In this study, nanoscale Pt films were obtained by flash RF sputtering depositions that used short RF plasma times to obtain 3-5 nm thick Pt films. The ToRuS precursor and H_2 co-precursor were then used to thermally deposit Ru with a 100°C substrate temperature, 21 °C ampoule temperature, and 40°C chamber and line temperature. The process used will be described and methods for overcoming observed challenges discussed. An analysis of the Ru deposition on the Pt will be presented. Ru growth conditions on 500 nm thermal SiO_2, obtained using the same deposition conditions, will be analyzed to inform our assumptions of growth rate on Pt. Sample characterization techniques used in this work include in-situ and ex-situ spectroscopic ellipsometry, sheet resistance, and scanning electron microscopy.

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AF-TuP-33 Plasma-Enhanced Atomic Layer Deposition of Ruthenium Using Ru(EtCp)$_2$ & O_2-Plasma on Platinum*, **G. Bruce Rayner, Jr.**,* The Kurt J. Lesker Company*; B Johs,* Film Sense*; B Liu,* The Pennsylvania State University*; N O'Toole,* The Kurt J. Lesker Company*; D Potrepka,* U.S. Army Research Laboratory

Ruthenium is a noble metal that continues to be of considerable interest as an electrode material for microelectronic device applications. Thermal and plasma-enhanced atomic layer deposition (PEALD) of Ru using molecular O_2 gas and O_2-plasma requires controlled exposure conditions to ensure the elemental phase is obtained. The Ru precursor utilized for this work was bis(ethylcyclopentadienyl)ruthenium [Ru(EtCp)$_2$].

To address nucleation delay during Ru PEALD using Ru(EtCp)$_2$ and O_2-plasma at 300°C, platinum seed layers were used as starting surfaces for subsequent Ru PEALD nucleation and growth [1]. Pt PEALD using trimethyl(methylcyclopentadienyl)platinum (MeCpPtMe$_3$) and O_2-plasma was performed at 300°C in the same reactor prior to Ru growth. The effects of Pt seed layer thickness on Ru PEALD nucleation and growth, as well as O_2-plasma exposure conditions were investigated in-situ by ellipsometry in real-time to optimize process conditions. Depth-profile XPS confirmed the presence of a Ru film with no oxygen, and the Pt seed layer. SEM and AFM images suggested an island nucleation growth mode. Ru surface roughness measured by AFM showed a systematic decrease with increasing Pt seed layer thickness. The films were also characterized ex-situ by ellipsometry, x-ray reflectometry (XRR), and transmission electron microscopy (TEM) to determine thickness and morphology.

The nucleation delay for film growth could be directly observed by changes in the in-situ ellipsometric data. Without the Pt seed layer, essentially no Ru film growth was observed. Even a 20-cycle Pt seed layer (0.2 nm thick) enabled the growth of a Ru film, though the resulting Ru film thickness and properties were strongly dependent on the Pt seed layer thickness.

Since it is the critical parameter for many applications, the Ru film resistivity was determined by ex-situ four point probe (4pp) measurements. The Ru film resistivity was also estimated from the in-situ ellipsometry data analysis, using a Drude optical model. A linear correlation was observed between the ex-situ 4pp and in-situ ellipsometry resistivity measurements, demonstrating that in-situ ellipsometry measurements could be used to optimize the conductivity properties of thin Ru films.

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AF-TuP-34 Atomic Layer Deposition of Ru Thin Films Using 'Rudense' as a Ru Precursor and Oxygen Gas as a Reactant*, **Dae Seon Kwon**, C An, S Kim,* Seoul National University, Republic of Korea*; H Song,* Seoul National University, Repubic of Korea*; S Cho, S Cha,* Seoul National University, Republic of Korea*; T Furukawa, T Hayakawa,* TOSOH Corporation, Republic of Korea*; K Kawano,* TOSOH Corporation, Repubic of Korea*; C Hwang,* Seoul National University, Republic of Korea

Ru attracts much attention as a potential electrode for the next-generation dynamic random access memory (DRAM) capacitor due to its promising properties such as low resistivity (~7 μΩ·cm) and high work function (~4.7 eV). Atomic layer deposition (ALD) is the most suitable method among numerous thin film growth techniques to grow uniform and conformal film over three-dimensional structures. Upon Ru deposition by ALD, selecting appropriate Ru precursor is crucial, because the film growth behaviors and its properties are highly affected by the Ru precursor used. Currently, metal-organic precursors like Ru(EtCp)$_2$ and (Ru(EtCp)(η^5-CH$_2$C(Me)CHC(Me)CH$_2$)) (RuDER) are widely used, but problems such as long incubation time and low growth rate still exist. Therefore, it is necessary to develop Ru precursor with improved performance. A new Ru precursor, Rudense (Ru(EtCp)(η^5-CH$_2$C(Me)CHC(Me)O)) (TOSOH Co.), was developed, which was adopted to grow Ru film via an ALD method in this study. The ALD behavior of Ru thin films using Rudense and O_2 as a Ru precursor and a reactant, respectively, was examined at temperatures ranging from 250 to 270°C. At 250°C, the self-limiting growth was confirmed by controlling the Ru precursor and O_2 feeding time. A saturated growth rate of 0.09 nm/cycle and very low incubation cycles (<20) were obtained, which are highly improved results compared with the results from RuDER. Also, well crystallized Ru phases and low resistivity (~ 70 μΩ·cm) were observed from an extremely thin film (< 3 nm). Chemical and structural analysis, such as X-ray photoelectron spectroscopy(XPS), time of flight secondary ion mass spectrometry(ToF-SIMS) and atomic force microscopy(AFM) measurements were conducted to examine the deposited films in more detailed manner. Finally, a high enough step coverage (> 90 %) was also obtained from the Ru thin film on a capacitor hole with a dimension of diameter of 120 nm and depth of 2400 nm.

AF-TuP-35 *In-situ* Half-Cycle Analysis of Atomic Layer Deposited Zinc Oxide as Channel Layer in Thin Film Transistor*, **Harrison Kim**, A Lucero, S Kim, J Kim,* The University of Texas at Dallas

Thin film process monitoring of atomic layer deposition (ALD) has been adopted as the versatile technique to identify both chemical and physical properties of ALD films. However, currently no tool is suitable to monitor the sub-nm device physics even if we are already in the era facing beyond 10 nm node semiconductor processes.

Hence, we have developed an ultra-high vacuum (UHV) cluster tool equipped with thermal processing, plasma surface treatment, thin film deposition, and electrical characterization which can all be performed *in-situ*. With this feasibility, it is possible to witness the genuine changes in interface states without any ambiguity arising from the oxidation or contamination from the atmosphere. Initial results are demonstrated by depositing low temperature ALD zinc oxide (ZnO). Thin film transistors (TFTs) with inverted-coplanar structure were prepared. ALD Al_2O_3 is used as gate insulator with aluminum defined gate and source/drain electrodes. Diethylzinc (DEZ) and water (H_2O) is used as the precursors to grow ALD ZnO at 100°C. DEZ and H_2O half-cycle analysis is carried out to study ALD ZnO behavior which is used as the channel layer in the TFTs. 45 ALD cycles to deposit ZnO was specifically chosen as it is the regime where ALD ZnO shows first switching behavior in vacuum (on/off ratio: ~10^2). Subsequently, one full ALD cycle shifts the threshold voltage (V_{th}) negatively. Additional DEZ half-cycle further results in a negative V_{th} shift along with a simultaneous increase in on and off current. Moreover, H_2O half-cycle decreases off current, making ALD ZnO film more semiconducting (on/off ratio: ~10^4). By using ozone as another oxidant, role of hydrogen as a shallow donor will also be discussed. We believe that our findings support the fundamental understanding on the origination of dominant n-type doping seen in ZnO.

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AF-TuP-36 Investigation of Low Temperature Silicon Nitride Deposition using Hexachlorodisilane and Ultra-High Purity Hydrazine*, **Antonio Lucero**,* The University of Texas at Dallas*; A Kondusamy,* University of Texas at Dallas*; S Hwang, X Meng, H Kim,* The University of Texas at Dallas*; D Alvarez, J Spiegelman,* RASIRC*; J Kim,* The University of Texas at Dallas

Silicon nitride is playing an increasingly important role in the semiconductor industry for use in self-aligned patterning, 3D integration, and memory applications. Conventional silicon nitride deposition relies on either high temperature or plasma to generate reactive species. Both techniques can deliver high quality films in terms of wet etch rate, uniformity, and dielectric properties.[1] However, modern applications demand lower deposition temperatures (< 400°C) and improved conformality over high-aspect ratio structures. Newly available ultra-high purity hydrazine sources have been successfully used to deposit metal nitrides at low temperature.[2] In this work we study the low temperature thermal ALD growth characteristics of silicon nitride using hydrazine and hexachlorodisilane (HCDS) and evaluate the physical properties of the films. Thermal ALD results with hydrazine will be compared to those from films deposited using PEALD with HCDS and ammonia in the same temperature range.

Silicon nitride films are deposited using a thermal ALD reactor from 250-400°C. Hydrazine is supplied from a BRUTE hydrazine source. Growth with hydrazine shows saturation behavior, with growth per cycle (GPC) gradually increasing with hydrazine exposure. GPC from 0.4-0.5 Å/cycle is observed at 400°C with refractive index of 1.813. X-ray photoelectron spectroscopy analysis is used to confirm film stoichiometry: SiN films with low oxygen (< 2%) and chlorine (< 1%) impurities can be achieved. These results are similar to those for films deposited with HCDS and NH_3 using PEALD at 360°C. Film density and wet etch rate results are compared for films deposited at different temperatures. Nucleation behavior on hydrogen terminated silicon, hydroxyl terminated silicon, and hydrazine treated silicon will be discussed.

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AF-TuP-37 Remote Plasma-Enhanced Atomic Layer Deposition of Metallic TiN Films with Low Work Function and High Uniformity*, Y Zhu, F Li, Y Shen, J Zhang,* ***Xiao Chen**,* Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, China

Thermal stability of metal/*n*-GaN contact is critical for its applications in microelectronic and optoelectronic devices . Metal Ti is generally used to make ohmic contact on *n*-GaN after high temperature annealing, and the key factor is to form TiN at the interface. To reduce the processing temperature and improve the reliability, metallic titanium nitride (TiN) thin film has been proposed to substitute traditional metals (such as Ti) in the contact structures, due to its low work function and high blocking effect. For this novel approach, the first step is to fabricate high quality TiN films. Here we adopted remote plasma-enhanced atomic layer deposition (RPEALD) method to deposit TiN films under well-controlled conditions. Stoichiometric TiN films (Ti: N ~ 1: 1) with low oxygen contamination (<5%) have been deposited uniformly on 2” substrates in a large temperature range of 250 ~ 400 . The work function of TiN films is quite low (~ 3.7 ± 0.1 eV) comparing to metal Ti (~4.33 eV), and almost independent to the growth temperature and substrates. Furthermore, thin TiN film exhibits good blocking effect on metal diffusion. Strong Fermi edge and high conductivity indicate excellent metallic property of the TiN films. This study of TiN film growth paves the way to establish low temperature process and improve the thermal stability of ohmic contacts for wide band gap semiconductor-based devices.

AF-TuP-38 In Situ Surface Reaction Mechanism Studies on ZrO_2 Atomic Layer Deposition from Tetrakis(ethylmethylamino)zirconium*, W Xu,* Colorado School of Mines*; K Sharma, D Hausmann,* Lam Research Corp.*;* ***Sumit Agarwal**,* Colorado School of Mines

The continued downscaling of modern semiconductor devices has led to the introduction of high-*k* dielectric materials. Atomic layer deposition (ALD) has emerged as a very promising technique for depositing high–*k* thin films. Among the various candidates for the high-*k* dielectric materials, ZrO_2 has been widely investigated for alternative gate dielectric materials because of its high dielectric constant, high breakdown field, excellent thermal stability, and compatibility with Si processing. Understanding the surface reaction mechanisms during the ALD of ZrO_2 will assist in controlling and optimizing the growth process, and therefore, advance the development of new ALD processes and precursors.

Herein, we report on the surface reaction mechanisms during ZrO_2 ALD using tetrakis(ethylmethylamino)zirconium (TEMAZ) as the Zr precursor. TEMAZ was chosen because, unlike $ZrCl_4$, the surface reaction produces no corrosive byproducts. Oxygen plasma, O_2, H_2O, and C_2H_5OH were used as the oxygen sources to grow the ZrO_2 films. The corresponding surface reactions during the ALD process were monitored using in situ attenuated total reflection Fourier transform infrared spectroscopy, which allows us to identify the surface reaction sites and adsorbed surface species that lead to film growth. In addition, the growth per cycle was measured using in situ four–wavelength ellipsometry.

In both O_2-plasma-based ALD and O_2-based ALD, the main reactive sites for TEMAZ are surface carbonates that are formed after exposure of the hydrocarbon terminated surface obtained after the TEMAZ cycle to these oxygen sources. Previously, we had also identified surface carbonates as the reactive sites for O_3- and O_2 plasma-based ALD of TiO_2 and Al_2O_3. In the H_2O-based ALD process, as expected, -OH groups were the reactive sites for TEMAZ (see Figure 1) and there was minimal carbon incorporation in the film. In C_2H_5OH-based ALD, the amide ligand terminated surface obtained after the TEMAZ cycle reacts with C_2H_5OH, forming surface $-OCH_2CH_3$ groups (see Figure 2). However, the ligand-exchange reaction is not complete in the subsequent TEMAZ cycle with net incorporation of $-OCH_2CH_3$ groups. Even up to a temperature of 300°C, we did not observe the decomposition of the $-OCH_2CH_3$ groups via *b*-hydride elimination mechanism.

AF-TuP-39 Wafer-scale Characterization of Atomic Layer Deposited Zinc Oxide Thin Films using a Temperature Gradient Combinatorial Approach*, H Kim, A Lucero, S Kim,* ***Jiyoung Kim**,* The University of Texas at Dallas

Electrical properties (*e.g.* resistivity or carrier concentration) of atomic layer deposited (ALD) zinc oxide (ZnO) can be easily modulated depending on the process conditions. However, complex transport behavior and insufficient characterizations make it difficult to comprehend the inherent nature of the electrical properties of ALD ZnO clearly. Thus, the combinatorial approach is suggested as one of the possibility to address this challenge. Since various growth conditions can be processed through a single experiment, the combinatorial approach helps to screen large structural or compositional differences rapidly. It provides a high-throughput methodology to develop or optimize material properties as desired.

Therefore, a rapid methodology to correlate electrical properties of ALD ZnO with nanostructures and compositions is developed through combinatorial study. Systematic study on the temperature dependent ALD ZnO is performed by intentionally introduced temperature gradient in the process reactor. A gradual temperature gradient (204°C to 224°C) over the 100-mm wafer is successfully achieved. Then, we acquired comprehensive information on structural, compositional, and electrical properties through a single experiment. X-ray diffraction (XRD) confirmed that ALD ZnO crystallized preferentially along the (002) orientation at a higher process temperature. Based on XRD and using Scherrer equation, we calculated the grain size that gradually varies as a function of process temperature: higher the process temperature, larger is the grain size. E_2 (437 cm^{-1}) peak in Raman spectroscopy is strongly correlated with the ZnO crystallinity as determined by XRD. Lastly, we found that ALD ZnO crystallinity and its grain size determines the film resistivity. This could be attributed to the enlarged conducting zinc oxide domain that increases carrier concentration. Hall mobility effect on conductivity is not considered significantly since its variations over the 100-mm wafer is negligible. An efficient wafer level characterization of ALD deposited material is demonstrated and feasibility of the combinatorial approach, in terms of visualization and interpretation of the material properties, is also shown.

This work was supported by the Creative Materials Discovery Program on Creative Multilevel Research Center (2015M3D1A1068061) through the National Research Foundation(NRF) of Korea funded by the Ministry of Science, ICT & Future Planning

AF-TuP-40 Study of Hollow Cathode Plasma Enhanced Atomic Layer Deposited Silicon Nitride: Relationship between Film Properties and Wet Etch Rate*,* ***Harrison Kim**, X Meng, A Lucero, L Cheng, S Kim, Y Byun, S Hwang,* The University of Texas at Dallas*; M Telgenhoff, B Hwang,* Dow Chemicals*; J Kim,* The University of Texas at Dallas

Plasma-enhanced atomic layer deposited (PEALD) silicon nitride (SiN_x) gathered great attention amongst as it can be grown at lower process temperature (< 400°C) with exceptional wet chemical resistance (wet etch

rate, WER< 2 nm/min in dilute hydrofluoric acid). However, despite the fundamental difference in growth mechanism between plasma-enhanced chemical vapor deposition (PECVD) and PEALD, study of film properties affecting WER of SiN_x has been primarily limited to the PECVD grown SiN_x. Moreover, irrespective of the type of Si precursor or type of plasma co-reactants used, research have been done mostly to evaluate the effect of hydrogen bonding density on WER.

Herein, we not only highlight the effect of hydrogen bonding concentration on the bulk film densities influencing the WER of PEALD grown SiN_x, but also provide insight on the influence of chemical bonding states of hydrogen or the effect of the residual impurity from the precursor. A customized ALD system installed with hollow cathode plasma source was employed to study SiN_x comprehensively. Hexachlorodisilane (HCDS, Si_2Cl_6) is adopted as Si precursor since it is the most commonly used precursor type for more than a decade owing to its compatibility with both thermal ALD and PEALD. Then, we explore the effect of process temperature (270°C - 360°C) and plasma gas composition (N_2/NH_3 or Ar/NH_3) on WER of SiN_x. Accordingly, we found the changes in hydrogen bonding states and reduction in hydrogen bonding concentration arises from either (1) thermal activation or (2) plasma co-reactant environment. Moreover, we propose mechanisms that affect the WER of SiN_x: hydrogen bonding states and residual impurity content. As a proof of principle, overall correlations are shown. Our findings highlight the significance of designing growth conditions properly through optimizing the process temperature, plasma gas compositions, and choice of Si precursor or type of plasma co-reactants to achieve lower WER.

AF-TuP-41 Investigation of Stability of Boron Oxide and Phosphorus Oxide Thin Films Grown by PALD*, **Bodo Kalkofen**, K Huang, M Silinskas,* Otto von Guericke University, Germany*; S Beljakowa,* Friedrich-Alexander-Universität, Germany*; B Garke,* Otto-von-Guericke University, Germany*; M Lisker,* IHP, Germany*; E Burte,* Otto von Guericke University, Germany

Plasma-assisted atomic layer deposition (PALD) was carried out for growing thin oxide films containing dopants for silicon, germanium, and SiGe. Boron oxide and phosphorus oxide films were deposited as source layers for p type doping and n type doping, respectively. Tris(dimethylamido)borane (TrisDMAB) was used as boron containing precursor and tris(dimethylamido)phosphine (TrisDMAP) as phosphorus containing precursor. The experiments were carried out in a commercial PALD reactor build by Sentech Instruments GmbH, Berlin. Dosing was achieved by "vapor-draw" into a nitrogen carrier flow by fast acting valves. Oxygen radicals in the PALD processes were generated by a remote inductively coupled plasma source.

The boron and phosphorus containing oxide films were highly unstable in ambient air and showed to some extent remarkable degeneration patterns after contact to air (see examples in Fig.1 and Fig.2). The development of the film degradation with time in air was investigated in detail. Films were stabilized by mixing them with stable oxides (e.g. antimony oxide) or by applying capping films of varying thickness. The films and film stacks were measured by spectroscopic ellipsometry and composition of the film stacks was analyzed in detail by x-ray photoelectron spectroscopy (XPS) and secondary-ion mass spectrometry (SIMS).

AF-TuP-42 Effects of Substrate Temperature and Oxygen Deficiency on the Electronic Properties and Optical Dispersion of MgO Thin Films*, **Yus Rama Denny**, T Firmansyah,* University of Sultan Ageng Tirtayasa, Indonesia*; S Lee,* Chungbuk National University*; H Kang,* Chungbuk National University, Republic of Korea

The electronic and optical dispersion of magnesium oxide (MgO) thin films were investigated by means of X-ray photoelectron spectroscopy (XPS), reflection electron energy loss spectroscopy (REELS) and ultra-violet photoelectron spectroscopy (UPS). MgO thin films were prepared on Si substrates by using electron beam evaporation deposited at different substrate temperature and oxygen flow rate. The O 1s peak from XPS spectra showed that the hydrate MgO, Mg(OH)2, was detected in the surface of MgO thin film at room temperature (RT) grown without oxygen partial pressure and it was decreasing at substrate temperature above 300°C. Meanwhile, the hydrate MgO peak was not found in the film deposited under oxygen partial pressure. The UPS results showed that the work functions of the MgO thin films were 4.69, 5.2, 4.65, and 4.29 eV for the films deposited at RT, 300°C, 400°C, and 500°C, respectively. The REELS spectra revealed that the band gaps of MgO thin films were varied with different substrate temperature and oxygen flow rate. The optical properties were also examined REELS data using Tougaard-Yubero model. The dispersion behavior of the refractive index from REELS results was studied in terms of the single-oscillator Wemple-DiDomenico model. The results showed that the different substrate temperature of MgO thin films caused a change in the dispersion parameters in contrast to the static values of refractive indices and dielectric constant which remained the same. Our work demonstrated that the substrate temperature and oxygen deficiency played a crucial role in improving the electronic properties of MgO thin films and REELS is an efficient tool to study the optical properties of a material obtaining the optical parameters.

AF-TuP-43 Design of Hierarchical Metal Oxide Nanowires with Tunable Orientation by Atomic Layer Deposition*, **Susanta Bera**, S Kwon,* Pusan National University, Republic of Korea

Fabrication of metal oxide semiconductors thin films having hierarchical arrangement are the most exciting prospect for optoelectronic application. One of the novel hierarchical nanostructures are branched metal oxide nanowires (NWs) representing a critical building block of the nanomaterials which greatly enhances the optical, electronic and mechanical properties. A variety of fabrication approaches have been investigated to form high-quality hierarchical NWs, including several bottom-up solution or gas-phase processes. However, ability to control the feature size, density, and orientation of the morphology within each level of the hierarchy over large area is a key challenge. However, atomic-scale precision can control the features of the morphology over a macroscopic area. But, attempting the approach can lead to dramatic variations in the morphology during coating on nonplanar surface due to inability to control the parameters of the deposition process. However, atomic layer deposition (ALD) is one of the powerful technique which allows subnanometer precision in film thickness, interfacial composition, morphology, and microstructure of different levels of hierarchy. Herein, we demonstrate the use of ALD to design hierarchical metal oxide nanowires with tunable orientation via controlling each level of hierarchy on wide range of substrates. In this work, some chemical and physical parameters are found to play key role on growth of the hierarchical thin films. In the next step, sol-gel assisted thin layers of $BiVO_4$ was coated on the hierarchical thin films and proposed to use as a photoanodes for photoelectrochemical water splitting. It is found that the hierarchical films show enhanced photoelectrochemical performance. We demonstrate that the hierarchical morphologies are beneficial for efficient light harvesting as well as additional direct conduction pathway to reduce the charge recombination.

AF-TuP-44 Development of High Performance ALD_TiN Process System*, **Jinho Jeon**, J Kang, C Shin, Y Park, S Kim,* Wonik IPS, Republic of Korea

In the past two decades, there has been a significant paradigm shift in Memory Devices. Specifically, (DRAM: Planer -> RCAT -> BCAT, FLASH: Planer -> 3D V-NAND (24nm), and LOGIC: HK/MG -> FinFET (14nm) -> GAA). These new innovations and technologies represent significant improvements from the current systems. Looking at it from the perspective of the Metal Process, we can analyze the ALD_TiN Film used in DRAM Cell Capacitor supporter and 3D NAND W/L barrier metal.

In order to increase the capacities of DRAM Cells, the number of Capacitor Nodes has been increased. In order to prevent bending issues of nodes (high Aspect ratio), ALD_TiN has to be created in high temperature for High Density, Good Step Coverage to be functional. To satisfy these need, the use of different Capacitor materials and innovations around shift from ZAZ to ZAZA….. are being thoroughly researched. In 3D V-NAND, as height of ON Stack increases, W/L (high surface area /Gate W B/M) Gapfill becomes increasingly difficult. The combination of low temperature ALD-TiN / ALD-W is being used to solve the complicated Gate Gapfill Process.

In response to the evolving Device, the research facility has successfully developed a TiCl4 gas base's ALD_TiN Film using the New Platform, achieving greater productivity and stability.

By developing the Low Thickness TiN Film used in 3D-NAND W/L B/M under 430~450 degrees, results of Step coverage above 98%, Film Continuity under 35A, and Density above 4.5g/cc have been successfully achieved. Also, by developing the TiN Film used in DRAM Capacitor (Storage and Plate) in high temperature of above 520~650 degrees, result of Good Step Coverage above 96% has been successfully achieved. This allowed for Cell Capacitor's stability.

Through multiple simulations of Shower Head, Gas Path and chamber designs optimized for ALD Process, system that stabilizes gas purging and pumping was created. The resulting high quality TiN Film has D/R=0.30A~0.45A/cycle and Cl level (SIMS/count) of less than 3xE-3.

AF-TuP-45 Deposition of Thin (0.5 – 42 nm) Alumina Films by ALD to Determine their Optical Constants from 190 – 1688 nm, ***Dhruv Shah**, D Patel, D Jacobsen, J Erickson, M Linford,* Brigham Young University

Atomic layer deposition (ALD) is widely used in the semiconductor industry to provide atomic level control of film thickness and uniformity. Here we report thermal ALD (332 ºC) of thin films of alumina from water and trimethyl aluminum (TMA) precursors. The alumina deposition was optimized by varying the dose and purge times for both precursors with an aim to obtain uniform film thickness and growth per cycle (GPC). Films of varying thickness (0.5 – 42 nm) were characterized by spectroscopic ellipsometry (SE) and X-ray photoelectron spectroscopy (XPS). XPS clearly showed an increase in surface aluminum content with increasing number of ALD cycles. The film thickness was measured by spectroscopic ellipsometry (SE), where film growth was extremely linear over the entire range probed (5 – 500 deposition cycles). The SE data from multiple thin films were used to build an optical model in a multi-sample analysis that included parameterized optical constants for alumina and film roughness. This model yielded a single set of optical constants for alumina over a wide range of thicknesses (0.5 – 42 nm) and wavelengths (190 -1688 nm). Because of the importance and frequency of alumina deposition by ALD, these optical constants should be useful to others in the field.

AF-TuP-46 Investigation of the Si doping effect on the Ga_2O_3 Films Prepared by Atomic Layer Deposition, ***Hong-Ping Ma**, H Lu, T Wang, H Chen, X Li, J Chen,* Fudan University, China*; J Zhu,* Tongji University, China*; D Zhang,* Fudan University, China

Precise control dopant composition and systematic study the doping effect are critical to the production of functional films with desired properties. In this study, we make the original try to use atomic layer deposition (ALD) to fabricate Si-doped Ga_2O_3 films. Optical spectrometry, Hall measurements, X-ray photoelectron spectroscopy and several other measuring techniques were applied to characterize and analyze the optical, electrical and structural properties of the doped films. The experiment results indicated that the content of the Si has an obvious influence on the photoelectrical properties of Ga_2O_3 films. The refractive index of Ga_2O_3 films was decreased with the increasing of the Si content. The Ga_2O_3 energy gap can be tuned from 4.75 to 4.92 eV through Si doping. The average transmittance was larger than 95% from ultraviolet to visual wavelength for all these Si-doped Ga_2O_3 films although the optical transparency was reduced after the Si doping. These results suggesting that the Ga_2O_3 film-based devices such as transparent electrodes, photodetectors or thin film transistors can be further optimized the structural quality and conductivity by improving ALD process.

AF-TuP-47 Magnetoelectric Properties of Atomic Layer Deposited ZrO_2-HfO_2 Thin Films, ***Kristjan Kalam**, H Seemen, P Ritslaid, A Tamm, K Kukli, M Mikkor,* University of Tartu, Estonia*; R Stern,* National Institute of Chemical Physics and Biophysics*; S Dueñas, H Castán,* University of Valladolid

ZrO_2 and HfO_2 have been materials of interest due to their several potential applications, for example in microelectronics as a memory material [1]. In this study, ZrO_2-HfO_2 films were grown by atomic layer deposition (ALD) on planar Si(100) and TiN substrates by alternately applying certain amounts of constituent binary oxide growth cycles. $ZrCl_4$ and $HfCl_4$ were used as zirconium and hafnium precursors, respectively. The oxidizer was H_2O.

Films with various compositions were grown, cation ratio Hf/Zr varied from 0.2 to 10 as measured by X-ray fluorescence spectrometer. Some films were grown as solid solutions and some as nanolaminates. The film thicknesses, measured by spectroscopic ellipsometry, varied between 9 and 22 nm. A nanolaminate, where 8 nm of HfO_2 is deposited on Si(100) and 10 nm of ZrO_2 is deposited on top of HfO_2, is ferromagnetic, measured with vibrating sample magnetometer. The same sample deposited on a TiN substrate was subjected to a Sawyer-Tower measurement and exhibited ferroelectric-like behavior.

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AF-TuP-48 Selective Film Stripping Techniques for In-FilmTrace Metal Analysis Using Inductively Coupled Plasma Mass Spectrometry (ICP-MS), ***Jaya Chowdhury**, J Huang,* ChemTrace*; K Fu,* Chemtrace*; P Sun, L Shi,* ChemTrace

Atomic layer deposition (ALD) of stacked films often entail thin film deposition based on the sequential use of a gas phase chemical processes[1]. Possibilities for atomic layer depositions to leave some un-reacted precursor elements in the form of impurities can be high. In order to achieve ultra-high purity products, essentially free from trace metals and organic impurities, they need to be fully qualified at the precursor level[2] as well as upon deposition of films[3].These films require full characterization for process optimization to eliminate device critical contaminants in the mature process[4]. The impact of not doing so can be very costly in terms of low yielding and unreliable final product. One of the technical challenges for in-film trace metal contamination analysis is the lack of selective film stripping sample preparation methods.

In this paper, different film surface and in-film trace metal analysis techniques will be described. Results will be discussed as part of a case study for W/TiN/SiOx stacked film wafers. Different stripping chemistries (acid, base, peroxide, etc.) and stripping conditions (etch time, chemical ratios, etc.) studied for target film removal will be elaborated upon. Using the optimized selective film stripping sample preparation recipe and ICP-MS, trace metals in the W film layer have been analyzed with efficient film removal selectivity and satisfactory method detection limits.

Keywords: Selective film stripping, trace metals, device critical contaminants, ICP-MS, wafer films

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AF-TuP-49 Study on Silicon-nitride ALD Process at Low Temperature by a High Density Multiple-ICP Source, ***Ho-Hyun Song**, H Chang,* KAIST, Republic of Korea

Plasma sources, such as CCP (Capacitively Coupled Plasma), ICP (Inductively Coupled Plasma), etc., have been widely used for fabrication processes in the semiconductor, flat-panel display, and solar-cell industries. In next-generation semiconductors, the necessity of high concentration nitride film deposition due to decrease of gate line-width and low temperature process using high density plasma with good step coverage at high aspect ratio have been required.

We have developed 7-coil multiple ICP sources (for 300 mm wafer), generating high-density & uniform nitrogen plasma by delivering high power (~10 kW) at low temperatures (300 ~ 550 K). Also, we have improved the plasma source to a magnetized-ICP source for generating more high density plasma. Using this source, a silicon nitride film was deposited on a 300 mm wafer by PE-ALD (Plasma Enhanced Atomic Layer Deposition) method. We also have conducted PE-ALD process experiments at low temperature conditions (300 ~ 550 K) and have analyzed the properties of deposited silicon nitride films. In order to analyze the characteristics such as composition ratio according to the depth of the thin film, we performed SIMS and XPS analysis. Through this study, it has been confirmed that the silicon nitride film, deposited by our sources, was very similar to that of the general LP-CVD process, and also the good step coverage was confirmed. We also have repeated the same experiment and the same analysis for SiCN thin film deposition.

AF-TuP-50 Self-Organized Growth of TiO_2 Anatase Nanorods on Graphene Nanoplatelets by Atomic Layer Deposition, ***Damiano La Zara**, F Grillo, M Kreutzer, J van Ommen,* Delft University of Technology, Netherlands

Understanding the spontaneous organization of atoms on well-defined surfaces promises to enable control over the shape and size of supported nanostructures. Atomic layer deposition (ALD) is an established gas-phase technique for the layer-by-layer deposition of conformal thin films in applications that require atomic-level precision. Given its unparalleled precision and scale-up potential, considerable research effort has been put in expanding its capability to the deposition of nanostructures other than thin films such as nanoparticles (NPs). However, the formation and growth of NPs is mediated not only by ALD surface chemistry but also by non-equilibrium phenomena such as adatom and NP diffusion and aggregation. Since such mechanisms are a strong function of reaction conditions and adlayer-support interactions, control over the NP size can be achieved only under certain system-dependent conditions. Nonetheless, if properly

understood, unconventional growth pathways can expand the range of nanostructures that can be synthesized by ALD. After achieving control over the NP size, the natural next step in the advancement of ALD of NPs is the synthesis of shape-controlled NPs and, in particular, of 1D nanocrystals such as nanorods.

Here, we report on the bottom-up formation of TiO_2 anatase nanorods on gram-scale batches of graphene nanoplatelets via $TiCl_4/H_2O$ ALD carried out at temperatures as low as 300 °C. We show that nanorods as large as 200 nm form even after only 5 cycles, indicating that the growth is dominated by diffusive aggregation rather than by a layer-by-layer mechanism. In particular, complex structures such as V-shaped and curved nanorods are observed. Prolonged annealing experiments show that the sequential nature of the ALD process is crucial for the nanorods formation. Statistical analysis of the shape of the nanostructures at different exposure times reveals a competitive process between growth pathways leading to either symmetric growth, and thus NPs, or asymmetric growth, and thus nanorods. In particular, the population of the different observed nanostructures is a non-linear function of the exposure time of $TiCl_4$ and H_2O even at saturation conditions. The number of cycles affects mostly the number rather than the size of the nanorods. Crucially, high-resolution transmission electron microscopy reveals that the TiO_2 nanocrystals can undergo oriented attachment and that the width of the nanorods is bound by {011} facets. Finally, analysis of the relative lattice orientation clearly shows an in-plane rotational alignment between the lattices of the TiO_2 nanocrystals and graphene nanoplatelets.

AF-TuP-51 Surface Reaction Routes of HCDS on SiO_2 using Density Functional Theory*, **Ki-Yung Kim**, D Shin, Y Kim,* Korea University of Technology and Education, Republic of Korea

HCDS (Si_2Cl_6) is still the choice of silicon ALD process in semiconductor industry mainly because of its self-limiting reaction and cost benefit. HCDS, however, does not follow the typical and sequential 'adsorption-reaction' process because of its low surface adsorption energy; the adsorbed molecule would rather desorb from surface than react with it. We try to rationalize its ALD characteristics by considering the kinetic energy of molecules and the succeeding reaction routes. Temperature should be raised to increase the number of molecules with high kinetic energy. This high thermal energy, however, can transform the reaction process from ALD to CVD. We found that the succeeding reaction routes could still be self-limiting at this high temperatures.

AF-TuP-52 Quadrupole Mass Spectrometer for ALD Process Monitoring - Challenges and Solutions*, **Uwe Meissner**,* ALD, Germany

The performance and reliability of Quadrupole Mass Spectrometry (QMS) Systems have been improved significantly over the last few years, and as such employed extensively in a range of semiconductor manufacturing applications as Residual Gas Analyzers (RGA).

Today, RGA systems are widely used to monitor, optimize and control different vacuum-based processes. New innovations in RGA technology and products can provide significant analytical benefit to enable optimization and monitoring for Atomic Layer Deopisition (ALD) and Atomic Layer Etch (ALE) processes.

There are significant developments with respect of improving sensitivity, detection limits and robustness of the QMS (RGA) systems. We will present solutions for improved ion source technology and system robustness. We will discuss specific requirements and solutions for QMS (RGA) applications for Thermal ALD and Plasma Enhanced (PE) ALD processes.

AF-TuP-53 Develop Inhibitor-Utilizing Atomic Layer Deposition for Synthesizing Few-layer Molybdenum Disulfide Thin Films*, **Woojin Jeon**,* Dankook University, Republic of Korea*; Y Cho, S Jo,* Samsung Advanced Institute of Technology*; J Ahn,* Korea Maritime and Ocean University, Republic of Korea*; S Jeong,* Soongsil University, Korea

We present a novel synthesis technique to produce high-quality MoS_2 thin films by utilizing an inhibitor for Mo precursor adsorption in an atomic layer deposition (ALD) process. The spectroscopic and microscopic analysis results revealed the dependence of the crystal and chemical structure of the deposited MoS_2 films on the concentration of the Mo precursor adsorbed on the substrate in the initial stage of the ALD process. The mechanism for this dependence was examined theoretically and experimentally. Based on this, we successfully synthesized highly crystalline few-layer MoS_2 samples on SiO_2.

ALD Applications
Room 107-109 - Session AA3+AF+EM-WeM
AA+AF+EM

Moderator: Iian Buchanan, Versum Materials, UK

8:00am **AA3+AF+EM-WeM-1 Fabrication of TiO_2 Interconnected Nanotubes by ALD and Synthesis of g-C_3N_4/Au/TiO_2 Heterostructure for Photocatalytic Water Splitting**, ***Li-Chen Wang***, *L Tsai, C Liu, T Perng,* National Tsing Hua University, Republic of China

Recently, the catalysis science has ascended to a new horizon due to the advent of novel nanotechnologies such as atomic layer deposition (ALD) with the capability of fabricating a marvelous panoply of nanomaterials. The sequential and self-limiting gas-solid surface reactions of the ALD process enable to deposit extremely conformal and ultrathin film on a wide variety of templates, favoring the innovative design of various nanostructured photocatalysts. Herein, we report a controllable fabrication of a hybrid photocatalyst comprising graphitic carbon nitride (g-C_3N_4), Au nanoparticles, and TiO_2 hollow fibers for photocatalytic water splitting. Titanium tetrachloride ($TiCl_4$) and H_2O were used as precursors for the ALD process to uniformly deposit a thickness-controllable TiO_2 thin film on hollow polysulfone fibers (PSFs). In order to minimize the e^--h^+ pair recombination, the TiO_2 hollow fibers were further decorated with Au nanoparticles by chemical reduction and then coated with a g-C_3N_4 nanolayer by pyrolysis of urea at a certain elevated temperature. For comparison, Au/TiO_2 hollow fibers and Au/g-C_3N_4 nanosheets were also prepared and individually used as photocatalysts for water splitting. It was demonstrated that the photocatalytic efficiency of the g-C_3N_4/Au/TiO_2 heterostructure could be influenced by the thickness of the TiO_2 thin film which can be tailored by the ALD cycle number. TiO_2 with perfect conformality on the porous PSF template also offers a large surface area of the hybrid catalyst and efficient trapping of the reflected photons within the interconnected nanotubes of the hollow fibers. More importantly, the surface plasmon resonance (SPR) effect of Au nanoparticles and the g-C_3N_4/Au/TiO_2 heterostructure that could effectively increase the separation of e^--h^+ pairs further enhance the photocatalytic efficiency of g-C_3N_4/Au/TiO_2 for water splitting when compared to those of Au/TiO_2 and Au/g-C_3N_4.

8:15am **AA3+AF+EM-WeM-2 Nano-energetic Materials Fabricated by Atomic/Molecular Layer Deposition**, ***Hao Feng***, Xi'an Modern Chemsitry Research Institute, China

As key components to improve energy densities, metal nanoparticle based energetic materials are widely used in many energetic systems, for example, as additives for propellants and explosives. Metal nanoparticle based energetic materials have fairly large surface areas and are extremely reactive. Proper surface modification improves the safety and stability of these materials and may also enhance their energy releases. By applying atomic layer deposition (ALD) or molecular layer deposition (MLD), surfaces properties of the metal nanoparticles can be dramatically changed and their energy release patterns can be effectively tuned at minimum losses of the energy densities.

Zr nanopowder is a very promising high energy metal fuel. However, this material is extremely sensitive to electrostatic discharges, which greatly jeopardizes its applications. By applying ALD/MLD surface modification, metallic Zr nanoparticles can be encapsulated by uniform layers of metal oxides, polymers, or carbon. The thicknesses of the encapsulation layers can be precisely controlled. The electrostatic sensitivity of Zr nanoparticles can be tuned in a wide range by varying the type and thickness of the ALD coating, which significantly enhances the safety in handling, storage, and utilization of this high energy material.

Metal nanoparticle based thermite materials feature very exothermic solid-state redox reactions. However, reaction rates of traditional thermite mixtures are limited by reactant diffusion velocities. Core-shell structured nanothermite materials can be synthesized by depositing certain types of metal oxides (oxidizers) on Al nanoparticles. The oxidizer layers deposited on the Al nanoparticles are conformal and their thicknesses can be precisely controlled by adjusting the number of ALD cycle. Reaction rates of the core–shell structured nanothermites synthesized by ALD are several times faster than the mixture of nanopowders. The enhanced reaction rate is ascribed to the intimate fuel-oxidizer contact as a result of the exquisite core–shell nanostructure and excellent conformity of the oxidizer shells.

8:30am **AA3+AF+EM-WeM-3 Atomic Layer Deposition of Alumina on Lactose Particles for Modified Release: Effect of Co-reactants and Substrate Crystallinity**, ***Damiano La Zara***, Delft University of Technology, Netherlands; *D Zhang, M Quayle, G Petersson, S Folestad,* AstraZeneca, Sweden; *J van Ommen,* Delft University of Technology, Netherlands

Atomic layer deposition (ALD) is an established technique for the synthesis of thin films for various applications ranging from semiconductors to energy storage devices. Recently, it has been gaining attention in the pharmaceutical field to modify the particle properties, for example the drug release. Compared to the conventional methods of drug particle coating, ALD has a number of advantages: control over the amount of deposited material, conformality, and its solventless nature. A few studies about ALD of metal oxides, including Al_2O_3, TiO_2 and ZnO, on acetaminophen, lactose and budesonide particles showed that the deposition of nanoshells can effectively slow down the drug release. However, the dependence of the film growth on pharmaceutical particles on the ALD operating conditions has not yet been investigated. Furthermore, the relationship between the properties of the coating (e.g, uniformity, conformality) and the dissolution behaviour of the resulting core-shell structures is not clear. Therefore, as the dissolution profile strongly depends on the coating quality, understanding how process parameters (e.g., number of cycles, co-reactants and substrate surface) affect the coating uniformity and conformality is crucial.

In this work, we study the effect of co-reactants, namely H_2O and O_3, on the Al_2O_3 growth on two kinds of lactose particles (i.e., fully crystalline lactose and crystalline lactose with micronization-induced amorphous surfaces) and evaluate the dissolution behaviour. The ALD process is carried out at ambient conditions in a fluidized bed reactor for a low number of cycles (i.e., from 4 to 14) using trimethylaluminum (TMA) as a metal precursor. Time-of-flight secondary ion mass spectrometry and Transmission Electron Microscopy (TEM) show that TMA/O_3 ALD on crystalline lactose particles offers greatly improved control over the coating uniformity and conformality compared to TMA/H_2O ALD. In fact, by causing severe agglomeration of the particles, water deteriorates the fluidization quality and thus the homogeneity of the coating process. In-vitro dissolution tests reveal more sustained release for the O_3-based process than for the H_2O-based one, thus underlining the benefit of O_3 in providing uniform and conformal coatings. However, little to no difference between TMA/O_3 and TMA/H_2O ALD is observed on lactose particles with amorphous surfaces. In fact, such amorphous surfaces firstly are inherently inhomogenous across the particles and secondly present micropores, as suggested by BET measurements. This inevitably leads to non-conformal films regardless of the co-reactant and moreover results in both surface and subsurface growth.

8:45am **AA3+AF+EM-WeM-4 A High Vacuum Plasma Enhanced Atomic Layer Deposition System for Depositing Very Reactive Metals**, ***Feng Niu***, SVT Associates, Inc.

Most of metal elementals deposited by ALD or PEALD so far are less electropositive or relatively stable. Very reactive metals which are defined as highly electropositive elements(electronegativity c <1.8) including alkaline, alkaline earth, group III, some transition and rare earth metals are needed for applications such as batteries, improved adhesion, barriers, etc.. However they have been proved very difficult to deposit in a conventional thermal ALD or PEALD reactor due to thermodynamic limitation, impurity requirements and unavailability of proper precursors and reducing agents.

A new high vacuum PEALD system achieving base pressure at level of 10^{-8} Torr range with a high efficiency hydrogen plasma source was developed and applied to deposit highly reactive metals. The system has demonstrated deposition of pure Mg metal using commercially available Bis(ethylcyclopentadienyl) magnesium ($Mg(CpEt)_2$).[1] Self-limiting performances of Mg was evaluated(Figure1).Results for film characterizations such as surface morphology by atomic force microscopy (AFM), and film composition especially O impurity by x-ray photon-electronic spectrometer (XPS) (Figure2) will also be presented. A binary sequence surface chemistry is suggested that the hydrogen radicals serve to strip the ligands from the metal precursor according to the general overall reaction scheme: $Mg(CpEt)_2+H_2$*--Mg+2HCpEt.

This system should also be excellent for deposition of many other very reactive metals such as Sr, Ba, Ti, Nb, Zr, Hf, Li, Na, etc., and for borides, carbides and nitrides where the materials are extremely sensitive to contaminants such as oxygen, moisture, carbon oxides, etc…

[1] US patent # US 9828673 B2.

9:00am **AA3+AF+EM-WeM-5 Plasma Properties of High Pressure ALD**, *C Qu,* University of Michigan*; **Pulkit Agarwal**, Y Sakiyama, A LaVoie,* Lam Research Corp.*; M Kushner,* University of Michigan

Plasma enhanced atomic layer deposition (ALD) of high quality dielectric films ultimately depends on controlling the fluxes of plasma produced reactive species onto the substrate and into features. In a typical plasma enhanced ALD cycle of SiO_2, the Si-containing precursor is usually deposited in a non-plasma environment. The oxidation step is then conducted by an oxygen containing plasma such as Ar/O_2. In order to produce high fluxes of the oxidizing radicals, which requires high power deposition, while having ion energies onto the wafer with below-damaging energies, the capacitively coupled plasmas are typically operated at pressures of many Torr. Theses pressures with high power produce high radical fluxes, while the collisional nature of the sheath results in low ion energies. There are several challenges in optimizing this system, including uniformity of reactant fluxes, controlling ion energies and minimizing damaging UV/VUV fluxes.

Results from a computational investigation of high pressure capacitively coupled plasmas designed for plasma enhanced ALD of SiO_2 will be discussed, with the goal of providing insights to the tradeoffs to simultaneously optimizing deposition conditions. Consequences of varying fluxes on uniformity of deposition in moderate aspect ratio features will also be discussed. The modeling platforms used in this study are the Hybrid Plasma Equipment Model (HPEM) and the Monte Carlo Feature Profile Model (MCFPM). The example system uses Ar/O_2 mixtures at pressures of 1-5 Torr, with power deposition of up to a few kW. The fundamental plasma properties of this operating regime (e.g., plasma and radical densities, electron temperature, reactive fluxes to the substrate, sources of ionization), ion energy and angular distributions (IEADs) to the substrate will be discussed. Feature scale modeling will correlate the reactive fluxes to deposition uniformity.

* Work supported by LAM Research Corp. and the DOE Office of Fusion Energy Science.

9:15am **AA3+AF+EM-WeM-6 Remote Plasma Atomic Layer Deposition of Gallium Oxide Thin Films using Trimethylgallium and Oxygen Plasma**, *H Hao, Y Shen, J Zhang, **Xiao Chen**,* Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, China

Because of its large band gap and many other excellent properties, gallium oxide (Ga_2O_3) is being considered as an important oxide semiconductor for large power transistors, UV optoelectronics and solar cells, etc. Particularly, amorphous Ga_2O_3 is now attracting great interest as gate dielectric and surface passivation layer in transistors. In this work, we have deposited high quality Ga_2O_3 thin films by remote plasma atomic layer deposition (RP-ALD) with trimethylgallium (TMGa) and oxygen plasma. The deposition rate was constant at 0.36Å/cycle within a wide process window from 100 to 400 ℃. X-ray photoelectron spectroscopy (XPS) indicates the presence of gallium, oxygen, and carbon elements with content of ~37.4, ~54.5 and ~8.1 at % respectively in the Ga_2O_3 thin films deposited on silicon substrate at 250℃. The carbon impurity in the film was reduced by ~ 34% comparing with previous reported results[1]. Atomic force microscopy shows smooth surface morphology with a small root-mean-square roughness of 0.156nm. Furthermore, Ga_2O_3 films were successfully deposited on silicon, sapphire and GaN surfaces, indicating the low substrate selectivity that is beneficial to the III-V device fabrication . X-ray diffraction reveals no any crystallization happened in the amorphous Ga_2O_3 films after annealed at a high temperature up to 900℃, under O_2 atmosphere for 90 sec in a rapid thermal annealing system. The excellent thermal stability and high uniformity of Ga_2O_3 thin films deposited by RPALD are very critical to further improve the stability of III-V devices.

Reference:

1. Donmez, I.; Ozgit-Akgun, C.; Biyikli, N. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **2013,** 31, (1), 01A110.

9:30am **AA3+AF+EM-WeM-7 Impact of Substrate Biasing during Plasma-enhanced Atomic Layer Deposition on Dielectric Breakdown of Al_2O_3 Thin Film**, ***Hyun Soo Han**, M Winterkorn, Y Kim, K Lee, T Yong, K Bae, W Park, P Schindler, F Prinz,* Stanford University

The plasma as reactants in atomic layer deposition process enables a great flexibility in processing conditions and a wide spectrum of material properties. In this study, we demonstrate the tunable electrical property of Al_2O_3 thin film through the substrate biasing during the plasma-enhanced atomic layer deposition. We modulate the substrate bias voltage from 0 to 150 V and evaluate its impact on growth per cycle, mass density and electrical breakdown strength. By applying substrate bias of ~ 20 V during the deposition, an impressive breakdown strength of 0.96 V/nm is achieved, which is approximately 11% higher value than that of the film prepared without substrate bias. Our results demonstrate that the plasma energy control via substrate biasing in the plasma-enhanced atomic layer deposition process is able to be a promising technique in optimizing materials' properties for various electronic or optoelectronic devices.

9:45am **AA3+AF+EM-WeM-8 Growth Mechanism of High-k Y_2O_3 on GaAs(001)-4×6 using *in-situ* Cycle-by-Cycle ALD and Synchrotron Radiation Photoelectron Spectroscopy**, *C Cheng,* National Chia-Yi University, Republic of China*; **Wan-Sin Chen**, Y Cheng, L Young, H Wan,* National Taiwan University, Republic of China*; C Yang,* National Tsing Hua University, Republic of China*; K Lin,* National Taiwan University, Republic of China*; T Pi,* National Synchrotron Radiation Research Center, Republic of China*; J Kwo,* National Tsing Hua University, Republic of China*; M Hong,* National Taiwan University, Republic of China

Atomic layer deposited (ALD) high-k dielectrics on semiconductors with thickness from sub-monolayer (ML) to nano-meter (nm) has become a norm in the fabrication of metal-oxide-semiconductor field-effect transistors (MOSFETs).[1,2] The high-performance nano-electronic devices demand scaled-down nm thick oxide layers. Moreover, a low interfacial trap density (D_{it}), the most critical property for the device, depends on the initial oxide growth on semiconductor. Literature contains many studies on ALD oxide films on semiconductors, but few studies have investigated the oxide growth mode in the embryo stage. Thus, the present investigation is motivated to reach the fine region of a single precursor molecule in contact with a single surface atom of a semiconductor substrate. We specifically selected the system of ALD-Y_2O_3 on freshly molecular beam epitaxy (MBE) grown pristine GaAs(001)-4x6. The oxide film is a single-domain single-crystalline cubic phase with a surface normal (110).[3,4] The D_{it} is low of mid 10^{11} $cm^{-2}eV^{-1}$, having a flat D_{it} distribution within the GaAs band gap without a peak bulge in the mid-gap.[5] We have studied the interfacial electronic structure with the film sub-ML to nanometers thick using *in-situ* synchrotron radiation photoelectron spectroscopy (SRPES). In this talk, we will present the growth mechanism of ALD-Y_2O_3 adsorption on GaAs(001)-4×6 with different cycles of deposition in an atomic scale. The pristine p-type MBE-GaAs(001)-4×6 surface was grown in an integrated ultra-high vacuum (UHV) growth/analysis system.[6] After each MBE and ALD deposition, the sample was *in-situ* transferred to National Synchrotron Radiation Research Center (NSRRC) for SRPES measurements with a UHV portable chamber, in which the vacuum is maintained below 5 x 10^{-10} torr. In the embryo stage, we found that $Y(EtCp)_3$ precursors mainly undergo a charge transfer to the faulted As atoms on the GaAs(001)-4x6 surface. Upon H_2O co-reactant deposition, followed N_2 purge, the footed As atoms are readily removed. Moreover, the oxygen atoms in H_2O take over the bonding role with the underneath Ga atoms and lines of Ga-O-Y bonds stabilize the Y_2O_3 film on the GaAs substrate. After one-monolayer Y_2O_3 formed, the coordinatively unsaturated Y-O pairs of Y_2O_3 open the next ALD cycle of alternated $Y(EtCp)_3$ and H_2O process.

[1] J. W. Elam *et al.*, *Chem. Mater.***15**, 3507 (2003).

[2] M. Retala and Markku Leskelä, *Handbook of Thin Films* Volume 1, 103 (2002).

[3] Y. H. Lin *et al.*, *Materials***8**, 7084 (2015).

[4] S. Y. Wu *et al.*, *Microelectron. Eng.***147**, 310 (2015).

[5] T. W. Chang *et al.*, *Microelectron. Eng.***178**, 199 (2017).

[6] Y. H. Chang *et al.*, *Microelectron. Eng.***88**, 440 (2011).

ALD Fundamentals
Room 113-115 - Session AF1-WeM
Plasma ALD I

Moderators: Dennis Hausmann, Lam Research, Jonas Sundqvist, Fraunhofer Institute for Ceramic Technologies and Systems IKTS

8:00am **AF1-WeM-1 Role of Low and Medium Energy Ions in PEALD Processes**, ***Marceline Bonvalot**, C Vallée, S Belahcen, V Pesce, A Chaket,* LTM-UGA, France*; R Gassilloud,* CEA-Leti, France*; P Gonon, A Bsiesy,* LTM-UGA, France

Plasma assistance in ALD has proven to be of primary importance for the production of materials with improved properties as compared to standard ALD. Indeed, Plasma Enhanced ALD (PE-ALD) enables efficient impurity removal, improved control of film stoechiometry, higher deposition rates

through reduction of purge time, lower substate temperatures and a wider choice of precursors. Moreover, ionic or radical species produced in the plasma can induce reactions which cannot occur under standard thermal ALD conditions. The plasma step in PEALD can also be used as a method for in-situ surface treatment to modulate the nucleation time of precursors on different substrates. This last point has proven to be attractive for the direct selective growth on patterned surfaces [1].

But high energy ion bombardment from the plasma may also induce damages on materials properties and make it difficult to obtain conformal films in high aspect ratio features, thus loosing a key ALD asset. This can be limited with remote plasma sources or by using an intermediate grid between the two electrodes of a capacitive discharge. However, medium/low energy ions and associated fluxes are thereby significantly reduced, even if they may positively contribute to materials properties.

In PECVD, this problem is solved with ICP sources and substrate biasing, but a similar set-up in PEALD has been seldom reported: Profjit et al [2] have shown that substrate biasing in PEALD helps tailor metal oxide properties. Here, we have investigated the specific impact of low/medium energy ions (10-100 eV) on 15 nm TiN and TiO_2 properties for microelectronic applications. These investigations have been carried out in a FlexAL PEALD tool equipped with an ALE (Atomic Layer Etching) bias system developed by Oxford. A very low power (1-10 W) can be applied on the substrate to allow low DC self-bias voltage determining ion energies. Plasma active species are identified by in-situ Optical Emission Spectrometry and growth is monitored by in-situ spectroscopic ellipsometry. The impact of ion assistance on TiO_2 insulating or TiN conducting properties (measured by 4 point probe) is discussed and related to film microstructural properties (density, crystallinity). Finally, the advantages of ion assistance for conformal thin film processing (mainly metallic) in high aspect ratio structures is presented.

[1] : R. Vallat et al.*Journal of Vacuum Science & Technology* A 35, 01B104 (2017); doi: 10.1116/1.4965966

[2] : H.B. Profijt et al. *ECS Trans*. 50 (2013) 23-34

8:15am **AF1-WeM-2 Energetic Ions during Plasma ALD and their Role in Tailoring Material Properties*, Tahsin Faraz*, *K Arts,*** Eindhoven University of Technology, Netherlands*; H Knoops,* Oxford Instruments Plasma Technology, UK*; S Karwal, E Kessels,* Eindhoven University of Technology, Netherlands

The contribution of highly reactive radicals towards film growth is a well-known feature of plasma-enhanced ALD (PEALD). On the other hand, the ions generated by the plasma can also play a significant role in PEALD which has been relatively less explored. The extent to which ions can influence the deposition process depends on a variety of ion characteristics. Recently, we demonstrated how material properties of oxides and nitrides grown using PEALD at fixed temperatures can be tailored by controlling ion energies with RF substrate biasing.[1] In this contribution, we report on the measurements of ion energy characteristics to investigate their role in tailoring material properties.

We analyzed ion energy distributions (IEDs) of plasmas typically used for PEALD (e.g. O_2, H_2, N_2, etc.) in a commercial 200-mm remote inductively-coupled-plasma (ICP) ALD system equipped with RF substrate biasing. IEDs were measured using a gridded retarding field energy analyzer (RFEA) for plasma exposures without and with substrate biasing. Performing such measurements is essential towards understanding how a given PEALD process can be influenced by energetic ions. PEALD with substrate biasing yielded relatively broad IEDs with low and high energy peaks centered at high energies in contrast to narrow single peaks centered at ≤30 eV observed for PEALD without any biasing. This showed how a growing film surface in RF-biased plasmas is subject to a range of ion energies, ΔE, where the maximum ion energy, $E_{i,max}$, can significantly exceed the mean ion energy, $\langle E_i \rangle$. On the basis of such studies, we determine the ion energy regimes that induce changes in material properties at a constant deposition temperature. Furthermore, varying the duration of RF substrate biasing applied during plasma exposure can alter the total energy dose of ions per cycle, $E_{i,dose}$, which was also demonstrated to be a factor influencing the deposition process.

Analyzing growth rate and properties (e.g., density, refractive index, resistivity, etc.) of several materials as a function of the aforementioned parameters derived from IEDs has provided more insight on the relation between ion characteristics and the ensuing properties, e.g., identifying ion energy thresholds between property improvement and degradation. Datasets will be presented for relevant material examples illustrating how controlling ion energy characteristics during PEALD provides a platform for synthesizing thin-films with desired properties.

[1]Faraz *et al.*, Tuning Material Properties of Oxides and Nitrides by Substrate Biasing during Plasma-Enhanced ALD on Planar and 3D Substrate Topographies, *ACS Appl. Mater. Interfaces* **10**, 13158 (2018)

8:30am **AF1-WeM-3 Role of Plasma Chemistry on Structure and Properties of Low Resistivity PEALD TiN Films*, Igor Krylov*,** *D Ritter, M Eizenberg,* Technion - Israel Institute of Technology, Israel

Titanium nitride (TiN) is probably the most popular metal grown by atomic layer deposition (ALD). The commonly used titanium precursors for TiN ALD growth are metalorganic compounds and volatile halides. Halide precursors (e.g. $TiCl_4$) allow deposition of highly crystalline TiN films with low resistivity at both thermal activated (~200 µOhm·cm) and plasma-enhanced (~150 µOhm·cm) regimes. However, the deposited films suffer from halide contamination leading to degradation of microelectronic devices. At the same time, halide contamination isn't present in TiN films deposited by metalorganic precursors. However, these films are often amorphous (or with poor crystallinity) and exhibit high oxygen contamination. Consequently, such films result in higher electrical resistivity, compared to the films deposited using the halide precursors.[1]

Recently, we reported plasma enchased (PE) ALD process resulting in low resistivity (~100 µOhm·cm) TiN film. These films were deposited from the TDMAT precursor and $N\text{-}_2$/Ar plasma mixture.[2] Such resistivity is comparable or even lower than that reported for PEALD processes using halogen based precursors.[1]

Here, we will report the effect of reactive gas (N_2, NH_3, H_2 or N_2/H_2) on the structure and properties of PEALD TiN films, grown from the TDMAT precursor. We will show that grain orientation of TiN can be tuned by both plasma chemistry and substrate choice. Consequently, deposition of either (001) or (111) single oriented TiN films may be obtained (Fig. 1 and 2). Such single oriented TiN films serve as effective "seed" layers for subsequently grown ALD films (Fig. 3). Effect of substrate (Al_2O_3, HfO_2, TiO_2, Ta_2O_5, MoO_x, WO_3, SiO_2) and plasma chemistry on the preferential orientation of TiN films will be discussed (Fig. 4). Based on experimental data, a qualitative model of TiN nucleation and growth will be presented for the PEALD process.

Plasma gas has a strong effect on TiN film quality (Fig. 5). The lowest resistivity of ~80 µOhm·cm was obtained for TiN films deposited from NH_3 plasma. In addition, NH_3 plasma results in the highest TiN deposition rate. The superior characteristics achieved by NH_3 plasma will be discussed.

References:

[1] V. Miikkulainen, M. Leskela, M. Ritala and R.L. Puurunen, J. Appl. Phys. **113**, 021301 (2013)

[2] I. Krylov, E. Zoubenko, K. Weinfeld, Y. Kauffman, D. Ritter, and M. Eizenberg, J. Vac. Soc. Technol. A (in preparation, 2018)

8:45am **AF1-WeM-4 Effect of Oxygen Plasma and Growth Temperature on the Densification of Plasma-Enhanced Atomic Layer Deposited Silicon Dioxide Film*, Donghyuk Shin,*** *H Song, H Park, D Ko,* Yonsei University, Republic of Korea

Silicon dioxide (SiO_2) has been widely used in silicon-based electronics for various applications. In particular, plasma-enhanced atomic layer deposition (PE-ALD) technology for SiO_2 film has attracted attention due to its high film uniformity, conformality and excellent step coverage compared to conventional thermal oxidation process. In addition, plasma exposure step in PE-ALD cycle enabled a low-temperature process by promoting the chemical reaction between the reactant gas and precursor. However, film properties of plasma-enhanced atomic layer deposited low-temperature SiO_2 such as wet etch rate (WER) differs from high-temperature thermal oxide. Several researchers have proposed post thermal annealing or plasma treatment to improve the quality of PE-ALD SiO_2 film [1,2]. Nevertheless, it is not clear yet how oxygen plasma treatment or growth temperature affects the densification of the PE-ALD SiO_2 films, especially at low temperatures of 200°C or below.

In our experiments, PE-ALD SiO_2 films, using Di-isopropylaminosilane ($SiH_3N(C_3H_7)_2$), namely DIPAS) as a Si source, were deposited on Si (100) substrates at various temperature of 50, 100 and 200°C with different in-cycle O_2 plasma (RF, 27.12MHz) time. O_2 plasma power was 400W and reactor pressure was maintained at 2 torr. Post plasma treatment was also executed to examine the film densification effect.

The thickness of SiO_2 films were measured by Spectroscopic ellipsometry (alpha-SE model, J. A. Woollam Co. Ltd.) to evaluate growth per cycle (GPC)

and WER. Wet etch test was carried out using 100:1 dilute hydrofluoric (DHF) solution maintained at 22°C and a WER of a thermal oxide was found to be 1.0 Å/sec. As shown in Fig. 1, GPC of the SiO_2 film decreases as with the process temperature and in-cycle O_2 plasma time. WER also decreased with increasing process temperature and in-cycle plasma time, showing much greater decrease along with in-cycle plasma time. In addition, X-ray reflectivity (XRR) analysis was conducted to confirm the film thickness measured with Ellip sometry, and to further obtain the film density. As the wet etch rate decreased with increasing growth temperature or plasma treatment time, the density of PE-ALD SiO_2 film increased slightly from 2.20, generally similar to the film density value of silicon dioxide, to 2.34. Our study discusses the impact of oxygen plasma treatment and growth temperature on PE-ALD SiO_2 film properties such as GPC, WER, and density.

Reference

[1] D. Hiller et al., J. Appl. Phys. 107, 064314 (2010).

[2] Kim et al., J. Vac. Sci. Technol. A 33, 1 (2015).

Fig 1. WER and GPC of PE-ALD SiO_2 films along with varying in-cycle plasma time and growth temperature.

9:00am **AF1-WeM-5 On the Co-reactant for Atomic Layer Deposition of Metals: Hydrogen/Nitrogen-based Plasmas for Cobalt ALD***, **Martijn Vos**, E Kessels, A Mackus,* Eindhoven University of Technology, Netherlands

The choice of the co-reactant used in an ALD process is critical, since it greatly affects the properties of the deposited material as well as the technological feasibility of the process. For metal ALD, a wide range of gases and chemicals have been explored as co-reactants, with O_2, H_2, and NH_3 being the most common choices (both in thermal and plasma ALD). In this work, it is investigated in detail what the effect of the co-reactant is on the ALD behavior, material properties and reaction mechanism for Co ALD. A connection is made between the plasma composition and the properties of the deposited layers, thereby gaining detailed insight in the influence of the various plasma species.

Cobalt is a transition metal which is receiving increasing interest, mainly for applications in metal interconnects. Co is used as liner, thereby replacing the conventional Ta, while it is also being explored as local interconnect or contact material (replacing Cu or W). Here, we address ALD of Co using the $CoCp_2$ precursor and different hydrogen- and nitrogen-based plasmas.[1,2] In particular, an AB (i.e. two-step) process with NH_3 plasma, an AB process with H_2/N_2 plasma and an ABC process with sequential H_2 plasma and N_2 plasma are compared.

Using quadrupole mass spectroscopy (QMS), H_2, N_2 and NH_x are identified as the main species in both the NH_3 and H_2/N_2 plasma, used for the AB processes. In addition, the release of HCp (C_5H_6) is observed during the plasma exposure of both AB processes. This is in contrast to the ABC process, where fragments of the Cp ring are detected. Furthermore, it has been found that both the NH_3 plasma and the H_2/N_2 plasma result in high-purity Co films. On the other hand, films deposited using the ABC process contain considerable amounts of C, O and N contamination (5-8 at.%). This difference in material properties suggests that the presence of NH_xspecies in the plasma is required for effective impurity removal. Moreover, variation of the H_2/N_2 ratio in the H_2/N_2 gas mixture shows that the film purity and resistivity are correlated to the amount of NH_x in the plasma. Overall, the results indicate that the choice of co-reactant is important for obtaining high-quality Co films and that NH_x species play a crucial role in the ALD growth.

9:15am **AF1-WeM-6 Plasma-enhanced Atomic Layer Deposition of Tungsten Films using Tungsten Chloride Precursor***, H Kim, **Seunggi Seo**, Y Lee, I Oh,* Yonsei University, Republic of Korea*; B Shong,* Hongik University, Korea, Republic of Korea

Tungsten (W) is a hard, refractory, and relatively inert metal, with widespread applications such as making filaments, filling contact holes and vias in microelectronic circuits, high-temperature technology, medicine, aviation, military uses, sport equipments. Atomic layer deposition (ALD) is a vapor phase thin film deposition technique based on sequential, self-limited surface reaction between chemical species. ALD enables deposition of thin films with high material quality, good uniformity, high conformality, and sub-nanometer thickness controllability. Furthermore, plasma-enhanced ALD (PE-ALD) which uses radicals as a reactant has been investigated as an attractive deposition method in terms of processing temperature and film quality. The most commonly used precursor for vapor deposition of W is WF_6, a highly reactive gas that often produces toxic hydrofluoric acid (HF) as a byproduct. WF_6 is also reactive toward common semiconductor device materials such as Si, Al, or Ti, and thus can lead to spontaneous etching during device fabrication. Therefore, fluorine-free tungsten precursors have recently received attention. In this work, we fundamentally investigated PE-ALD process of W on SiO_2 substrate, using tungsten chloride (WCl_x) precursor and hydrogen plasma. Various analytic techniques such as X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), rutherford backscattering spectrometry (RBS), 4-point probe, and field emission scanning electron microscopy (FE-SEM) were utilized, as well as density functional theory (DFT) calculations. Our PE-ALD W process showed typical ALD growth characteristics with a growth rate of 0.24 Å/cycle. W thin film deposited by our process showed low Cl impurity (< 1%) and low resistivity (~ 5.22×10^{-4} Ωcm).

9:30am **AF1-WeM-7 Tailoring Molybdenum Carbide Properties by Plasma and Ion Energy Control during Plasma Enhanced ALD***, A Bol, **Eldad Grady**, M Verheijen, T Faraz, S Karwal, W Kessels,* Eindhoven University of Technology, Netherlands

Molybdenum carbide (MoC_x) exhibits a high mechanical and thermal stability together with a metallic like electrical conductivity, making it attractive for various applications. As an IC diffusion barrier MoC_x is ideally amorphous and dense, while for superconductivity the cubic δ-$MoC_{0.75}$ shows the highest transition temperature (14.3 K) for MoC_x films.[1] The ability to separately control the crystallinity and density of MoC_x allows for tailoring film properties to the specific application. In this work, we present the first extensive study on how film density and crystallinity of MoC_x can be tailored independently during plasma-enhanced ALD (PEALD) by controlling either the plasma exposure time or the ion energy.[2] We investigated MoC_x films grown using $(^tBuN)_2(NMe_2)_2Mo$ as the precursor and H_2/Ar plasma as the co-reactant at temperatures between 150°C and 300°C.

PEALD of MoC_x at 300°C using a plasma time of 20s yielded a mass density of 7.0 g/cm^3, which increased to 8.0 g/cm^3 upon increasing plasma time to 80s, while film crystallinity remained relatively unchanged. The trend in mass density was reflected by a significant decrease in film porosity and resistivity (272 to 143 μΩ−cm) which was also accompanied by a corresponding change in material composition owing to a decrease in C/Mo ratio (0.96 to 0.78) and film [N] content. In order to investigate the effects of varying the energy of ions impinging on the substrate, a radio-frequency bias voltage was applied to the substrate in the 20s plasma exposure step at 300°C. The measured mean ion energy increased from 25 eV for non-biased plasma to 125 eV with -100V bias. The elevated ion energy resulted in a higher mass density of 8.2 g/cm^3 together with an increase in film crystallinity, with crystallite size doubling in comparison to non biased deposition. The increase in density and crystallinity was reflected by a decrease in film porosity, resistivity (272 to 143 μΩ−cm) and C/Mo ratio (0.96 to 0.79). The effects of varying temperature and ion energies at 300°C on the film chemical and physical properties will be discussed.

From these and other results to be reported, it can be concluded that longer plasma time densifies the film but has little effect on crystallinity, while substrate bias densifies and crystallises the MoC_x film. Both longer plasma exposure and bias are successful in mitigating impurities in the film and lowering the film resistivity. This work opens new processing opportunities at low temperatures for the integration of tailor-made MoC_x thin films into a wide range of applications.

[1] Sathish et al., Solid State Comm. 177, 33 (2014)

[2] Profijt et al., JVSTA, 31, 01A106 (2013)

9:45am **AF1-WeM-8 Atmospheric-Pressure Plasma-Enhanced Spatial ALD of In_2O_3:H***, **Yves Creyghton**, A Varanasi, F Roozeboom, P Bolt, P Poodt,* Holst Centre - TNO, Netherlands

Hydrogen-doped indium oxide (In_2O_3:H), a transparent conductive oxide first developed in 2007, has recently attracted strong attention as a replacement for tin doped indium oxide because of its high mobility (>100 cm^2/Vs) and high transparency (>90%) in the visible region of the spectrum. Sputtered In_2O_3:H has been demonstrated successfully but one of the challenges remaining is the damage induced by energetic ion-bombardment which may give rise to point defects [1]. High-quality In_2O_3:H layers were obtained previously using time-sequenced ALD at 100°C with cyclopentadienyl indium and a mixture of H_2O and O_2 followed by solid phase crystallization at 150-200°C in N_2 [2].

In the scope of large-area and high-throughput applications at low temperature we developed a plasma enhanced spatial ALD process for In_2O_3:H using tri-methyl indium (TMI) as precursor and a new type of Dielectric Barrier Discharge (DBD) plasma source for the supply of reactive

co-reactants. The DBD plasma is generated very proximate (<200 µm) to the substrate without interacting electrically with the substrate. The highly uniform line-shaped plasma provides high concentrations of radicals while neutral gas and ion temperatures remain low. Depositions have been realized using a rotary spatial ALD reactor. Layer growth, electrical, optical and structural properties were investigated as a function of gas composition (H_2, H_2O, O_2 and N_2), gas flow rate and temperature in the range 100-200°C.

Best results without post-annealing were obtained in H_2O-H_2-N_2 plasma at temperatures above 140°C which is just above the transition temperature from amorphous to polycrystalline growth. The thickness of ~140 nm (1600 cycles) as determined by spectroscopic ellipsometry has less than 3% non-uniformity for films deposited at 150°C. Carrier mobility values as high as 85 cm^2/V.s for films grown at 150°C and 110 cm^2/V.s at 175°C with resistivity values of only 10^{-3} Ω.cm have been determined by Hall measurements. A transparency of ~90% in the visible region of the spectrum and ~85% on average was observed in the spectral range of 300-1800 nm for temperatures in the 150-175°C range. XRD and SEM analysis of the thin films showed that the layers deposited are polycrystalline. The average size of the crystals increases from ~35 nm to ~70 nm with increasing temperature. Current research is focused on the optimization of the thermal budget including options offered by solid-phase crystallization of amorphous layers.

[1] B. Demaurex et al., Appl. Phys. Lett. **101** (2012) 171604.

[2] B. Macco, ACS Appl. Mater. Interfaces **7** (2015) 16723-16729.

ALD Fundamentals
Room 113-115 - Session AF2-WeM
Plasma ALD II

Moderators: Markku Leskela, University of Helsinki, Finland, Jihwan Ahn, Seoul National University of Science and Technology

10:45am **AF2-WeM-12 Low-Temperature Plasma-Enhanced ALD of Highly Conductive Niobium Nitride Thin Films with RF Substrate Biasing**, ***Yi Shu***, *A O'Mahony,* Oxford Instruments Plasma Technology; *H Knoops,* Oxford Instruments Plasma Technology, UK; *A Kurek,* Oxford Instruments Plasma Technology; *T Miller,* Oxford Instruments Plasma Technology, UK; *O Thomas, C Hodson,* Oxford Instruments Plasma Technology

Low-temperature superconductivity of Niobium Nitride (NbN) enables the utilization of NbN thin films in numerous quantum information applications. Recently, plasma-enhanced ALD (PEALD) of NbN thin films has been studied extensively[1,2,3], aiming for high quality NbN thin films deposition with precise thickness control at low process temperature (e.g. <400°C). These processes still require a long plasma exposure time (>40 s) and relatively-high deposition temperatures (>300°C) to eliminate impurities for the optimum film properties, such as high superconducting transition temperature (T_c) and low normal-state resistivity. On the other hand, it has been shown that RF substrate biasing applied during PEALD deposition can increase ion energy and influence film properties including stress[4], crystallinity[5], density[6], and resistivity[7]. Following above results, bias-enhanced PEALD of NbN thin films deposition with (t-butylimido)-tris(diethylamido) niobium (TBTDEN) and remote H_2/Ar plasma is investigated in this work.

This study was carried out in an Oxford Instruments Plasma Technology FlexAL ALD tool equipped with an RF-biased table (13.56 MHz, substrate biasing up to 100 W power, -350 V resulting DC bias voltage), where independently controlled RF substrate biasing was applied along with mixed H_2/Ar plasma generated by inductively-coupled plasma (ICP) RF power. Coupons of silica samples were used as substrates. Film quality was evaluated by film resistivity at room temperature (RT), which was calculated from sheet resistance measured by the four-point probe method (FPP), and film thickness measured by ex situ spectroscopic ellipsometry (SE).

Different plasma parameters were investigated, e.g. RF bias power ranged from 0-75 W, and plasma duration ranged from 10-50 s. Benefit from the RF biasing, RT resistivity as low as 142 µΩ*cm was observed with NbN thin films deposited at 250°C, by PEALD process with a 20 s plasma exposure time. Moreover, such conductivity, which is corresponding to high superconducting transition temperature (T_c) [1], was found to remain with films grown at lower process temperatures down to 120°C.

[1] Ziegler *et al*., *Supercond. Sci. Technol.***26**, 025008 (2013)

[2] Sowa *et al*., *J. Vac. Sci. Technol. A*. **35** 01B143 (2013)

[3] *Hinz et al*., *Supercond. Sci. Technol.* **25** *075009*(2010)

[4] Profijt *et al*., *J. Vac. Sci. Technol. A*. **31** 01A106 (2013).

[5] Ratzsch *et al*., *Materials* **8**, 7805-7812 (2015).

[6] Profijt *et al*., *Electrochem. Solid-State Lett*. **15**, G1-G3 (2012).

[7] Faraz *et al*., presented at AVS ALD2017(2017).

11:00am **AF2-WeM-13 Low-temperature Plasma Assisted Atomic Layer Deposition of Cadmium Telluride**, ***James Pattison,*** University of Maryland; *B VanMil, A Hewitt,* U.S. Army Research Laboratory; *N Strnad,* University of Maryland; *Y Chen, P Wijewarnasuriya,* U.S. Army Research Laboratory

Cadmium telluride (CdTe) is an important group II-VI semiconductor that can be alloyed with the semi-metal HgTe to create $Hg_{1-x}Cd_xTe$ (MCT) based semiconductor materials, with a band gap tunable from 0 to 1.5 eV. MCT is the incumbent technology used in long-wave infrared (IR) imaging. Surface passivation is critical for the next generation of infrared focal plane arrays (FPAs) used for imaging in the long-wave infrared (8-12 mm band). As device dimensions decrease in newer FPA designs, the surface area to bulk volume ratio increase, and the surface recombination of charge carriers in MCT photodiodes can limit the performance of FPAs, ultimately degrading the diode signal-to-noise ratio. CdTe is an ideal passivation material for MCT due to being very close in lattice match to $Hg_{0.78}Cd_{0.22}Te$ (band gap of 115 meV equal to 10.6 mm), having similar thermal expansion coefficient, and being transparent to long wave infrared. The high-aspect ratio features present in next-generation FPAs present a challenge to current state of the art CdTe passivation by molecular beam epitaxy, which deposits material in a line-of-sight fashion. Atomic layer deposition of CdTe provides conformal coverage of these features with atomic-level thickness control, overcoming this challenge. The temperature of any MCT processing step, including passivation, must occur at low enough temperatures to avoid outgassing of mercury from the MCT device, which is catastrophic to performance. Past work on CdTe ALD and CdTe MOCVD has relied upon thermal deposition processes (> 220°C) that are incompatible with MCT device processing. Here we present preliminary results from our novel plasma-assisted ALD process for deposition of CdTe on silicon and MCT device substrates at a variety of temperatures (from 50 to 200°C) compatible with MCT device processing. Optical characterization by dynamic in-situ spectroscopic ellipsometry (iSE) during growth provides growth-per-cycle and insight into the nucleation and deposition mechanisms. X-ray photoelectron spectroscopy (XPS) confirms the presence of CdTe and examination of other contaminants within the ALD film. X-ray diffraction was used to study the orientation of ALD films on both HgCdTe and silicon substrates. Transmission electron microscopy was used to characterize the film thickness, orientation, and chemistry.

11:15am **AF2-WeM-14 Improved Deposition Rate of Low T PEALD Silicon Nitride Using Amines**, ***Sungsil Cho***, *S Chang, J Park,* Entegris Inc., Republic of Korea; *B Hendrix, T Baum, J Giolitto,* Entegris Inc.

Plasma-enhanced atomic layer deposition (PEALD) of silicon nitride (SiNx) films using silicon-halide precursors and plasma-activated ammonia (NH_3) is well-known and characterized. In this presentation, we dramatically improved the efficiency of the process by catalyzing the precursor dose with an amine. Specifically, hexachlorodisilane (Si_2Cl_6) and tetrabromosilane ($SiBr_4$) were used to deposit SiN films via plasma-activated NH_3 at a deposition temperatures from 250-450°C. The deposition rate was increased 2-3X by modifying the pulse sequence, as shown in Figure 1.

The results of amine catalyzed PEALD-SiNx films were compared to conventional PEALD-SiN films. Figure 2-A shows that the growth rate of the NH_3 catalyzed PEALD-SiN film from Si_2Cl_6 saturated at 2.8~3.0 Å/cycle; this was 2~3 times higher growth rate than the normal PEALD-SiN film (~1Å/cycle) process. This increase may be attributed to the amine catalyst leading to a lower activation energy, influencing the surface reaction of the Si compound. A similar 2X enhancement in growth rate was observed for $SiBr_4$.

In terms of the characterization of the amine catalyzed PEALD-SiN film, we found that the wet etch rate (WER) of the amine catalyzed PEALD-SiN film was generally higher than that of the normal PEALD-SiN film process. The WER of the SiN film was improved as plasma exposure time or plasma power was increased. Furthermore, the amine catalyzed PEALD-SiN film showed excellent conformality on silicon oxide trench structures with high aspect ratios (AR~11:1), as shown in Figure 3-A. We also observed that the SiN film was uniformly etched down the sidewall and at the bottom of the via structure.

11:30am **AF2-WeM-15 Improved Adhesion and Electrical Properties of Plasma-Enhanced ALD Platinum through Cycle-by-Cycle Hydrogen Plasma Treatment**, ***Martin Winterkorn***, *J Provine, H Kim, P Schindler, T Kenny, F Prinz,* Stanford University

Insufficient adhesion of platinum thin films to their underlying substrates is a cause of concern in many applications such as biomedical and MEMS devices. We report on significantly improved adhesion of plasma-enhanced ALD platinum films on multiple substrates through in-situ cycle-by-cycle hydrogen plasma treatment. Further, we demonstrate a novel method for quantifying adhesion, which involves the deposition of a highly stressed overlayer and a subsequent liftoff procedure. The effect of the hydrogen plasma treatment on film resistivity and uniformity have also been characterized, and an extreme substrate dependence has been observed, with the most extensive treatment condition resulting in a 8% decrease in resistivity compared to no treatment on Al_2O_3 substrates, but a 78% increase on SiO_2 substrates.

All films were deposited at 270°C in an Ultratech / Cambridge Nanotech Fiji ALD reactor, using trimethyl(methylcyclopentadienyl)platinum(IV) as the precursor and remote O_2 plasma as the oxidant, with 400 cycles resulting in approximately 20 nm thick films as confirmed by X-ray reflectivity measurements. The plasma treatment consisted of an additional 10 seconds of H_2 plasma and 10 seconds of O_2 plasma after each cycle, with purge times of 5 seconds. Various conditions were investigated, performing the treatment during all 400 cycles, only the first 200 cycles, only the first 50 cycles, or not at all (numbers 4 through 1, respectively).

Adhesion was evaluated using tape lift-off, and a novel method that mimics real application in MEMS fabrication processes: Two-layer photoresist is patterned with arrays of squares of various sizes on top of the platinum film, followed by e-beam evaporation of a 200 nm thick Pt layer which has a high tensile stress of 640 Mpa. A lift-off procedure is then carried out on the sample, which includes submerging it in solvents and ultrasonic agitation. In case of insufficient adhesion, individual patterned squares delaminate at the interface between the ALD platinum layer and the substrate. The fraction of delaminated squares at various sizes, as observed by optical microscopy, can then be used as a quantitative indication for adhesion strength.

11:45am **AF2-WeM-16 Low Temperature SiNx Film Deposition by Plasma Enhanced Atomic Layer Deposition with Trisilylamine**, ***Sun Jung Kim***, *S Yong, Y Choi, H Hwangbo, H Chae,* Sungkyunkwan University (SKKU), Republic of Korea

Recently, the degree of integration density of semiconductor devices is continuously increasing and critical dimension (CD) also is reduced to less than 20nm. In the nanoscale devices, silicon nitride (SiN_x) layers are essential and critical for the fabrication of nanoscale devices and it is important to control SiN_x film thickness at atomic level. Atomic layer deposition (ALD) processes are applied for the atomic layer thickness control. It is also known that the low process temperature for SiN_x film deposition less than 400°C is becoming an issue in ALD processes maintaining growth per cycle (GPC) of 1.0Å/cycle or above [1].

In this study, we developed SiN_x plasma-enhanced atomic layer deposition (PEALD) films with trisilylamine (TSA) as a Si precursor and NH_3 in inductively coupled plasma (ICP) reactor for low temperature deposition high GPC. Reactive radicals and ions are generated in ICP environment and make low temperature processing possible. The GPC was measured as high as 1.2Å/cycle at 350℃ of substrate temperature. The ratio of nitrogen and silicon (N/Si) was determined as high as 1.33 at an optimized condition. We also investigated chemisorption path of TSA on SiN_x film during first-half reaction of PEALD process with a reference of adsorption analysis of TSA on Si (100) surface [2].

References

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[2] B. W. Bush, A. H. Marquis, O. Egwu and J. H. Craig Jr., Surf. Interface Anal., Vol. 40, Is. 10, pp.1402-1405 (2008).

ALD Fundamentals
Room 113-115 - Session AF1-WeA
In-situ Monitoring and Analysis

Moderators: Christophe Detavernier, Ghent University, Belgium, Christian Dussarrat, Air Liquide

1:30pm **AF1-WeA-1 In Situ IR Spectroscopic Investigation of Thermal and Plasma-Enhanced ALD of Pt: Temperature Dependency of the Growth Rate*, Michiel Van Daele*, *C Detavernier, J Dendooven,* Ghent University, Belgium

The O_2-based processes of Pt using the $MeCpPtMe_3$ precursor have become a model system for oxidative noble metal ALD processes. The thermal process is characterized by a narrow temperature window (250-300°C; below this temperature range the growth rate quickly diminishes), while PE-ALD process has a much larger temperature window. An intriguing question is why the growth diminishes below 250°C for the thermal process. It has been suggested in literature that the precursor ligands dehydrogenate on the catalytic Pt surface and form a carbonaceous layer causing surface poisoning. However, direct identification of the surface species to support this hypothesis is missing. This is mainly because IR light is absorbed by metals, which complicates in-situ IR spectroscopy studies in transmission. In this work, in situ reflection IR spectroscopy is used during O_2 and O_2 plasma based ALD processes at different deposition temperatures to shed light on the reactions that take place on the surface during the processes.

The ALD setup used for this work is shown in Fig. 1. It concerns a pump type ALD chamber that is connected to a Bruker Vertex 70v IR spectrometer. To ensure steady state growth conditions, a sputtered Pt film is used as the substrate. Substrate temperatures of 100, 200, and 300°C are used. FTIR spectra are taken after every precursor and reactant pulse. Consecutive spectra are subtracted, giving difference spectra for each half cycle. Positive (negative) features in Fig. 2 are due to added (removed) surface groups.

We have found evidence that CH_3 and C=C containing species are present on the surface after precursor exposure at low substrate temperatures (<150°C), poisoning the surface during thermal ALD. These species are removed by O_2 plasma which enables PE-ALD below 150°C through combustion reactions. Above 150°C, no CH_3 groups were detected and the C=C vibrations diminished for both the thermal and PE-ALD process which indicates dehydrogenation reactions and ligand restructuring. Both processes show the presence of CO combustion products after precursor exposure. In addition, the PE-ALD FTIR spectra indicate the presence of ether and ester combustion products after precursor exposure, likely due to a higher amount of surface oxygen for the PE-ALD process compared to the thermal process. We conclude that the restructuring and dehydrogenation of the precursor ligands is necessary to allow the dissociation of molecular O_2 on the Pt surface, explaining the need for high substrate temperatures for the thermal Pt process.

1:45pm **AF1-WeA-2 Growth Mechanisms and Diffusion Behavior of Molecular Layer Deposition Films Deposited by Cyclic Azasilanes, Maleic Anhydride, and Water*, Ling Ju*, *N Strandwitz,* Lehigh University

Molecular layer deposition (MLD) using N-(2-aminoethyl)-2,2,4-trimethyl-1-aza-2-silacyclopentane (AZ), maleic anhydride (MA), and H_2O is used to grow hybrid organic-inorganic films.[1] The growth rate (~ 90 Å/cycle in the steady state at 100 °C) is much larger than for MLD/ALD chemistries that involve exclusively surface reactions, indicating that precursor diffusion into the MLD film plays a key role in the large growth rate.[1]

In-situ quartz crystal microbalance (QCM) measurement monitors the mass gains during individual reactions, and provides detailed information of precursor diffusion behavior by varying the precursor sequence, substrate temperature, and purging time. The mass profiles during the AZ and MA reactions are consistent with these two precursors diffusion into and out of the MLD films. The growth also displays a strong dependence on the substrate temperature and purge times of AZ and MA, that is consistent with the effects of the sub surface reactions. Diffusion coefficient and diffusion depth of different precursors were quantified. These studies provide better understanding of the structures and growth behavior of the MLD films, and avenues for basic studies of the effects of specific chemical functionalities on growth.

1 L. Ju, B. Bao, S. W. King and N. C. Strandwitz, J. Vac. Sci. Technol. A **35,** (2017).

2:00pm **AF1-WeA-3 *In-situ* RAIRS Investigation of the Oxidation and Reduction of Cu using UV/O_3 and Ethanol*, Luis Fabián Peña,*** The University of Texas at Dallas*; M Todd,* Versum Material, Inc*; Y Chabal,* The University of Texas at Dallas

Copper is the most widely used material in semiconductor interconnect technology because of its superior conductivity and resistance to electromigration. Although several methods to deposit copper oxide on nanostructured surfaces with high aspect ratio have been developed using ALD,[1,2] a reduction step is required to convert the deposited copper oxide film into metallic copper. Promising results have been demonstrated using ethanol as the reduction agent but little experimental data is available on the reduction pathways; the reaction mechanisms and surface chemistry are poorly understood.

In this work we use *in-situ* reflection absorption infrared spectroscopy (RAIRS) to investigate each step of the oxidation (UV/O_3) and reduction (ethanol (EtOH)) process to achieve an ideal Cu metal surface in an ALD environment.

To understand the reduction of copper oxide thin films with ethanol, we investigate the role of ethanol partial pressure on the oxide reduction rate by monitoring the surface species after each dose. To illustrate, the IR spectra in **Fig. 1** shows that the initial reaction begins by reducing the concentration of surficial C≡O species (2209 cm^{-1}) and this frequency is red shifted to (2175 cm^{-1}) as the extent of dipole coupling is reduced after subsequent ethanol exposures. At the same time, the reduction of CO_2 (2337 cm^{-1}) takes place after the 2nd EtOH exposure at which point the reduction of Cu_2O also begins to take place (636 cm^{-1}). Eventually, 4 consecutive EtOH exposures are enough to reduce the oxide on Cu (632 cm^{-1}). Having established an understanding on the reactions taking place on the surface, the process is optimized to reduce by-product re-deposition using an ALD-like binary process with EtOH and nitrogen.

References

[1] Alnes, M. E., Chem. Vap. Deposition, 18: 173–178

[2] Waechtler, T*.,* J. Electrochem. Soc. *2009 156(6):H453-H459*

2:15pm **AF1-WeA-4 Real Time GISAXS Study of the Effects of Plasma Gas Chemistry on Growth of InN Films by Atomic Layer Epitaxy*, Neeraj Nepal*,** U.S. Naval Research Laboratory*; V Anderson,* The American Society for Engineering Education*; S Johnson,* U.S. Naval Research Laboratory*; S Rosenberg, J Woodward, A Kozen,* The American Society for Engineering Education*; C Wagenbach,* Boston University*; D Meyer, B Downey, J Hite, V Wheeler,* U.S. Naval Research Laboratory*; Z Robinson,* SUNY College at Brockport*; D Boris, S Walton,* U.S. Naval Research Laboratory*; K Ludwig,* Boston University*; C Eddy, Jr.,* U.S. Naval Research Laboratory

III-N semiconductors have found application in a variety of technologies, however, the requisite heteroepitaxy on foreign substrates, miscibility gaps, substrate versatility and low strain heterojunctions challenge material developments. Among III-Ns, InN has the lowest growth temperature, which represents a significant challenge to epitaxial growth of single phase In containing layers. To address this, the growth temperature has to be reduced. Plasma assisted atomic layer epitaxy (ALEp) offers a new low temperature growth approach to achieve epitaxial thin films [1]. At reduced growth temperatures, plasma driven non-thermal equilibrium kinetics on nucleation and growth process is critical for improved material quality. As conventional, ultra-high vacuum growth monitoring methods generally difficult to employ, we have shown that using high intensity x-rays to monitor the evolution of grazing incidence small angle x-ray scattering (GISAXS) features directly correlate with the surface roughness, impurities, and electrical properties of the thin film [2].

In this paper, we present real time GISAXS Study of plasma gas chemistry and its effect properties on growth in the synthesis of high quality InN films by ALEp on a-plane sapphire substrate at 250°C. The total gas flow through the plasma source (N_2 +Ar = 275 sccm) was kept constant while the N_2 flow was varied from 15 to 95 sccm. During the initial cycles of InN growth on a-plane sapphire, the specular peak broadens and the correlated peak (CP) start to evolve along the native wing with different correlated length scales (CLSs). At N_2= 95 sccm surface scattering is higher and it appears to increase with N_2 flow fraction. During growth CLS remains constant at 11.56 nm for 94 sccm N_2 while it increases from 9.72 to 12.56 nm for 15 sccm of N_2. Separation between the diffuse scattering rod and CP is smaller for lower N_2 flow at the end of the growth. Lower N_2 flow through plasma increases reactive nitrogen species on the growth surface, which initiate

coarsening by converging nucleation islands. Consistent with *in situ* GISAXS, post-growth atomic force microscopy shows that surface roughness decreases from 0.35 nm to 0.12nm by decreasing N_2 flow fraction from 34% to 5%. Post-growth x-ray photoelectron spectroscopy indicates shows no carbon for all films. In this paper we present plasma characterization results to understand the influence of relative gas flow on species production and their effect on growth besides structural, morphological, and electrical properties of ALEp grown InN films.

[1] Nepal et al., Cryst. Growth and Des. **13**, 1485 (2013).

[2] Nepal et al., J. Vac. Sci. Technol. A 35, 031504 (2017).

2:30pm **AF1-WeA-5 Low-Temperature Plasma-Enhanced Atomic Layer Deposition of Cobalt Thin Films using Cyclopentadienylcobalt-dicarbonyl and N_2-H_2 Plasma**, ***Pouyan Motamedi,*** *K Bosnick,* National Research Council Canada, Canada*; K Cadien, J Hogan,* University of Alberta, Canada

The field of thin and ultrathin metallic thin films has attracted a great amount of attention, owing to their various applications, including microelectronics, enhanced solar absorbers, and catalysts for growth of carbon nanotubes. In most cases, achieving the capacity to deposit a conformal thin film on a three-dimensional structure is an important factor. Plasma-enhanced atomic layer deposition (ALD) offers potential for growth of conformal thin films with a precise control over the thickness, and its capability for deposition at relatively low temperatures. A survey of the literature reveals that the field of growing metallic thin films via ALD is relatively under-studied. Specifically, cobalt has several applications as a magnetic material, and is being increasingly considered to be used as an interconnect in nanofabrication. Unfortunately, the amount of research available on ALD of cobalt thin films is extremely limited. Here, we demonstrate that, using an organometallic precursor and nitrogen plasma, cobalt thin films can be deposited at temperatures as low as 240°C. The deposited films show no sign of carbon and oxygen impurities. A comprehensive characterization analysis was performed on the films, in order to study their composition, physical properties, surface properties, and crystal structure. In addition, in-situ spectroscopic ellipsometry was utilized to observe and analyze the growth rate and optical properties of the films, as a function of growth cycles. All these analyses were performed for the growth temperature range of 120-500°C. The general conclusion was that the specific combination of the precursors and the recipe was very successful in deposition of smooth, crystalline, and chemically pure cobalt thin films with resistivity and optical properties close to those of the bulk material. A wealth of useful information was gathered about the growth mechanism of metals using ALD, which can be potentially applied to other metallic thin films.

2:45pm **AF1-WeA-6 A Surface Science Toolbox for Understanding Atomic Layer Epitaxy**, ***Charles R. Eddy, Jr.***, *S Rosenberg, J Woodward,* U.S. Naval Research Laboratory*; D Pennachio, C Palmstrøm,* University of California, Santa Barbara*; N Nepal,* U.S. Naval Research Laboratory*; V Anderson,* Kennesaw State University*; S Johnson,* U.S. Naval Research Laboratory*; C Wagenbach, K Ludwig,* Boston University*; A Kozen, S Walton, D Boris, V Wheeler,* U.S. Naval Research Laboratory

Atomic Layer Epitaxy (ALEp) is a promising subset of atomic layer processes (ALPs) which has the potential to open a new realm of non-equilibrium semiconductor growth. In ALEp, the objective is to grow crystalline, epitaxial layers on a crystalline substrate for active regions of electronic and optoelectronic devices. This requires expansion of the ALD processing space to higher temperatures and adds constraints of crystallinity and purity (electronic grade requires impurity concentrations less than ppm). While ALEp has been shown to maintain the self-limiting nature of ALD at temperatures up to 500°C, the additional materials quality criterion requires a more complete understanding of the ALEp process if it is to be fully successful. In this regard, it is essential to develop a set of surface science tools that can be employed either *in situ* or *in vacuo* to ensure that atmospheric exposure does not influence or interfere with observed process mechanisms.

In this work, we highlight the development and early application of a suite of *in situ* or *in vacuo* characterization techniques aimed at providing surface and near-surface structure assessments [reflection high energy electron diffraction/low energy electron diffraction (RHEED/LEED) and grazing incidence small angle x-ray scattering (GISAXS)] as well as surface chemistry assessments [(x-ray photoelectron spectroscopy (XPS), resonant ion trap mass spectrometry (RIT-MS) and reflection-absorption infrared spectroscopy (RAIRS)]. We present select results from these characterizations during efforts to develop ALPs for GaN surface preparation for epitaxy and for early ALEp growth of heteroepitaxial AlN and InN films on GaN and Al_2O_3 substrates as a function of plasma pulse conditions. As an example, GISAXS measurements have revealed a distinction in the growth mode of InN on sapphire vs. GaN substrates for an otherwise identical ALEp process, with the former proceeding by correlated island growth with short range order and the latter by long range order evolution on properly prepared surfaces. Further, the duration of the plasma pulse is shown to influence the growth mode between a bimodal distribution of islands for short pulses to a single mode distribution for intermediate pulses to etching for the longest pulses. Changes in plasma chemistry are also found to affect growth mode and film quality. These changes are correlated to independent measurements of plasma properties in an effort to establish plasma process – film property relationships. A combination of RAIRS and RIT-MS will be presented to further illustrate the role of plasma chemistry.

3:00pm **AF1-WeA-7 Investigation of the Temperature Dependence of Plasma-assisted Atomic Layer Epitaxy Growth of InN on GaN using *in situ* Grazing Incidence Small-angle X-ray Scattering**, ***Jeffrey M. Woodward,*** *S Rosenberg,* The American Society for Engineering Education*; N Nepal, S Johnson,* U.S. Naval Research Laboratory*; C Wagenbach,* Boston University*; A Kozen,* The American Society for Engineering Education*; Z Robinson,* SUNY College at Brockport*; K Ludwig,* Boston University*; C Eddy, Jr.,* U.S. Naval Research Laboratory

Plasma-assisted atomic layer epitaxy (ALEp), a variant of atomic layer deposition in which relatively higher temperatures are utilized to promote surface diffusion for epitaxial growth, offers several potential advantages over conventional methods such as metalorganic chemical vapor epitaxy and molecular beam epitaxy for the growth of III-N materials and device structures. These advantages include significantly lower growth temperatures and highly controlled layer thicknesses, the latter of which is the result of the sequential pairs of self-terminating and self-limiting reactions that constitute the growth process. However, plasma-assisted ALEp is a relatively new method for III-N growth, and significant efforts will be required to better understand the nucleation and growth kinetics. To this end, grazing incidence small-angle X-ray scattering (GISAXS) has been previously utilized for the study of surface morphology during the plasma-assisted ALEp growth of InN[1] and AlN[2] on a-plane Al_2O_3 substrates. GISAXS is a non-destructive technique that can probe electron density fluctuations of length scales ranging from approximately 1 nm to 250 nm in an integral manner, making it well-suited to the study of epitaxial growth. The resulting intensity distribution from a collection of scattering objects is related to the form factor and structure factor, which are the Fourier transforms of functions describing the object shape and spatial arrangement, respectively.

In this work, we present *in situ* GISAXS studies performed at the Cornell High Energy Synchrotron Source during the plasma-assisted ALEp growth of InN on bulk GaN substrates, using 180°C, 250°C, and 320°C growth temperatures. We analyze the intensity distributions in order to extract information about the evolving morphologies. The data indicates that the InN islands are cylindrical, with mean inter-island spacings that scale with temperature. While deposition on GaN at 180°C was found to yield comparable inter-island spacings to those previously reported for deposition on a-plane Al_2O_3 at low temperatures[1], deposition on GaN at 250°C produced islands with increased spacing compared to a-plane Al_2O_3 at the same temperature. The inter-island spacing at 180°C was approximately constant throughout the growth process, which may indicate that such temperatures are insufficient for island coalescence. In contrast, the inter-island spacings at 250°C and 320°C were found to increase with growth time.

[1] N. Nepal et al., J. Vac. Sci. Technol. A **35**,031504 (20107)

[2] V. R. Anderson et al., J. Vac. Sci. Technol. A **35**, 031508 (2017)

3:15pm **AF1-WeA-8 In situ Investigations on the Crystal Structure Dependent ALD Film Growth of TiO_2**, ***Martin Knaut***, *M Albert, J Bartha,* Technische Universität Dresden, Germany

The ALD of TiO_2 from titanium tetraisopropoxide (TTIP) and water or ozone is a widely known and well-reviewed ALD process.[1-3] Nevertheless, there are papers reporting inhomogeneous film growth or non-ideal surface reactions which might cause CVD effects.[3-6] Additional, Kim et al. published an impact of the crystal structure of TiO_2 films on the density of surface hydroxyl groups and thus on the amount of chemisorbing TTIP molecules correlating with the film growth per cycle.[7] In this paper we present detailed in situ based investigations on the TiO_2 film growth and its interaction with process parameters and film properties. Quartz crystal microbalances were used to monitor the TiO_2 deposition at temperatures

between 200 and 300°C showing a spontaneous thickness and substrate temperature dependent change in GPC (marked by black dots in figure 1). This change in GPC corresponds to the crystallization of amorphous TiO_2 films into an anatase phase which was confirmed by atomic force microscopy and Raman spectroscopy measurements. A detailed analysis of the mass changes during single ALD cycles revealed an impact of the crystal structure on the amount of chemisorbing precursor molecules and so on the growth per cycle. While Kim et al. addressed this effect to a higher density of surface hydroxyl groups this work shows that the change in film growth is also related to an enhanced thermal decomposition of TTIP molecules on an anatase film resulting in a non-saturating CVD-like film growth once the film crystallizes. To enable linear and reproducible processes Al_2O_3 buffer layers have been applied to suppress film crystallization even at elevated temperatures and thicknesses. This approach allows to deposit thick amorphous TiO_2 films with a constant growth per cycle (see figure 2).

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ALD Fundamentals
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Process Development

Moderators: Woojin Jeon, Dankook University, Harm Knoops, Eindhoven University of Technology

4:00pm **AF2-WeA-11 Water Assisted ALD Process for Y_2O_3 Thin Films and Evaluation of the Y_2O_3 Containing Metal-insulator-capacitor Structures**, ***Nils Boysen***, *L Mai, E Subasi, C Bock, A Devi,* Ruhr-University Bochum, Germany

The development of new ALD processes involving promising metal-organic precursors and mild process conditions is important to gain advances in creating ultra-thin films with superior functional properties for various micro- and optoelectronic applications. ALD is the method of choice for these functional applications, as the deposition of conformal, dense and pure films at low temperatures and mild oxidizing conditions is possible, which renders ALD as an indispensable method for modern microelectronic devices. In this context, the development of a new ALD process for the material Yttrium(III) oxide is highlighted, as Y_2O_3 exhibits a large band-gap of 5.5 – 5.8 eV with a dielectric constant of k = 14-18, while also possessing a high thermal stability and a high mechanical strength, which makes this material a suitable choice for application as high-k gate dielectric in metal-oxide-semiconductor field-effect transistor (MOSFET) based devices. Among the reported precursors for the ALD of Y_2O_3 there are certain drawbacks, which include a narrow ALD-window, high deposition temperatures and low growth rates. To tackle some of these issues, we developed a new water assisted ALD process for the fabrication of ultra-thin Y_2O_3 films under mild process conditions involving the highly reactive precursor Tris(*N,N'*-diisopropyl-2-dimethylamido-guanidinato) Yttrium(III) [$Y(DPDMG)_3$]. Furthermore, detailed film characterization with a special focus on the functional properties of the Y_2O_3 thin films were performed and the results are highlighted. The Y_2O_3 thin films were deposited in a self-limiting ALD growth mode ranging from 175°C to 250°C (Figure 1) resulting in smooth, polycrystalline and oxygen-rich thin-films with low level of contamination (Figure 2). To prove the functionality of the yttria thin films in terms of dielectric applications, 20 nm Y_2O_3 thin films were used as the insulating material in Au/Ti/Y_2O_3/n^+-Si(100) capacitors which revealed a very high breakdown field between 4.0 and 7.5 MV/cm accompanied by a low leakage current density of about 10^{-7} A/cm² at 2 MV/cm (Figure 3)[1]. The dielectric permittivity in this capacitor stack was estimated to be k =11. The oxygen-rich features on the surface of the thin-films render this material promising as a passivation layer for metal oxide thin film transistors (MOTFT), to enhance their stability and electrical performance. The promising performance of our yttria films renders the new ALD process as a potential alternative to other established ALD processes for the deposition of yttria by successfully lowering the deposition temperature, while retaining growth rate and thin-film purity.

4:15pm **AF2-WeA-12 New Plasma-enhanced Atomic Layer Deposition Process for SnO_2: Process Development and Evaluation of SnO_2 for TFT Applications**, ***David Zanders,*** *L Mai, E Subasi, C Bock, A Devi,* Ruhr-University Bochum, Germany

Tin (IV) oxide (SnO_2) is a promising n-type semiconducting material with excellent electrical and optical properties.[1,2] Hence, thin films of SnO_2 are employed in a broad range of devices such as photovoltaic cells[3] and thin film transistors (TFTs)[4]. With respect to TFTs, SnO_2 as a channel layer material is exceptionally attractive due to its high mobility and transparency. As the properties of metal oxide semiconductor thin films for optoelectronic applications are highly dependent on the deposition process, a wise choice must be made to this effect. Atomic layer deposition (ALD) and plasma enhanced ALD (PEALD) are favourable for such applications owing to the low processing temperatures, precise control of thickness as well as dense and conformal coverage over complex device geometries.

Herein we report a new and promising PEALD process using a new tin alkyl precursor for the deposition of SnO_2 thin films. The liquid precursor is volatile and thermally robust as evidenced by thermal analysis (Fig. 1) and temperature dependent NMR studies. The application of this precursor in a PEALD process using oxygen plasma resulted in high quality SnO_2 layers. The self-limiting ALD growth characteristics and the saturation behavior were confirmed at different substrate temperatures ranging from 60 – 150°C (Fig 2). The films were characterized by XRR, AFM, RBS, NRA and XPS to evaluate the structure, morphology and composition. The as-deposited SnO_2 films were amorphous and stoichiometric. The functional properties in terms of optical bandgap was determined to be 3.6 eV from UV-Vis measurements. Finally bottom-gate bottom-contact TFTs were fabricated using the SnO_2 as a channel layer. Mobilities up to 10 $cm^2V^{-1}s^{-1}$ were achieved at low deposition temperatures (T = 60°C) thus making this PEALD process very attractive for flexible electronics. The devices also show a high I_{on}/I_{off} ratio of 10^7, which is more than sufficient for digital circuits.[5]

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4:30pm **AF2-WeA-13 Hollow Cathode Plasma-Enhanced Atomic Layer Deposition of Silicon Nitride using Pentachlorodisilane (PCDS) and Hexachlorodisilane (HCDS)**, ***Xin Meng***, *H Kim, A Lucero, S Hwang, J Lee, Y Byun, J Kim,* The University of Texas at Dallas*; B Hwang, X Zhou, J Young, M Telgenhoff,* Dow Chemicals

Plasma-enhanced ALD (PEALD) is an attractive method of depositing silicon nitride (SiN_x) due to its ability to grow high-quality films at low temperatures (≤400°C) for various applications [1]. Unlike other silicon precursors, chlorosilane precursors can be applicable to either thermal ALD process in combination with ammonia (NH_3), hydrazine (N_2H_4) or plasma-enhanced ALD process using NH_3 plasma. The use of chlorosilane precursors is also considered a practical approach for high-volume manufacturing (HVM). Among the reported chlorosilane precursors, hexachlorodisilane (HCDS, Si_2Cl_6) is a promising candidate due to its higher surface reactivity as well as the demonstration of a distinct self-limiting growth behavior in ALD SiN_x process [2]. Nevertheless, it is desirable to find an alternative chlorosilane precursor with a higher reactivity and a higher growth per cycle than HCDS.

In this work, a novel chlorodisilane precursor, pentachlorodisilane (PCDS, HSi_2Cl_5), was investigated for the growth of SiN_x via hollow cathode PEALD. Well-defined self-limiting growth behavior was successfully demonstrated over the growth temperature range of 270−360°C. At identical process conditions, PCDS not only demonstrated approximately >20% higher GPC than that of HCDS, but also delivered a better or at least comparable film quality determined by characterizing the refractive index, wet etch rate, and density of the films. Fourier transform infrared spectroscopy (FTIR) spectra suggested that N−H bonds were the dominant hydrogen-containing bonds in the SiN_x films without a significant amount of Si−H bonds originating from the precursor molecules. We contribute the significant improvement in GPC to the enhanced reactivity of the proposed precursor

molecular structure simply by a hydrogen atom substitution. The minor change in the molecular structure can render a lower steric hindrance, a higher polarity of the precursor molecule, and an additional precursor adsorption reaction pathway via Si−H bonds cleavage.

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