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.

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