

## ALD Fundamentals

### Room Plaza D - Session AF1-TuM

#### ALD Fundamentals: Precursors and Process Development (8:00-10:00 am)/Precursors and Mechanism (10:45am-12:00 pm)

**Moderators:** Sean Barry, Carleton University, Canada, Simon Rushworth, EpiValence, UK, Markku Leskela, University of Helsinki, Finland, Ravindra Kanjolia, EMD Performance Materials

8:00am **AF1-TuM-1 Photo-assisted ALD of Oxides and Metals, Ville Miikkulainen, K Väyrynen, University of Helsinki, Finland; V Kilpi, Picosun Oy, Finland; K Mizohata, J Räisänen, M Ritala, University of Helsinki, Finland**

#### INVITED

Photo-assisted ALD, i.e. activation of ALD chemistry by UV and visible-range photons provides many potential advantages, such as lower deposition temperature, novel growth chemistries, selective area deposition, and elimination of film defects. However, there are only a few reports available on the topic, materials deposited being e.g. ZnO, Al<sub>2</sub>O<sub>3</sub> and Ta<sub>2</sub>O<sub>5</sub>. [1-3] The main challenges are the reactor design and the complexity of the heterogeneous photochemistry. The reactor must ensure intensive light on the substrate while avoiding film growth on the optical components.

Our research group at University of Helsinki has been developing photo-assisted ALD processes for oxide and metal films. Customized Picosun™ R-200 ALD reactor with two alternative UV sources is employed. Pulsed Xenon lamp and VUV deuterium lamp allow a wide range of wavelengths. Nitrogen curtain flow is used to protect the optical window from film deposition.

A single-source approach with metal alkoxides has proved itself an effective method for depositing metal oxides. We have deposited oxides of Ti, Zr, Hf, Nb, and Ta from the corresponding alkoxides with the sequence alkoxide-purge-illumination. [4] In this presentation, results on process characteristics and film properties will be discussed. Area-selectivity of the photo-assisted Ta<sub>2</sub>O<sub>5</sub> ALD was demonstrated by depositing a University of Helsinki emblem with two aluminum shadow masks. Resolution does not allow device level patterning but can be exploited to protect contact areas, for example.

Regarding photo-assisted ALD of metals, supplementary parameters must be considered. The deposited material is optically absorbing and electrically conductive, and typically reduction of the metal is required upon an ALD cycle. In this presentation, experimental results on photo-assisted ALD of Ru and Cu will be discussed.

Semiconductor Research Corporation (SRC) and Finnish Centre of Excellence in Atomic Layer Deposition (ALD CoE) are acknowledged for funding. Picosun provided the customized reactor for the project.

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8:30am **AF1-TuM-3 Oxidation State Discrimination in the Atomic Layer Deposition of Vanadium Oxides, Matthew Weimer, I Kim, P Guo, Argonne National Laboratory; R Schaller, Argonne National Laboratory, Northwestern University; A Martinson, A Hock, Argonne National Laboratory**

Tunable control over the oxidation state of transition metal oxides (or sulfides) remains a significant challenge in ALD. Traditionally, the oxidation state of the metal precursor or strength of oxidant dictates the final oxidation state of the metal, and stoichiometry of elements, in the resulting film. In this work, a single vanadium 3<sup>+</sup> precursor performs self-limiting growth of thin films that span common oxidation states of vanadium, 3<sup>+</sup>, 4<sup>+</sup>, and 5<sup>+</sup>. ALD of V<sub>2</sub>O<sub>3</sub>, VO<sub>2</sub>, and V<sub>2</sub>O<sub>5</sub> are realized via four distinct reaction mechanisms accessed at the same temperature by judicious choice of oxygen sources and co-reactants. Saturation behavior in all cases, the O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O/O<sub>2</sub>, and H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub> processes, is observed by *in situ* quartz crystal microbalance (QCM) and surface chemistry is studied

with quadrupole mass spectrometry. As expected O<sub>3</sub> oxidizes vanadium fully to the 5<sup>+</sup> state to grow crystalline V<sub>2</sub>O<sub>5</sub>. Growth with O<sub>2</sub> has not observed and self-termination with H<sub>2</sub>O occurs after less than 250 cycles corresponding to film growth of ~ 5 nm as measured by spectroscopic ellipsometry. When H<sub>2</sub>O and O<sub>2</sub> are introduced in sequence, synergistic growth of amorphous V<sub>2</sub>O<sub>5</sub> occurs. In this synergistic process, a clear distinction between non-oxidative protic ligand exchange, the H<sub>2</sub>O reaction, and metal oxidation, the O<sub>2</sub> reaction, is demonstrated in either reaction order. In addition, it is apparent from these results that this vanadium precursor requires an oxidation mechanism in sustained ALD film growth.

In an extension of this approach, we can produce films with the intermediate vanadium 4<sup>+</sup> oxidation state, VO<sub>2</sub>, through reducing equivalents – H<sub>2</sub> gas. In traditional A/B-type ALD, H<sub>2</sub>O<sub>2</sub> produces an amorphous mixed 4<sup>+</sup>/5<sup>+</sup> oxide that is easily reduced to vanadium 3<sup>+</sup> oxide, V<sub>2</sub>O<sub>3</sub>, or oxidized to vanadium 5<sup>+</sup> oxide, V<sub>2</sub>O<sub>5</sub>, by varying the atmosphere of a low temperature anneal. Phase pure VO<sub>2</sub> is not readily accessible. When H<sub>2</sub> is dosed after H<sub>2</sub>O<sub>2</sub> during growth, amorphous films of VO<sub>2</sub> are grown that can be crystallized with a low temperature, 350 °C, anneal. These VO<sub>2</sub> films show the characteristic temperature dependent Raman spectroscopy response in the expected temperature range, Figure 1, of the well-known insulator to metal transition (IMT) for VO<sub>2</sub>. Conformal films of VO<sub>2</sub> were grown on indium-tin oxide (ITO) nanorods in this method, Figure 1, in order to modify the phonon response of the ITO nanorods. A distinct blue-shift of the wavelength of all absorption spectral features above the IMT transition temperature is observed and can be modulated through VO<sub>2</sub> film thickness.

8:45am **AF1-TuM-4 Controlled B Doping in ZnO Atomic Layer Deposition using Boric Acid in Methanol as the B Source, Yan Zhang, A Mane, Argonne National Laboratory; J Liu, O Farha, Northwestern University; K Kovi, Argonne National Laboratory; J Hupp, Northwestern University; J Elam, Argonne National Laboratory**

ZnO is a well-known transparent conducting oxide with applications in numerous fields including microelectronics, solar cells, sensors, and light emitting diodes. There is fundamental scientific interest as well as commercial incentive to engineer ZnO and improve the electrical and optical properties. Towards this end, research efforts have been devoted to introducing trivalent Al or B atoms as dopants in ZnO thin films using various deposition methods. Atomic layer deposition (ALD) has the advantages of precise thickness control on the atomic scale, excellent conformity on high aspect ratio substrates, and relatively low deposition temperatures. These characteristics make ALD an attractive approach for fabricating ZnO-based devices. One of the major challenges in the ALD of ZnO:B is the lack of suitable boron-containing precursors. Ideally, the B precursor should have a high vapor pressure and reactivity, be safe to handle, and should yield a high B doping efficiency.

In this work, we have used for the first time a solution of boric acid in methanol (BA-MeOH) as the B precursor for ZnO:B ALD. Although BA has a room temperature vapor pressure of only ~10<sup>-5</sup> Torr, in methanol the BA forms trimethyl borate (TMB), which has a much higher vapor pressure of ~100 Torr. Moreover, the reaction between DEZ and TMB is nearly as favorable as that between DEZ and H<sub>2</sub>O. Encouraged by these properties, we proceeded to study the ALD of ZnO:B using *in-situ* quartz crystal microbalance measurements (Fig. 1a) and found that the BA-MeOH added mass and inhibited the subsequent ZnO ALD in a manner very similar to ZnO:Al ALD using trimethyl aluminum. Furthermore, the doping level was well controlled by varying the B deposition cycle percentage in each ALD supercycle between 1% and 8%. Next, the doping efficiency, electrical properties, and optical properties of ALD ZnO:B films were investigated. We achieved a high mobility of 18 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> with a low carrier concentration of 4×10<sup>19</sup> cm<sup>-3</sup> using a boron cycle percentage 1% (Fig. 1b). Future work will incorporate these ALD ZnO:B films into devices such as thin film transistors and diodes.

9:00am **AF1-TuM-5 Atomic Layer Deposition of Cobalt(II) Oxide/Hydroxide Thin Films, Tomi Iivonen, E Tirkkonen, K Mizohata, K Meinander, M Leskelä, University of Helsinki, Finland**

Cobalt(II) oxide (CoO) and cobalt(II) hydroxide [Co(OH)<sub>2</sub>] have recently emerged as candidates for several applications related to energy storage, such as lithium ion batteries (LiCoO<sub>2</sub>), supercapacitors (NiCoO<sub>x</sub>) and (photo)electrochemical water splitting [CoO / Co(OH)<sub>2</sub>]. As the basis of these applications is the redox chemistry of cobalt, it is important to be able to control the oxidation state of Co during the deposition process.

Currently, majority of the reported ALD processes for cobalt oxide are based on ligand combustion chemistry, using either oxygen plasma or

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ozone. However, while the use of oxygen plasma or ozone enables facile deposition of oxide films, in the case of cobalt, the control of its oxidation state is lost due to unavoidable formation of  $\text{Co}^{3+}$ .

Here we report a deposition process for  $\text{CoO} / \text{Co(OH)}_2$  films based on the use of *bis*-trimethylsilylamido cobalt  $[\text{Co(BTSA)}_2]$  and water vapor. As  $\text{Co(BTSA)}_2$  is reactive towards water, the films can be deposited without cobalt being oxidized during the surface reactions. The process can be used to deposit  $\text{CoO} / \text{Co(OH)}_2$  in a temperature window of 75–250 °C. The growth per cycle –value (GPC) is strongly dependent on the deposition temperature, ranging from 1.2 Å to 0.25 Å (Figure 1A). The hydrogen content, and thus the amount of  $\text{Co(OH)}_2$  present in the films varies with the applied deposition temperature, as evidenced by Time-of-Flight Elastic Recoil Detection Analysis study (Figure 1B). X-ray photoelectron spectroscopy confirms that the oxidation state of Co in the films is +II.

9:15am **AF1-TuM-6 High Purity Indium Oxide Films Prepared by Modified ALD using Liquid Ethylcyclopentadienyl Indium**, *Fumikazu Mizutani, S Higashi*, Kojundo Chemical Laboratory Co.,Ltd., Japan; *T Nabatame*, National Institute for Materials Science

## Introduction

Among various precursors, cyclopentadienyl indium (CpIn) is one of the most promising precursors for atomic layer deposition (ALD) of high purity indium oxide films, because cyclopentadienyl group (Cp) in CpIn is very easily eliminated from indium by reacting with hydroxyl group during ALD process [1]. However, CpIn is solid at room temperature, while liquid precursor is demanded for use in commercial ALD instrument [2]. Therefore, we prepared liquid ethylcyclopentadienyl indium (EtCpIn), which is expected to have similar ALD characteristics, and investigated its ALD process for depositing high purity oxide films.

## Experiments

EtCpIn was synthesized by using modified procedure for CpIn, and  $^1\text{H-NMR}$  spectra of the EtCpIn supported its estimated structure (Fig. 1).

Indium oxide films were deposited onto Si wafer at 150 °C. Argon was used as a carrier and a purging gas. EtCpIn, plasma oxygen, and water were employed as reactants. EtCpIn was held in a stainless steel cylinder heated to 120 °C. Oxidizing reactants in the ALD cycles were exposed in two ways: water followed by plasma oxygen (WpO), and only plasma oxygen (pO).

Thicknesses of the films were measured by spectroscopic ellipsometer. Purities of the films were investigated using radio frequency glow discharge optical emission spectrometry (RF-GDOES).

## Results and Discussion

Fig. 2 shows the relationship between film thickness and the number of ALD cycle for WpO and pO. Growth rates of the films (WpO, pO) were almost the same (0.03 – 0.04 nm/cycle), and quite small compared with the case of CpIn [1]. The difference is caused by the plasma, which was not used in CpIn case [1]. Since we used plasma oxygen to obtain high purity films, hydroxyl groups were completely oxidized and disappeared before EtCpIn exposure, and no Cp elimination was occurred during EtCpIn exposure.

Fig. 3 shows depth profiles of indium oxide films by WpO process and by pO process. Very small amount of carbon incorporation is seen in pO film, while no obvious incorporation is detected in WpO film. These results indicate that Cp were completely eliminated by reacting with hydroxyl group, though still non-negligible amounts is remain by plasma oxidation.

## Summary

A novel liquid precursor, ethylcyclopentadienyl indium, for atomic layer deposition of indium oxide films was synthesized, and high purity indium oxide films were deposited using water and plasma oxygen as oxidizing reactants.

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9:30am **AF1-TuM-7 A New Scandium Precursor for the ALD of Scandium Oxide**, *Jean-Sébastien Lehn, C Dezelah, D Moser, R Kanjolia*, EMD Performance Materials

Scandium oxide is a high- $\kappa$  dielectric material with potential application in microelectronic capacitor structures. Additionally, scandium-containing Tuesday Morning, July 18, 2017

mixed oxides, such as  $\text{GdScO}_3$ ,  $\text{DyScO}_3$  or  $\text{Al}_x\text{Sc}_{(2-x)}\text{O}_3$  are also interesting high- $\kappa$  dielectric materials. Scandium precursors containing acac, Cp, MeCp, or amidinate ligands have been used previously for the ALD of scandium-containing thin films.<sup>1-5</sup>

A new scandium precursor will be presented: bis(methylcyclopentadienyl)(3,5-dimethylpyrazolato)scandium(III). This precursor (hereafter called Sc-07) combines the advantages of a high vapor pressure (0.27 Torr at 100 °C) with a low melting point (< 40 °C), and a very good thermal stability. A low-melting precursor reduces the risk of clogging a line via condensation during use, and facilitates large-scale synthesis and purification via distillation to obtain ultra-high purity material.

Scandium oxide films were grown by ALD on a home-built system using Sc-07 and water, and the growth/cycle was high, at approximately 1.3 Å/cycle. The ALD window covers the range of 230-275 °C. Thanks to its high vapor pressure, ALD growth of Sc-07 could be obtained at a source temperature of 100 °C; film growth was observed even with the bubbler set at 80 °C. Vapor delivery compares well with other scandium precursors, such as the amidinate,  $\text{Sc(thd)}_3$  and  $\text{ScCp}_3$ , which were delivered at 140 °C, 115-119 °C, and 105 °C, respectively.<sup>1,2,5</sup>

The films have refractive indices of 1.8-1.9, which is consistent with the bulk value. XPS showed that carbon in the films was below detection limit, and that the Sc/O ratio corresponds to the expected  $\text{Sc}_2\text{O}_3$ , as shown in the attached XPS depth profiles. Detailed XPS energy scans show no evidence of nitride nitrogen.

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9:45am **AF1-TuM-8 ALD  $\text{Y}_2\text{O}_3$  Film Using Liquid Yttrium Precursor and Water**, *Akihiro Nishida, A Yamashita, M Hatase, T Yoshino, M Enzu*, ADEKA Corporation, Japan

Yttrium oxide ( $\text{Y}_2\text{O}_3$ ) is well-known as a stable compound having a wide band gap, high dielectric constant and high refractive index. It has been employed in several industrial applications as a ceramic, dielectric insulator, superconductor, optical film, protective film and buffer layer. However, almost all yttrium ALD precursors are solids at room temperature and thus undesirable for industrial use. Lowering the melting point is required in order to solve several problems such as a difficult purification process, clogging precursor delivery lines, and the generation of particles.

In this study, we carried out the investigation of several types of yttrium ALD precursors. As an example, we found that the yttrium precursor tris(sec-butylcyclopentadienyl)yttrium  $[\text{Y(sBuCp)}_3]$  is a liquid at room temperature.  $\text{Y(sBuCp)}_3$  showed a very clean TG curve without decomposition and residue. Over 2 months', long term thermal stability of  $\text{Y(sBuCp)}_3$  at 150°C was observed by TG-DTA measurement. Additionally, we demonstrated ALD  $\text{Y}_2\text{O}_3$  using  $\text{Y(sBuCp)}_3$  and water as the coreactant. The deposition temperature was varied from 200 to 400°C. It was also found that carbon and nitrogen contamination in each  $\text{Y}_2\text{O}_3$  film was not detected by XPS measurement when deposited at 200°C (Fig. 1). Furthermore, we verified that smooth films were deposited by XSEM measurement (Fig. 2). Therefore, we conclude that  $\text{Y(sBuCp)}_3$  is suited for manufacturing ALD processes compared to conventional solid precursors.

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10:45am **AF1-TuM-12 Thermal ALD of Gold Thin Films**, *M Mäkelä, T Hatanpää, K Mizohata, J Räsänen, M Leskelä, Mikko Ritala*, University of Helsinki, Finland

ALD gold thin films are desired for various applications including plasmonics and catalysis. In recent years a great amount of work has been invested into finding a suitable gold precursor for ALD. All the previously presented potential gold precursors are rather unstable thermally or have ligands that may complicate the film growth.[1,2] Until now there has not been a thermal ALD process of gold.

In this study a thorough analysis of a range of potential gold precursors was made and dimethyl(diethyldithiocarbamate)gold(III),  $\text{Me}_2\text{Au}(\text{S}_2\text{CNET}_2)$ , was found to exhibit exceptional stability and nearly complete one-step evaporation in thermogravimetric analysis. The compound was synthesized in-house and used in thermal ALD together with ozone. Ozone is a general co-reactant in ALD oxide processes but the instability of gold oxide allows the deposition of metallic gold with ozone.

The evaporation temperature of  $\text{Me}_2\text{Au}(\text{S}_2\text{CNET}_2)$  was 99 °C and the films were deposited at 120 °C and above. Self-limiting film growth was confirmed at 180 °C. Thermal decomposition of  $\text{Me}_2\text{Au}(\text{S}_2\text{CNET}_2)$  was observed only at 250 °C which is a very high temperature for a volatile gold precursor. The Au thin films were uniform, polycrystalline, continuous and conductive. Typical resistivity values of 40 nm thick films were 4 – 16  $\mu\Omega\cdot\text{cm}$ . Chemical composition of a film deposited at 180 °C was analyzed by time of flight elastic recoil detection analysis (TOF-ERDA) that showed the film to be pure and contain only 2.9 at.% oxygen, 0.85 at.% hydrogen, and 0.2 at.% of carbon and nitrogen each. This is the first thermal ALD process for gold and exhibits good growth characteristics and high film quality.

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11:00am **AF1-TuM-13 Nucleation Behavior of Ru on SiO<sub>2</sub> by Atomic Layer Deposition Using Cyclopentadienylethyl(dicarbonyl)Ruthenium and Oxygen**, *Guo Liu*, EMD Performance Materials; *C Dezelah*, EMD Performance Materials, USA; *D Moser, R Kanjolia*, EMD Performance Materials

Ru has been widely investigated for potential applications in microelectronics as an electrode material as well as for catalysis and other applications. The thermal Ru ALD process with O<sub>2</sub> is known to have a nucleation delay for many Ru precursors. It is important to understand the nucleation behavior of a Ru precursor to achieve uniform growth with precise thickness control. Ru ALD of cyclopentadienylethyl(dicarbonyl)ruthenium,  $\text{Cp}(\text{Et})\text{Ru}(\text{CO})_2$  or RUCCOE, has been reported to have high growth rates of 1.5-3 Å/cycle<sup>(1)</sup> or ~1.0 Å/cycle with an 80-90 cycle nucleation delay.<sup>(2)</sup> In this work, correlations of the complex nucleation behavior of RUCCOE with the deposition temperature, precursor dose, and argon carrier/purge gas flow rate etc. have been investigated.

There is a considerable variation in the nucleation delay even at the same deposition temperature of 300°C. This variation can be described by the average growth rate per cycle (GPC) over a fixed number of cycles. For examples, an increase in Ru pulse time can cause a rapid drop of the average GPC, and a small change in the purge gas flow rate for RUCCOE under deposition conditions 2 and 3 can significantly vary the average GPC for the same 2s. RUCCOE pulse time as shown in Figure 1.

The nucleation delay of RUCCOE also depends on the substrate as well as the deposition temperature in the range of 275-350°C. The lower the deposition temperature, the slower the nucleation process. Equal growth rate on native and 100nm thermal SiO<sub>2</sub> and true linear growth were not achieved until about 350°C, at which temperature a nucleation delay of 40-50 cycles has been observed.

The cause of this variable nucleation delay behavior is believed to be a result of CO adsorption on the substrate surface. CO is known to be capable of inhibiting Ru nucleation under certain deposition conditions.<sup>(3)</sup> RUCCOE loses CO at ~190°C but the partially decomposed precursor is thermally stable up to 350°C or possibly higher. CO evolved from RUCCOE can be partially absorbed on the substrate. An increase in the RUCCOE pulse time will increase the local CO concentration on the surface while a higher temperature can speed up CO desorption and thus change the Ru nucleation.

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11:15am **AF1-TuM-14 Mechanistic Aspects of Ru ALD Based on Ru(DMBD)(CO)<sub>3</sub> using Downstream Quadrupole Mass Spectrometry**, *Zhengning Gao*, Washington University, St. Louis; *R Kanjolia*, EMD Performance Materials; *P Banerjee*, Washington University, St. Louis

The precursor 2, 3 - dimethyl butadiene Ruthenium tri-carbonyl (Ru(DMBD)(CO)<sub>3</sub>), is a volatile molecule with favorable properties for the deposition of both Ru and RuO<sub>2</sub> films via ALD. The precursor can generate a vapor pressure of 1 Torr at 33 °C and completely volatilizes at 140 °C leaving no residue. Recently, the deposition of Ru and RuO<sub>2</sub> films have been demonstrated<sup>1</sup> using Ru(DMBD)(CO)<sub>3</sub>. The films demonstrate a higher growth rate and lower deposition temperature window as compared to other Ru precursors. However, the exact reaction mechanism for Ru(DMBD)(CO)<sub>3</sub> during every half-cycle remains largely unexplored. Knowledge of Ru(DMBD)(CO)<sub>3</sub> half-reactions is critical to design processes with faster nucleation cycles. Such approaches are particularly attractive for applications such as, battery charge collecting electrodes and seed layers for the Cu damascene process which demand high conductivity from ultra-thin films.

In this talk, we will discuss the mechanism of ALD of Ru(DMBD)(CO)<sub>3</sub> and H<sub>2</sub>O using *in situ* downstream quadrupole mass spectrometry (QMS). QMS provides a real-time analysis of reaction by-products produced due to incoming precursor interaction with functionalized surfaces. Using QMS, the by-product species can be identified and the amount quantified.

The QMS signal of the Ru(DMBD)(CO)<sub>3</sub> consists of three distinct species. First, the mass-to-charge ratio (m/e) of 67 corresponds to the DMBD ligand dissociating from the molecule. Second, a strong m/e = 16 is also observed as the DMBD further cracks into smaller fragments. Finally, m/e = 44 is observed and is related to CO<sub>2</sub> and HCOOH formation from the reaction of the tri-carbonyl groups with H<sub>2</sub>O. The QMS signal of these three species will be discussed in the context of varying process parameters such as Ru(DMBD)(CO)<sub>3</sub> and H<sub>2</sub>O pulse times and the temperature of the ALD process. Additionally, *ex situ* film characterization including atomic force microscopy and transmission electron microscopy will be presented to correlate the process signatures obtained via QMS to the film type and morphology.

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11:30am **AF1-TuM-15 Atomic Layer Deposition for Rhenium Based Materials**, *Jani Hämäläinen, M Mattinen, M Vehkamäki, K Mizohata, K Meinander, J Räsänen, M Ritala, M Leskelä*, University of Helsinki, Finland  
Many rhenium compounds are highly interesting for several applications. The last-stable-element-discovered rhenium metal is vital in superalloys for jet engines and in catalysis [1]. Re-Pt catalysts are, as an example, used in making lead-free, high-octane petrol [2]. Another potential use for the rhenium is for copper diffusion barrier layers in microelectronics [3]. The super-hard ReB<sub>2</sub> is tough enough to scratch diamond [4], whereas the “covalent metal” ReO<sub>3</sub> has an electrical conductivity comparable to silver [5]. In contrast, ReS<sub>2</sub> has recently emerged as a potential 2D material for various optoelectronic and electronic applications because of the unique and unusual behavior of the ReS<sub>2</sub> to retain a direct bandgap even in bulk form as the monolayers are effectively decoupled from each other [6].

Atomic layer deposition (ALD) is an established method in the semiconductor industry to prepare thin films in controllable and repeatable manner, even at monolayer level, on large and complex surfaces. Therefore, development of ALD processes for rhenium based materials could become highly beneficial for various applications. Here, recent progress in development of rhenium based materials by ALD at the University of Helsinki is presented. This includes the developed ALD processes for both Re metal and ReS<sub>2</sub> thin films using ReCl<sub>5</sub> with NH<sub>3</sub> and H<sub>2</sub>S based ALD chemistries, respectively. Both of these materials have been deposited by ALD for the first time. The grown films have been analyzed with several methods, including FESEM/EDX, GIXRD, AFM, TEM, XPS, TOF-ERDA, and 4-point probe.

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11:45am **AF1-TuM-16 Plasma-enhanced Atomic Layer Deposition of Silver using the Ag(fod)(PEt<sub>3</sub>)-precursor and NH<sub>3</sub>-plasma, *Matthias Minjauw, E Solano*, Ghent University, Belgium; *S Sree*, KU Leuven, Belgium; *R Asapu*, University of Antwerp, Belgium; *M Van Daele, R Ramachandran*, Ghent University, Belgium; *S Verbruggen, S Lenaerts*, University of Antwerp, Belgium; *J Martens*, KU Leuven, Belgium; *C Detavernier, J Dendooven*, Ghent University, Belgium**

Currently, there is a high interest in the fabrication of Ag nanostructures for applications in plasmonics, catalysis and nanophotonics. So far only a few Ag ALD processes have been reported in literature, due to the low thermal stability and insufficient volatility of Ag-precursors. The most promising Ag ALD process uses the Ag(fod)(PEt<sub>3</sub>)-precursor in combination with H<sub>2</sub>-plasma (H<sub>2</sub>\*), [1] and this resulted in the adoption of this process by several research groups in recent years. [2-5] In this abstract, we report a new process using the Ag(fod)(PEt<sub>3</sub>)-precursor in combination with NH<sub>3</sub>-plasma (NH<sub>3</sub>\*). This process offers a sixfold increase of the growth rate (0.24 nm/cycle) in the linear growth regime and an enhanced nucleation compared to the widely adopted H<sub>2</sub>\*-process (0.04 nm/cycle). The nucleation enhancement results in higher densities of smaller Ag nanoparticles, which is important for applications in catalysis and plasmonics.

The linearity and saturation behavior of the NH<sub>3</sub>\* and H<sub>2</sub>\*-process was confirmed on Au substrates. The conformality of the NH<sub>3</sub>\*-process was confirmed on complex 3D substrates. The nucleation and island growth mode of both processes was compared on SiO<sub>2</sub>-substrates by combining ex situ grazing-incidence small-angle X-ray scattering (GISAXS) and scanning electron microscopy (SEM). It was found that for the same amount of Ag per surface area on the substrate, the particle areal density is 9 times larger for the NH<sub>3</sub>\*-process compared to the H<sub>2</sub>\*-process, and the particle sizes are much smaller. X-ray diffraction (XRD) showed that the deposited Ag films were polycrystalline fcc Ag. X-ray photoelectron spectroscopy (XPS) indicated low impurity levels in the bulk of films grown with both processes. At the surface of films grown using the NH<sub>3</sub>\*-process, the nitrogen atomic concentration was ~20%. From in situ Fourier transform infrared (FTIR) spectroscopy experiments, clues were found that these impurities derive from nitrogen containing surface species generated during the NH<sub>3</sub>\*-pulse which are interacting with the precursor molecules during the precursor pulse. We hypothesize that these surface groups lead to a more efficient removal of the precursor ligands, resulting in a higher precursor surface coverage compared to the process using H<sub>2</sub>-plasma and hence explaining the enhanced nucleation and growth rate of the NH<sub>3</sub>\*-process.

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