ALD Fundamentals
Room On Demand - Session AF1

Precursors and Chemistry: Precursor Design, New Precursors, Process Development

AF1-1 Thermal Atomic Layer Deposition of Cobalt Metal Films: Synthesis and Characterization of Volatile, Thermally Stable Cobalt Precursors and Development of New Thermal Cobalt ALD Processes*, Nyi Myat Khine Linn,* *J. Hollin, Z. Devereaux, C. Winter,* Wayne State University

Miniaturization trends in microelectronics require thin films of transition metals and alloys by thermal atomic layer deposition (ALD), because thermal ALD can deposit ultrathin films with conformal coverage in high aspect ratio features and afford Angstrom-level thickness control. Recently, growth of cobalt metal thin films has gained attention due to numerous applications, such as replacing copper with cobalt in nanoscale devices. However, there have been limited reports of thermal ALD processes for cobalt metal because most cobalt precursors have low thermal stabilities (decompose at <250 ℃) and low reactivity toward common reducing agents. The overall goal of our project is the discovery of new cobalt ALD precursors and the development of new cobalt ALD processes. This cobalt process will be incorporated with other metal precursors to afford metal alloy thin films, such as $CoTi_x$ ($x = 0.18$-0.83). Different classes of cobalt(II) complexes, containing ligands such as β-ketoiminate, β-diketonates, and β-diketonate with neutral donors, were synthesized as potential ALD precursors. The volatility and thermal properties of these compounds were assessedby thermogravimetric analysis, melting point, and thermal decomposition studies. Cobalt metal ALD studies were carried out with substrate temperatures from 200 to 300 ℃ using a cobalt precursor and a nitrogen-based reducing agent. Cobalt nitride and cobalt metal films resulted. Film growth only occurred on metal substrates and not on insulators. Cobalt elemental composition on the substrates was first analyzed by X-ray photoelectron spectroscopy. Film thicknesses were measured by cross-sectional scanning electron microscopy and the phases of the films were characterized by grazing incidence X-ray diffractometry. Other film characterization data will be presented.

AF1-2 Atomic Layer Deposition of Ga_2O_3 Thin Films Using a Liquid Precursor Pentamethylcyclopentadienyl Gallium and Combinations of H_2O and O_3*, Makoto Mizui,* *N. Takahashi, S. Higashi, F. Mizutani,* Kojundo Chemical Laboratory Co., Ltd., Japan

Pentamethylcyclopentadienyl gallium (GaCp*) is a liquid precursor for atomic layer deposition of Ga_2O_3 thin films. GaCp* is a cyclopentadienyl compound having a pentahapto half-sandwich structure as well as ethylcyclopentadienyl indium (InEtCp), which we previously reported [1]. Recently, we reported that high-purity Ga_2O_3 thin film with negligible carbon residue was deposited by the ABC-type ALD process with GaCp*, H_2O, and O_2 plasma (WpO) [2]. In this study, we applied O_3 as an alternative oxidant in place of O_2 plasma, and we conducted the ABC-type ALD process with GaCp*, H_2O, and O_3 (WOz).

The decomposition temperature of GaCp* was estimated to be around 250 °C by using differential scanning calorimetry. In our recent study of the WpO process, the growth temperature was set to 200 °C [2]. However, O_3 oxidization was supposed to be weaken below 200 °C [3]. Therefore, the growth temperature was set to 230 °C in this study. Ga_2O_3 thin films were deposited on 50 mm Si wafer with native oxide films. During the WOz process, linear growth with no incubation time and with a growth per cycle (GPC) of ~0.1 nm/cycle was observed, when 2 s GaCp*, 0.5 s H_2O, and 250 s O_3 pulse times were applied. For the WOz process, a self-limiting surface reaction occurred when a GaCp* pulse time of 1.5-3 s, a H_2O pulse time of 0.4-0.6 s, and an O_3 pulse time of 180-300 s were applied. With a short O_3 pulse time less than 180 s, oxidation was clearly insufficient and resulted in thinner Ga_2O_3 films. The GPC of the WOz process was larger than the GPC of WpO process (0.06 nm/cycle [2]). The reason was supposed that hydroxyl group remained after an O_3 step, and more reactive points existed at the next GaCp* step.

The elemental depth profile was analyzed by using high-resolution Rutherford backscattering spectroscopy (HR-RBS). It clearly shows that Ga_2O_3 film with a stoichiometric composition (O/Ga = 1.5) was obtained by WOz process, and that carbon was detected only on the surface. This result is comparable with the WpO process [2], and it indicates that ALD Ga_2O_3 film with high purity and negligible carbon residue was possible by using O_3 as an alternative oxidant in place of O_2 plasma.

The Ga_2O_3 films by ABC-type ALD with GaCp*, H_2O, and O_3 was demonstrated. This result will expand the potential of GaCp* for attractive applications such as large-area displays.

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AF1-3 Synthesis, Structure and Property Evaluation of a New Class of Volatile Lanthanide Precursors Containing Enaminolate Ligands*, C. Winter,* ***Navoda Jayakodiarachchi,*** Wayne State University

Thin films of binary lanthanide oxides and lanthanide-containing ternary oxides have gained increased attention in the microelectronics industry due to their high dielectric constants, large band gaps, and small lattice mismatches with silicon, which make them excellent materials for gate dielectrics in semiconductor devices. Also, lanthanide oxide thin films are useful as protective and antireflection coatings, luminescent materials, and catalysis. Atomic layer deposition (ALD), which is a thin film deposition technique that affords Angstrom-level thickness control and high conformality in high aspect ratio features, is a promising technique to deposit lanthanide oxide thin films. However, lanthanide precursors available to deposit lanthanide oxide thin films by ALD remain limited, especially for water-assisted lanthanide oxide processes. Hence, designing new lanthanide precursors for ALD is a crucial driving force for the advancement of microelectronic devices and also for accessing new properties and applications associated with lanthanide oxide materials. We have prepared a new class of lanthanide precursors containing enaminolate ligands of the formula $[R_2NCH{=}C(tBu)(O)]^-$ by treatment of three equivalents of the potassium enaminolate salt with one equivalent of anhydrous lanthanide(III) chlorides. As representative examples, La, Pr, Nd, Er, Lu, and Y complexes were synthesized and characterized using NMR, IR spectroscopy, and CHN microanalyses. The molecular structures of selected complexes were determined using X-ray crystallography. The volatility and thermal stability of the new complexes were evaluated using thermogravimetric analyses, sublimation temperatures, and thermal decomposition temperature measurements to determine their suitability as ALD precursors. To study the effect of the ligand substituents on the volatility and thermal stability of the lanthanide enaminolate complexes, three ligand derivatives with different R group were employed (L^1, $NR_2 = N(CH_3)_2$, L^2, $NR_2 = N(CH_2)_4$, L^3, $NR_2 = N(CH_2)_5$). All of the lanthanide enaminolate complexes were volatile and sublimed between 95 and 160 °C at 0.5 Torr. Complexes with L^1 ligand showed the lowest sublimation temperatures (95 to 120 °C at 0.5 Torr), whereas complexes with L^2 and L^3 ligands sublimed at 140 to 160 °C at 0.5 Torr. Moreover, complexes with L^3 ligands showed higher thermal stabilities than those found in L^1 and L^2 complexes. Most importantly, these lanthanide enaminolate complexes were found to be reactive toward the water, which is a promising sign for the use of these precursors in future water-assisted ALD processes to deposit lanthanide-containing thin films.

AF1-4 Metal Selenides: From Precursor Synthesis to Atomic Layer Deposition*, Jaroslav Charvot,*** University of Pardubice, Czechia*; M. Barr,* Friedrich-Alexander University of Erlangen-Nürnberg, Germany*; R. Zazpe,* University of Pardubice, Czechia*; Y. Cao, V. Koch,* Friedrich-Alexander University of Erlangen-Nürnberg, Germany*; D. Pokorný, J. Macák,* University of Pardubice, Czechia*; J. Bachmann,* Friedrich-Alexander University of Erlangen-Nürnberg, Germany*; F. Bureš,* University of Pardubice, Czechia

Metal selenides possess interesting properties among various fields, as photovoltaics, thermoelectric materials, photocatalysis and many other. ALD is a technique that allows for film deposition of these materials with nanometer thickness, and which can even enhance the desired characteristics. Solution Atomic Layer Deposition (sALD) is an emerging method bypassing some of the gas ALD (gALD) limitations, and in which the gas-solid reaction system is substituted with reactions between the substrate surface and precursors dissolved in appropriate solvent.

The literature provides very few chemical methods for the controlled deposition of metal selenides. Essentially, the number of potential selenium precursors for deposition represents a bottleneck. Besides the highly toxic and unstable H_2Se, only bis(trialkylsilyl)selenides are established for selenides thin film manufacturing. This work presents various silyl- and stannylselenides with linear or cyclic structure for gALD and sALD depositions. The molecular structures can be tailored to achieve various trade-offs between volatility, reactivity, air stability or ease of synthesis, as required depending on the application.

Selected precursors are then tested in gALD and sALD to prepare metal selenides and compared. Both the choice of precursor molecule and the choice of technique (gALD vs sALD) can be used to adjust the results and optimize them towards either high growth or high substrate selectivity.

AF1-5 Investigating the Role of Sigma and Pi Bonding in Volatile Molybdenum(Vi) Precursors*, **Michael Land**, G. Bačić,* Carleton University, Canada*; K. Robertson,* Saint Mary's University, Canada*; S. Barry,* Carleton University, Canada

Several atomic layer deposition (ALD) processes that deposit molybdenum films use precursors with the bis(tert-butylimido)molybdenum(VI) framework. Most of the reported volatile molybdenum compounds are prepared via salt metathesis reactions of bis(tert-butylimido)dichloromolybdenum(VI) ($(tBuN)_2MoCl_2$) with anionic nitrogen-based ligands such as dimethylamide or amidinates. Recently, we investigated the volatility and thermal stability of the parent compound, $(tBuN)_2MoCl_2$, and the effect of neutral ligands including amines, phosphines, ethers, and carbenes [1]. Some of the coordinating ligands increased the volatility of this framework but were found to dissociate from the metal complex upon evaporation. This "ligand-assisted volatilization" is a convenient method to increase the volatility of a compound for purification (by sublimation) purposes but is not practical for ALD since ligand dissociation in the gas phase will cause inconsistent gas-phase concentrations.

Notably, the neutral N,N'-chelate ligands did not dissociate from the metal complex upon heating. Herein, we investigate a series of $(tBuN)_2MoCl_2$ complexes with neutral N,N'-chelates. Incorporation of 1,4-di-tert-butyl-1,3-diazabutadiene results in a volatile compound (**1**) with an onset of volatilization of 91 ºC (from thermogravimetric analysis, Fig. 1) and thermal decomposition beginning around 170 ºC, (from differential scanning calorimetry). We found we could easily increase the thermal stability as we proceed down the spectrochemical series towards "low spin ligands". For example, the corresponding 2,2'-bipyridine adduct (**2**), has a significantly increased thermal stability, with an onset of decomposition at 240 ºC. Although this increased stability comes at the cost of volatility (165 ºC); however, a similar thermal range (79 ºC for **1** and 75 ºC for **2**) is observed.

Several other ligands were also investigated with thermal stabilities ranging from 160 ºC for "higher spin ligands" to 273 ºC for "lower spin ligands". Increases in thermal stability appear to arise from a π-withdrawing effect, whereas decreases arise from a σ-donation effect: these opposing bonding effects were investigated computationally. These effects reduce and increase the basicity of the imido nitrogen atom, respectively, which controls the activation energy for the primary decomposition pathway; γ-H activation of the tert-butyl group (Fig. 2). Finally, all compounds have been characterized in the solid state, using traditional spectroscopic techniques, including single-crystal X-ray diffraction.

AF1-6 Unearthing Zinc Alkyls as Reducing Agents in Cobalt Metal ALD: Mechanistic Studies, Process Development and Thin Film Analysis*, **David Zanders,*** Ruhr University Bochum, Germany*; J. Liu,* Tyndall National Institute, University College Cork, Ireland*; J. Obenlüneschloß, C. Bock,* Ruhr University Bochum, Germany*; M. Nolan,* Tyndall National Institute, University College Cork, Ireland*; S. Barry,* Carleton University, Canada*; A. Devi,* Ruhr University Bochum, Germany

Cobalt-containing thin films and nanomaterials – in particular metallic Co – are garnering significant interest as next-generation interconnects to replace Cu in future nanoelectronic devices. A review of the current ALD processes for Co thin films reveals a surprising gap: No studies on the use of metal organic reducing agents has been reported.[1] This is surprising considering the ALD history of its "competitor" Cu and the reports on processes employing several Cu(I) and Cu(II) precursors being reduced with the well-known $Zn(Et)_2$.[2,3] However, deposition of copper using this Zn-containing reductant resulted in unwanted Zn contamination owing to the low thermal stability and CVD-type behavior of $Zn(Et)_2$.[4]

This presentation describes the development of an ALD process yielding Zn-free thin films of Co, employing $CoCl_2$(TMEDA) (previously used in the ALD of Co_3Sn_2 intermetallics[5]) as Co precursor and $Zn(DMP)_2$, an intramolecularly stabilized Zn(II) aminoalkyl compound,[6] as Zn precursor. The precursor pair has been chosen based on an initial reactivity study encompassing several Zn precursor candidates (Figure 1) which allowed us to hypothesize the mechanistic reaction steps that may be involved in thin film growth in the ALD process. The mechanisms of thin film formation are examined by detailed DFT calculations to support the proposed reaction paths.

A full process study was carried out on 2 inch Si(100) wafers (Figure 2).Typical ALD growth characteristics in terms of saturation were found for both Co and Zn precursor pulse and a strong dependency of the growth per cycle (GPC) on the deposition temperature was observed. The film thickness scaled linearly with the number of deposition cycles, confirming ALD behavior. Complementary RBS/NRA and XPS investigations on selected Co thin films confirmed their metallic nature and the absence of Zn. While other impurity levels were low as well, the C contamination amounted to 20 at.%. Nevertheless, resistivity measurements of Co thin films directly grown on insulating SiO_2 substrates yielded promising values of 15 - 20 µΩ cm.

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AF1-7 Deposition of Dielectric Y_2O_3 Thin Films by Thermal ALD Using a Homoleptic yttrium Formamidinate Precursor and Water*, **Nils Boysen**, D. Zanders, T. Berning, D. Rogalla, S. Beer, C. Bock, A. Devi,* Ruhr University Bochum, Germany

The atomic layer deposition (ALD) of Y_2O_3 thin films is widely known to be an important process not only for the application of Y_2O_3 as high-*k* oxide, but also for wear-, corrosion-resistive and hydrophobic coatings. These applications benefit from the intrinsic properties of ALD processes such as a high thin film uniformity, conformality and compositional quality. Such beneficial properties can only be exploited if the precursor chemistry and behavior is fine-tuned for a thoroughly optimized ALD process. In this study, we opted for the development of an ALD process for the formation of dielectric Y_2O_3 thin films using a homoleptic yttrium precursor $[Y(DPfAMD)_3]$ and compared the chemical nature of the precursor, ALD process characteristics and the resulting thin film quality to the already established processes using the parent amidinate $[Y(DPAMD)_3]$ and guanidinate $[Y(DPDMG)_3]$ precursors. Thermogravimetric analysis (Figure 1) of all compounds revealed superior evaporation behavior of $[Y(DPfAMD)_3]$ compared to $[Y(DPAMD)_3]$ and $[Y(DPDMG)_3]$, which ultimately resulted in considerably reduced precursor evaporation temperatures of only 95 °C in the corresponding ALD process and an enhanced ALD processing window reaching from 200 °C to 325 °C (Figure 2). Homogeneous, smooth and crystalline thin films were obtained at 300 °C with a GPC of 1.36 Å and contamination levels (C and N) were under the detectable limits of NRA (< 0.5 at.%) at this deposition temperature. XPS confirmed the low levels of impurities on the surface of the films and interesting similarities and differences were found in the O1s and Y3d core level spectra, where the contribution from yttrium hydroxides (Y-OH) as an intrinsic feature of the water assisted ALD process are possibly lower when using $[Y(DPfAMD)_3]$ compared to $[Y(DPAMD)_3]$ and $[Y(DPDMG)_3]$. The quality of the Y_2O_3 thin films was tested in metal-insulator-semiconductor (MIS) device structures, where a high permittivity of 13.9 at 1 MHz and a low breakdown field in the range of 4.2 to 6.1 MV cm^{-1} could be determined. The presented results clearly show that a rational choice of the precursor and only small changes within the ligand sphere of the precursor can have a considerable impact on its performance in the corresponding ALD process.

AF1-8 $(^tBuNH)SiMe_2NMe_2$ – a new *N,N'-κ_2*-monoanionic Ligand for Atomic Layer Deposition Precursors*, **Matthew Griffiths**,* Carleton University, Canada*; D. Zanders,* Ruhr University Bochum, Germany*; M. Land,* Carleton University, Canada*; J. Masuda,* Saint Mary's University, Canada*; A. Devi,* Ruhr University Bochum, Germany*; S. Barry,* Carleton University, Canada

Thanks to ALD precursor design research, today there exist volatile and thermally stable precursors for almost every element on the periodic table. While this has enabled materials of all different types to be deposited, there are still some shortcomings that arise from the incorporation of impurities into the deposited films. In many cases, these impurities are not only detrimental to the properties of the film, but they are introduced from the metalorganic precursor itself.

Amidinate precursors are one of the most popular classes of ALD precursor because they are easily synthesized and react cleanly with most co-reagents to deposit metal oxides, nitrides, sulfides, and other binary or ternary materials. In some cases, however, forming a metallic film using metal amidinates and a reducing co-reagent can leave significant amounts of carbon and nitrogen in the films. This has prompted a revitalized push to develop new precursors for refractory metals and many of the first-row transition metals. We hypothesized that a potential improvement to the amidinate system could be to make it slightly less strongly bound to the metal center by disrupting the resonance structure present in the ligand and thus allow for reduction on a surface to proceed more readily.

To furnish a stable ligand, we replaced the bridgehead carbon of the amidinates with silicon, giving a *gem*-diaminosilane (gDAS) which has the desired *N,N′-κ_2*-chelating motif and is monoanionic like the amidinates. The ligand $(^tBuNH)SiMe_2NMe_2$ ($R^1 = Me$, $R^2 = {}^tBu$) has been described only once for the first-row transition metals (Ni and Co); thus we decided to explore its potential across the periodic table.

Two Li compounds have been identified and perform well by thermogravimetric analysis (TGA). Due to the large steric bulk of this ligand, complexes that would contain more than two gDAS ligands have not been observed (Sc and Ti). When attempting to prepare $V(gDAS)_3$ we instead isolate only $V(gDAS)_2$. This +2 oxidation state is common for many of the first-row transition metals and this ligand forms thermally stable and volatile precursors of the type $M(gDAS)_2$. Where M = V, Mn, Fe, Co, Ni, Zn, and Mg, the compounds perform exceptionally well with residual masses by thermogravimetric analysis (TGA) below 5%, and 1 Torr temperatures between 110 and 115 °C. In particular the $Co(gDAS)_2$ complex is very thermally robust and performs very well during a TGA stress test. These compounds are the first of a family of precursors containing this type of monoanionic N-Si-N ligand and are prime candidates for ALD process development.

AF1-9 Aluminum Hydride Precursors for Atomic Layer Deposition of Aluminum Metal

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The growth of atomically precise, conformal aluminum (Al) metal films is desired due to their applications in microelectronics, plasmonics, energetic materials, and hydrogen storage processes. Thermal atomic layer deposition (ALD) can be employed to grow high-quality films through sequential and self-limiting surface reactions. Al metal possesses a very negative electrochemical potential ($Al^{3+} + 3e^- \leftrightarrow Al$, $E^o = -1.676$ V), which necessitates the use of powerful, thermally stable reducing agents as co-reactants during thermal ALD processes. There have been only two literature reports on the thermal ALD of Al metal films, both of which came from our laboratory. Considerable work remains to be carried out to develop strongly reducing co-reactants that can be used for Al metal ALD. In the present work, we will describe the synthesis, characterization of Al dihydride complexes of the formula $[LAlH_2]_n$ where L is a monoanionic, multidentate oxygen or nitrogen ligand. The applicability of these complexes as reducing agents in the thermal ALD of Al and other metal deposition processes will be overviewed.

AF1-10 Growth Mechanism of the Atomic Layer Deposition of ZnO Thin Films Using Bis(*n*-Propyltetramethylcyclopentadienyl)Zinc

Fumikazu Mizutani, *M. Mizui, N. Takahashi,* Kojundo Chemical Laboratory Co., Ltd., Japan*; M. Inoue, T. Nabatame,* National Institute for Materials Science, Japan

We have reported the atomic layer deposition zinc oxide thin films using cyclopentadienyl-based precursors, bis(*n*-propyltetramethylcyclopentadienyl)zinc, $Zn(Cp^{pm})_2$, which is expected to deposit high-purity ZnO thin films [1]. At that time, ZnO thin films were deposited at 200 °C on 150 mm Si wafers with native oxide films, and the ALD process consisted of alternating exposure to $Zn(Cp^{pm})_2$ and oxidants, H_2O followed by an O_2 plasma. Then, linear growth up to 50 cycles was observed with pulse times for $Zn(Cp^{pm})_2$, H_2O, and O_2 plasma of 0.1, 30, and 120 s, respectively [1].

However, after that, when the sample deposited up to 1000 cycles was analyzed by cross-sectional TEM, it was found that the film of SiO_2 containing a small amount of Zn was initially grown, and the island-shaped ZnO film was grown in the next stage. That is, since the precursor is adsorbed at a low density in the initial stage, it is considered that the SiO_2 film grew while taking in Zn in the precursor by O_2 plasma having a very long pulse time. And at the next stage, nucleation has started. In the ALD process design, the precursor pulse, H_2O pulse, and O_2 plasma pulse correspond to precursor adsorption, precursor oxidation, and surface hydroxyl group dehydrogenation, respectively. Among these, the H_2O pulse time and the O_2 plasma pulse time are quite long, so it is considered that the cause of the nucleation delay was insufficient precursor pulse time. On the other hand, since the ZnO film is deposited after nucleation, it seems that the extension of the precursor pulse time is sufficient only at the initial stage. Therefore, the precursor pulse time was extended to 1 s only in the first 10 cycles, and then ALD was performed up to 300 cycles with a precursor pulse time of 0.1 s to prepare a sample for evaluation of nucleation. When a cross-sectional TEM observation of this sample was performed, a conformal film was deposited. Thus, ALD without nucleation delay using this $Zn(Cp^{pm})_2$ was demonstrated.

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AF1-11 Ultrasonic Atomization of Titanium Isopropoxide at Room Temperature for TiO_2 ALD Thin Films

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Room temperature evaporation of titanium isopropoxide [$Ti[OCH(CH_3)_2]_4$, TTIP] precursor was performed using ultrasonic atomization technique for TiO_2 atomic layer deposition (ALD) thin films growth. Quartz crystal microbalance data show comparable results on the growth behavior between room temperature TTIP ultrasonic atomization and heated TTIP bubbler at 70 °C. The TiO_2 ALD saturation window is established for room temperature atomized TTIP exposure time and reactor temperatures. Room temperature atomized TTIP grown TiO_2 films show smooth surface morphology as well as TiO_2 anatase crystal structure before/after the annealing treatment. Two-dimensional TiO_2 film thickness mappings on a 150 mm diameter Si(100) wafer were performed by spectroscopic ellipsometry. The thickness variation of TiO_2 films by the room temperature atomized TTIP is less uniform than that of TiO_2 films by thermally vaporized TTIP, due to the incomplete evaporation of the TTIP liquid droplets, which is more difficult to transport than its vapor in the cross-flow configuration of ALD.

AF1-14 Designing Volatility Into Lead Precursors

Goran Bacic, Carleton University, Canada*; J. Masuda,* St. Mary's University, Canada*; S. Barry,* Carleton University, Canada

Volatility is a critical property of ALD precursors, but there is no reliable method to predict it. This was recently highlighted in our research when we discovered that bis[lead(II) *N,N′*-di-*tert*-butyl-1,1-dimethylsilanediamide] [(**4Pb**)$_2$] had good volatility (112°C/1Torr) despite being dimeric in the solid and vapor phases. Oligomerization usually decreases volatility, so we attempted to cleave the dimer to improve volatility by increasing steric bulk, adducting the monomer with a Lewis base, and by installing a pendant tertiary amine onto the ligand itself. None of these strategies produced a more volatile complex than (**4Pb**)$_2$. Indeed, even the monomeric derivative lead(II) N,N′-bis(1-(dimethylamino)-2-methylpropan-2-yl)-1,1-dimethylsilanediamide (**5Pb**) had slightly lower volatility (118 °C/1Torr). These counter-intuitive results led us to investigate the origins of high volatility with density functional theory (DFT) and experimentally with thermogravimetric analysis (TGA). In this talk, we will introduce and discuss our efforts to combine theoretical and experimental methods to predict precursor volatility.

Since volatility is governed by intermolecular interactions, which in turn are determined by the molecular electrostatic potential (ESP), we modeled vapor pressure against statistical properties of the ESP. To fit our models, we obtained a consistent set of measured vapor pressures for several known and novel lead precursors: the novel (**4Pb**)$_2$ and **5Pb** were compared to the recently reported acyclic lead(II) bis[bis(trimethylsilyl)amide] $(Pb(btsa)_2$, 127°C/1Torr) and the cyclic lead(II) *rac-N,N′*-di-*tert*-butyl-2,3-diamidobutane (**1Pb**, 94°C/1Torr), as well as more classical precursors (e.g., $Pb(tmhd)_2$, 166 °C/1 Torr). For the theoretical calculations, we developed an efficient and reliable DFT methodology (ωB97X-D3(BJ)//revPBE) which was benchmarked against high-level ab initio coupled-cluster calculations (DLPNO-CCSD). Statistical analysis revealed strong correlations between vapor pressure and the total variance ($\sigma_{\pm}^2$, $R^2 = 0.987$), absolute polar surface area (A, $R^2 = 0.983$), and standard deviation ($\prod$, $R^2 = 0.970$) of the ESP. With these results, we were able to explain how dimerization improves the volatility of (**4Pb**)$_2$, why the monomeric **5Pb** was less volatile, and which hypothetical lead precursors may be more volatile. Finally, we generalize our findings to qualitative design considerations, critically evaluate the limitations of our current approach, and outline the path toward a quantitative methodology to predict volatility.

AF1-17 Solution ALD: A Versatility Process for Various Material Growth*,* *Maissa Barr*, *B. Zhao, P. Von Grundherr, M. Uddin, V. Koch, M. Halik, J. Bachmann,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany

We have proposed and demonstrated a novel thin film deposition technique by transferring the principles of atomic layer deposition (ALD), known with gaseous precursors, towards precursors dissolved in a liquid. The technique can also be considered as a generalization of already established methods such as the ‘layer by layer’ growth or the ‘successive ion layer adsorption and reaction’ (SILAR). 'Solution ALD' (sALD) shares the fundamental properties of standard ‘gas ALD’ (gALD), specially the self-limiting growth and the ability to coat conformally deep pores. It has been already shown that it is possible to transfer standard reactions from gALD to sALD such as TiO_2 deposition . However, sALD also offers novel opportunities such as overcoming the need for volatile and thermally robust precursors.

To illustrate this, we establish sALD procedures for depositing films of non oxides layers such as Pb-compound deposition, MOF, selenides and sulfides. Those examples highlight how ionic, polar, or high-molecular weight precursors that only exist in the condensed phase are now rendered amenable to being utilized in surface-controlled thin film formation by sALD for depositing materials that would otherwise be more difficult or more expensive to achieve by gALD or hazardous. The deposition was achieved on small (2 cm*1 cm) and large samples (up to 10 cm*10 cm). The ALD behavior has been shown. The influence of the deposition parameters on the morphology, the crystalline structure and the chemical composition has been investigated by scanning electron microscopy, atomic force microscopy, grazing incidence x-ray diffraction and x-ray photoelectron spectroscopy. Additionally, the nucleation is studied in function of chemical pretreatment to control the gowth and allow selective deposition of CuS, ZnS and SnS.

This particular ALD process offer the growth of high quality and crystalline layers in middle conditions with the use of low cost and environmental friendly precursors.

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AF1-20 Routes to Novel Dielectric and Semiconductor Devices Using Cyclohexasilane*, Ramez Elgammal,* The Coretec Group

A newly developed "liquid silicon" precursor will be discussed. Cyclohexasilane (CHS; Si6H12) has been used to make silicon-based films (such as polysilicon, silicon nitride, silicon carbide and others), as well as silicon nanowires and quantum dots. CHS offers a more versatile, lower-cost and safer pathway to a variety of silicon based products being considered for flexible and printable electronics. One particularly interesting deposition method for CHS that has recently received interest is ALD.

There is a need for a silicon precursor that is not only cost effective, but one that can be readily chemically functionalized to develop advanced materials. CHS is one such silicon precursor that is a liquid at room temperature allowing for easier storage and handling. Cyclohexasilane has a moderate boiling point, 80 °C at 15 torr. It has long been considered to be the preeminent silicon precursor for a variety of applications including silicon anodes, solid state lighting, and a wide variety of semiconductor devices. CHS may also be used to create thin films of β-SiC on a variety of substrates under mild conditions.

Aside from those advantages, CHS allows for facile p-doping of materials and due to the methods of deposition and the deposition conditions amenable to a reagent such as CHS, continuous growth with the suppression of unintentional secondary deposits may be readily achieved. Moreover, it may be possible to use CHS to achieve solution growth to deliver high structural quality materials with significantly decreased capital and operational costs.

The use of CHS across a wide range of industries and applications will be discussed as will the advantages of this material over incumbent technologies.

AF1-23 Atomic Layer Deposition of Cupric Oxide Using Copper(II) Acetylacetonate*, Gabriel Bartholazzi*, *L. Black,* The Australian National University, Australia

Copper oxide is a well-known p-type semiconductor with potential applications in a range of fields, including photovoltaics, gas sensors, catalysis and water splitting. It is mainly found in two oxidation states, cupric oxide (CuO) and cuprous oxide (Cu_2O). In some applications, Cu_2O is preferred due to its larger bandgap of 2.1-2.6 eV compared to 1.3-17 eV for CuO. Cu_2O has been previously deposited by ALD using various combinations of precursors and reactants such as $Cu(OAC)_2$ and H_2O, $^n(Bu_3P)_2Cu(acac)$ and wet oxygen and Cu(I)(hfac) and H_2O. However, the copper precursors used in these processes suffer from some drawbacks such as poor stability ($Cu(OAC)_2$),adhesion problems due to fluorination (Cu(I)(hfac)) and small temperature window ($^n(Bu_3P)_2Cu(acac)$). Copper(II) acetylacetonate ($Cu(acac)_2$)appears to be a promising candidate due to its high stability, relatively low price and vapour pressure. Additionally, reports have shown that this precursor has a wide deposition window which is a very important feature when depositing in combination with other materials. $Cu(acac)_2$ has been reported in combination with O_3 to produce CuO and in a supercycle reaction with H_2O and a reducing agent to produce Cu. Conversely, the $Cu(acac)_2/H_2O$ process was reported not to result in film growth. Cu_2O films obtained from $Cu(acac)_2$ by ALD have yet to be reported. In this work, we demonstrate ALD of Cu_2O from $Cu(acac)_2$ and a combination of H_2O and O_2 as reactants. The depositions were carried out using a Beneq TFS-200 system. Double-side-polished silicon wafers were used as substrates. The $Cu(acac)_2$ precursor was held at 140°C. The precursor and reactant pulse times were varied in order to obtain the process saturation curves. Ex-situ spectroscopic ellipsometry was used to determine the film thickness and optical constants. Fourier-transform infrared spectroscopy (FTIR) and grazing incidence X-Ray diffraction (GIXRD) were used to determine the crystallinity and oxidation state. Film uniformity and roughness were assessed using atomic force microscopy. The results confirm self-limiting deposition behaviour with a growth per cycle of ~0.07 Å/cycle at 200°C. The relatively low growth rate may be due to the incomplete reaction of the precursor ligands, as some level of carbon impurities were detected by FTIR. Nevertheless, GIXRD and FTIR confirm that the desired Cu_2O oxidization state was obtained using this process. Films are crystalline and present a direct band gap of 2.6 eV.

The final submission will include additional results on the process optimization which are to be completed soon.

AF1-26 Low-Temperature Growth of Crystalline Tin(II) Monosulfide Thin Films by Atomic Layer Deposition Using a Liquid Divalent Tin Precursor*, Mohd Zahid Ansari,* Yeungnam University, Korea (Republic of)*; P. Janicek,* University of Pardubice, Czechia*; D. Nandi,* Yeungnam University, Korea (Republic of)*; S. Slang, M. Bouska,* University of Pardubice, Czechia*; H. Oh,* Yeungnam University, Korea (Republic of)*; B. Shong,* Yeungnam University, Czechia*; S. Kim,* Yeungnam University, Korea (Republic of)

Better-quality stoichiometric SnS thin films were prepared by atomic layer deposition (ALD) using a novel liquid divalent Sn precursor, N, N′-di-*t*-butyl-2-methylpropane-1,2-diamido tin(II) [Sn (dmpa)], and H_2S. A relatively high growth per ALD cycle (GPC) value of approximately 0.13 nm/cycle was achieved at 125 °C. Crystalline SnS films could be grown from room temperature (25 °C) to a high temperature of 250 °C. Density functional theory calculations were used to examine the surface reactions and self-limiting nature of the Sn precursor. Mixed phases of cubic (π) and orthorhombic (o) SnS films were deposited at low temperatures (25–100 °C), whereas only the orthorhombic phase prevailed at high growth temperatures (>125 °C) based on the complementary results of XRD, Raman spectroscopy, and XPS analyses. The optoelectronic properties of the SnS films were further evaluated by spectroscopic ellipsometry(SE) analysis. The results from the SE analysis supported the observed change from mixed π-SnS and o-SnS to o-SnS with increasing deposition temperature and allowed the determination of the energy bandgap (∼1.1 eV) and a relatively broad semi-transparent window (up to 3000 nm). Overall, this new ALD process for obtaining a good quality SnS is applicable even at room temperature (25 °C), and we foresee that this process could be of considerable interest for emerging applications.

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ALD Fundamentals
Room On Demand - Session AF10
ALD Fundamentals Poster Session

AF10-1 Datasets and Algorithms for Machine Learning-Driven Process Optimization Using ALD Growth Profiles*, **Angel Yanguas-Gil**, J. Elam,* Argonne National Laboratory

Process optimization is a crucial aspect of atomic layer deposition that is often carried out through a combination of trials and human expertise. In this work we explore how machine learning approaches, and in particular artificial neural networks, can help accelerate such optimization, potentially reducing it to a two step process.

Our goal is to use thickness values measured at different points of a reactor as well as dose timings as inputs to predict optimization targets such as dose times required to achieve full saturation or predicting growth profiles in areas that are not readily accessible. This data is usually obtained as part of the routine characterization process after each deposition. Our approach relies on two steps: we first use CFD simulations to generate growth profiles inside a reactor of a given geometry. The simulations depend on parameters that are generally not known, but when enough conditions are explored, they provided a dataset that covers the expected behavior of a wide range of ALD process. The resulting datasets are split into two different sets, one for training, and one for training, so that machine learning algorithms can be validated against data they have not been trained against. The second step is to train surrogate models using the training datasets to carry out a specific task. In this work we have explored primarily models based on artificial neural networks.

When trained and compared for tasks such as predicting saturation times, machine learning models based on artificial neural networks can accurately predict dose times, with a Pearson correlation accuracy exceeding 0.99 with respect to the testing dataset. When we apply this model to experimental data obtained for TMA/water growth in our cross flow reactors we also observe similarly a very good accuracy. We have generalized this model to situations involving more than one growth conditions, therefore extending the models to conditions where we are trying to optimize both saturation times simultaneously. Finally, we explore other relevant problems, such as the discrimination between self-limited and non-self limited growth, which can be casted as a classification task, and the case of process transfer across two different reactors.

AF10-2 Conducting Hafnium Nitride Films Fabricated by Atomic Layer Deposition With Cleaning Step and Post-Deposition Annealing in NH_3 Atmosphere*, **Seung Kyu Ryoo**, B. Kim, H. Park, Y. Lee, S. Lee, M. Oh, I. Lee, S. Byun, D. Shim, C. Hwang,* Seoul National University, Korea (Republic of)

As the scaling down of memory device kept proceeded, a highly integrated structure using high-*k* gate dielectrics (such as HfO_2) has attracted a great deal of interest to ensure high performance in the ultra-thin film (<10 nm). At the same time, HfO_2 compatible electrodes are also required to reduce degradation caused by the adverse interface properties between electrode and dielectric. Among various materials, hafnium nitride (HfN) is one of the most promising candidates, with superior compatibility with HfO_2, low bulk resistivity, and high thermal stability. For high-density memory application, all layers in the memory cell (dielectric, electrode) should be fabricated by atomic layer deposition (ALD) for conformal growth. However, it is challenging to obtain conductive hafnium nitride films grown by ALD because of the formation of the insulating phase (Hf_3N_4) or contamination of oxygen impurity (HfO_xN_y).

In this study, conducting hafnium nitride film with a low impurity (<5%) was deposited by ALD and post-deposition anneal (PDA). The ALD HfN films were deposited using TEMA-Hf($[HfN(CH_3)C_2H_5]_4$) as a Hf-precursor- and NH_3 as a reactant gas. The cleaning step, feeding only TEMA-Hf without NH_3 gas, was conducted before the main ALD cycle to decrease the impurity concentration in the grown hafnium nitride thin films. During this step, injected TEMA-Hf reacted with impurities and decreased the residual contamination gases inside the chamber without being deposited on the substrate. The PDA at temperature >900℃ under the NH_3 atmosphere further decreased impurities and promoted phase change from insulating Hf_3N_4 to conducting HfN. Finally, HfN film with a resistivity of $10^6 \mu\Omega\cdot cm$ could be achieved by such process optimizations.

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AF10-3 Higher Temperature ALD for HfO_2 Film using Hafnium Aminoalkoxide Precursors*, **Masako Hatase**, H. Sato, A. Sakurai, T. Yoshino, N. Okada, A. Nishida, A. Yamashita,* ADEKA CORPORATION, Japan

Hafnium oxide (HfO_2) is widely used in the semiconductor industry as a high-k dielectric in memory capacitors and as a gate insulator in field effect transistors. Recently, HfO_2 attracts additional attention as a possible candidate for CMOS-compatible and scalable ferroelectric memories. The properties of HfO_2 films vary depending on the crystallographic structures which can be controlled with deposition conditions. For example, higher deposition process is promising to obtain a higher dielectric constant phase. For the last decade or more, hafnium amide-, cyclopentadienyl- and chloride-based precursors have been commonly used as ALD precursors, but their thermal stabilities are insufficient for higher temperature use. Therefore, more thermally robust hafnium precursors for higher temperature ALD are considered to be advantageous.

In this work, several hafnium aminoalkoxide precursors have been investigated. As general hafnium alkoxide precursors $[Hf(OR)_4]$ have unoccupied cordination sites, we have introduced amine chelates in the molecule to complete the hafnium coordination sphere. Tetrakis(1-dimethylamino-2-propoxy)hafnium $[Hf(dmap)_4]$ is a viscous liquid at room temperature and has high vapor pressure (1.0 torr @ 153^{o}C). The thermal stability of $Hf(dmap)_4$ was found to be higher than that of TDMAH by 90^{o}C according to DSC measurement. We demonstrated ALD of HfO_2 using $Hf(dmap)_4$ with an O_3 coreactant. Self-limiting film growth on Si and SiO_2 substrates was observed at higher deposition temperature from 250^{o}C to 350^{o}C. A smooth HfO_2 film was confirmed by FE-SEM measurement (Fig. 2). Furthermore, carbon and nitrogen contamination in the HfO_2 film was not detected by XPS measurement when deposited at 375^{o}C (Fig. 3). We have also synthesized Tetrakis(1-dimethylamino-2-butoxy)hafnium $[Hf(dmab)_4]$ and Tetrakis(1-ethylmethylamino-2-propoxy)hafnium $[Hf(emap)_4]$, which are both thermally stable as well.

In conclusion, hafnium aminoalkoxide precursors are thermally robust and suitable for high temperature ALD of HfO_2 films. During the presentation, basic properties of the hafnium aminoalkoxide precursors and HfO_2 film quality will be discussed.

AF10-4 Plasma Enhanced Atomic Layer Deposition (PEALD) of Nickel Using Allyl Cyclopentadienyl Nickel as the Precursor*, **Elham Kamali Heidari**, K. Bosnick, J. Canlas, T. Patrie,* National Research Council, Canada

Owing to their excellent magnetic properties, low electrical resistivity, high thermal conductivity, high Curie temperature, excellent corrosion resistance and unique catalytic properties, nickel thin films and nanoparticles have found various applications ranging from information storage devices and electronics to energy storage, magnetic sensors and catalysis.

In the present study nickel thin films were deposited on silicon and sapphire substrates using allyl cyclopentadienyl nickel ($C_8H_{10}Ni$) as the precursor and N_2 and N_2/H_2 as the co-reactant plasma. This precursor was chosen due to its low melting point of 9 ^{o}C and high vapor pressure that provides the possibility of low temperature atomic layer deposition of nickel. PEALD was carried out by sequential exposure of the substrate to the precursor and plasma, followed by a purging time of 2 and 5s, respectively. The effect of substrate temperature as well as plasma composition and dose time was studied. X-ray reflectometry (XRR) studies showed that 200 ^{o}C is the optimum substrate temperature in terms of film thickness. Lower and higher temperatures resulted in a decrease in growth rate. Regarding the plasma composition, pure N_2 plasma leads to higher growth rates, but less Ni content in the film, while introducing 5% H_2 to the plasma results in lower growth rates but higher Ni concentrations. The optimum plasma does time is 15s. Lower dose times resulted in lower growth rates, while higher does times did not make changes to the thickness.

Finally, the optimum ALD Ni coated substrates were loaded in a CVD chamber for deposition of CNTs where Ni acts as the catalyst for nucleation and growth of CNTs. The scanning electron microscopy (SEM) as well as Raman spectroscopy studies showed that regardless of the plasma composition, CNTs are uniformly deposited all over the surface, showing the high effectiveness of the developed ALD process for deposition of well dispersed of Ni catalysts on the surface of both Si and sapphire. We believe the developed recipe can be applied for deposition Ni nanoparticles or thin films on different substrates for catalysis applications.

AF10-5 Enhancement of Ferroelectric Properties of $Hf_{0.5}Zr_{0.5}O_2$ Thin Films by Various Metal Electrodes*, In Soo Lee,* Department of Materials Science and Engineering and Inter-University Semiconductor Research Center, Seoul National University, Korea (Republic of)*; B. Kim, S. Hyun, H. Park, Y. Lee, S. Lee, M. Oh, S. Ryu, S. Byun, D. Shim, C. Hwang,* Seoul National University, Korea (Republic of)

Since the discovery of ferroelectric properties in HfO_2-based materials, $Hf_{0.5}Zr_{0.5}O_2$ (HZO) became one of the most prevalent ferroelectric thin films due to its excellent ferroelectricity with small film thickness and CMOS-compatibility [1]. Among various metal electrodes used as a bottom electrode, the HZO film showed the best ferroelectric properties when grown on the TiN bottom electrode [2]. However, a recent study revealed that the tungsten (W) metal electrode used as a bottom electrode and top electrode resulted in the highest remnant polarization (P_r). As a top electrode, W shows a low thermal expansion coefficient inducing an in-plane tensile strain to HZO film during rapid thermal annealing, facilitating the formation of o-phase [3].

In this study, ferroelectric HZO films were deposited by the atomic layer deposition (ALD) technique on the TiN and W bottom electrode. At the same time, Ru and TiN were used as top electrodes. The 10-nm-thick HZO film deposited on the W electrode with TiN as a capping electrode showed a substantial increase in the $2P_r$ value ($50.1\mu C/cm^2$), which increased by 31.4% compared to the case of conventional TiN/HZO/TiN films. Also, 10-nm-thick HZO film deposited on TiN electrode with Ru capping electrode showed an even higher $2P_r$ value ($63\mu C/cm^2$) at 4.6MV. Detailed characterization results for the interface structure and possible origin for such improvements will be presented.

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AF10-6 Simulating Ultrasmooth, Pinhole-free Thin Films with a Monte Carlo Model of Nucleation and Growth*, D. LaFollette,* University of Southern California*; **Kinsey Canova**, J. Abelson,* University of Illinois at Urbana-Champaign

The architecture of advanced microelectronic devices requires vacuum-deposited films that are only a few nm thick, pinhole-free, and smooth. However, film growth by ALD or low-temperature CVD often follows the Volmer-Weber mode that begins with nucleation of discrete islands that grow until the substrate is covered (“coalescence”). Film thickness and roughness at coalescence depend on several factors including the nucleation rate and the growth rate. To show the effects of these two parameters alone, we construct a Monte Carlo model that simulates film morphology as a function of (i) the nucleation rate of hemispherical islands at random positions on the bare surface and (ii) the constant film growth rate on those islands. Simulated films resemble AFM images of real films and reveal a remarkable power law relationship between the RMS roughness and the ratio of the nucleation and growth rates.

We next derive an analytical model based on Poisson point statistics at coalescence. It formally predicts the same power law trend that is observed in the Monte Carlo simulation. Both models estimate the required rates to grow a film within set limits of total thickness, roughness, and coverage.

Simulation results are compared to experimental data for HfB_2 films during the onset of growth; these match closely during some time periods but not over the entire process. The deviations presumably arise from the simplifying assumptions in the Monte Carlo simulation, which includes no kinetic parameters apart from the constant nucleation probability and growth rate. Therefore, the simulation can also be used as a tool to indicate the likely presence of additional kinetic factors, e.g., surface diffusion, in the growth process.

AF10-7 Revisiting Process Optimization in Atomic Layer Deposition: Going Beyond Growth Rate*, **Elham Rafie Borujeny**, K. Cadien,* University of Alberta, Canada

Atomic Layer Deposition (ALD) is a promising nanofabrication technique for depositing thin layers of a wide range of materials with atomic-level control over thickness, remarkable uniformity over large areas, and exceptional conformality on patterned structures. Optimized ALD processes consist of self-limiting reactions that introduce reactants or precursors to the substrate surface one by one in a cycle resulting in formation of a monolayer of target material on the surface. Conventionally, such optimized ALD processes are achieved by growing a number of trial films while varying the dose and the purge timings of the ALD cycle and obtaining growth per cycle (GPC) in each case. Once a stable GPC is obtained, the corresponding dose and purge timings are considered to be optimized and ensure self-saturation. One of the limitations of such GPC-based optimization strategy is that it requires significant resources (energy, material, and time) to repeat the experiments and obtain optimized cycle parameters in all deposition temperatures or conditions. In this work, we demonstrate a fast and versatile strategy to obtain self-saturating ALD cycle parameters at any deposition temperature or condition without needing to grow trial ALD films and obtaining GPC. Through a few examples, we show that our optimization approach results in self-saturating cycle parameters consistent with the GPC-based optimization approach and makes the resources available to obtain not only self-saturating ALD process parameters but also process conditions that are fine-tuned to obtain films with superior structure, property, and functionality. We also demonstrate that our optimization approach can provide a unique tool to investigate and design in-situ doping strategies for ALD films. Examples of successful doping of ALD films of emerging materials by using our approach are also provided.

AF10-8 Surface Reaction of Nb_2O_5 RT-ALD Explained by Using Quartz Crystal Microbalance Measurements*, **Kazuki Yoshida**, K. Saito, M. Miura, K. Kanomata, B. Ahmmad, S. Kubota, F. Hirose,* Yamagata University, Japan

Metal oxides are used as protective layers for metal components, organic electronics, and packaging films. Niobium pentoxide (Nb_2O_5) has been studied as protective layers for the cathode of the fuel cells. The ALD coated Nb_2O_5 exhibits excellent anti-corrosion[1]. However, a high-temperature process over 200 °C was necessary in the conventional technologies. Previously, we reported the room temperature (RT) ALD process of Nb_2O_5[2], but we have not discussed the detailed surface reaction in the RT-ALD process. In the present study, we use a quartz crystal microbalance measurement (QCM) to investigate its surface reaction, which enables the monitor of the quartz crystal surface mass variation during ALD. It is confirmed that the surface mass increased in the step-by-step mode, suggesting that the Nb_2O_5 was deposited in ALD mode. In this study, we discuss the surface reaction in the Nb_2O_5 RT-ALD from the surface mass variation.

A schematic of the RT-ALD surface mass variation monitoring system with a QCM sensor is shown in Figure 1. We used plasma excited humidified Ar as an oxidizing gas, *tert(*butylimido)tris(ethylmethylamido)niobium (TBTEMN) as precursors of Nb_2O_5. Any heaters or thermal sources were not installed to the chamber wall. TBTEMN container was warmed up around 80 °C to promote the niobium precursor evaporation. The exposure time of TBTEMN was 50 s, plasma excited humidified argon was 615 s. The evacuation steps of 180 and 60 s were inserted between TBTEMN and the plasma excited humidified argon exposure. For the QCM measurement, we used an ALD sensor (#750-717-G2, Inficon) with AT-cut quartz crystals which a resonance frequency was 6 MHz. The sampling rate was 2 Hz. The surface mass variation during the whole process was recorded in a data logger as voltage variation.

We confirmed the surface mass variation during 10 cycles of ALD. The mass variation curve exhibits the stepwise increase that indicates the ALD growth mode. To discuss the surface reaction in this process, we picked up a typical mass variation curve in 10 cycles, as shown in figure 2. The surface mass varied during the precursor adsorption and surface oxidization period. The number of reacted ligands of the precursor adsorption period is estimated as 2 or 3 from a mass variation ratio during one ALD cycle. In the conference, we propose a surface reaction model of Nb_2O_5 RT- ALD.

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AF10-9 Ir Studies on Low-Temperature Atomic Layer Deposition of Aluminum Nitride Using Plasma Excited Ammonia*, Kentaro Saito, K. Yoshida, K. Kanomata, M. Miura, B. Ahmmad, S. Kubota, F. Hirose,* 4-3-16 Jonan, Japan

Aluminum nitride (AlN) has been attracting much attention since it is also expected to be used as a gas barrier for organic light emitting diodes (OLEDs). In the conventional technologies, depositions of AlN were examined by chemical vapor deposition (CVD) and atomic layer deposition (ALD), although these were performed at a temperature of 200 °C and higher. A low-temperature deposition is demanded for flexible electronics since the OLEDs are not torelant to the high-temperature processes. In this study, the low-temperature ALD of AlN using trimethylaluminum (TMA) and plasma-excited ammonia is examined. We aim to modelize the surface reactions of the low-temperature AlN ALD with multiple internal reflection infrared absorption spectroscopy (MIR-IRAS).

A p-type Si substrate was used as a sample with a form of prism for MIR-IRAS. The size of the sample prism was 10×48 mm^2 whose resistivity was 10 Ωcm. The sample prism was set in an ALD reaction chamber. The prism was heated at 160 °C with a direct current passing. In the nitridation step, ammonia and argon were mixed with a volume ratio of 7 : 3, followed by being excited in a quartz tube with an RF power of 250 W and a frequency of 13.56 MHz. The flow rate of the mixed gas was 10 sccm. Ammonia molecules in the mixture were dissociated to NH radicals and fragments for the nitridation.

We observed the surface reaction to confirm the TMA adsorption on the AlN surface at 160 °C and examine if the plasma-excited ammonia causes nitridation on the TMA adsorbed surfaces. Fig. 1 shows IR absorbance spectra, measured from the TMA adsorbed surface with TMA exposures from 1000 to 200000 L at 160 °C. The presence of positive peaks at 2941, 2899, and 2830 cm^{-1} indicates that TMA was adsorbed on the surface at 160 °C. Fig. 2 shows IR absorbance spectra measured from plasma excited ammonia treated TMA adsorbed surface. The negative peaks at 2941, 2899, and 2831 cm^{-1} indicate the degeneration of hydrocarbon, which might be due to the nitridation. From this observation, we designed the process of AlN ALD and confirmed the AlN deposition by X-ray photoelectron spectroscopy. In the conference, we discuss the reaction model of AlN deposition based on the IR absorption spectra and XPS analysis.In the conference, we discuss the surface reaction of the low-temperature AlN ALD.

AF10-10 Atomic Layer Deposition of SiO_2 using BDEAS and O_3 as Precursor*, Yu-Hsuan Yu,* Taiwan Instrument Research Institute, National Applied Research Laboratories , Taiwan*; C. Kei,* Taiwan Instrument Research Institute, National Applied Research Laboratories, Taiwan

Silicon dioxide (SiO_2) is a common dielectric material in silicon microelectronic devices owing to its relatively low dielectric constant and large band gap. Science the size of microelectronic devices become smaller as the complexity of structure increase, the requirement on thickness and uniformity of SiO_2 coatings become stricter. Atomic layer deposition is known for precise thickness control and excellent step-coverage, which is a good candidate to fabricate SiO2 thin film. In this study, We deposited silicon oxide (SiO2) film by ALD using bis(diethylamino)silane (BDEAS) and ozone (O_3) as precursors. The SiO_2 film was deposited at several different temperatures which from 200℃ to 350℃. The thickness of SiO2 was measured by ellipsometer and TEM. The growth rate of SiO2 is from 0.13 (200℃) to 0.93 (350℃) Å/cycle.

AF10-11 Effect of Plasma Time in Plasma-Enhanced Atomic Layer Deposition on Wet Etching Properties of Aluminum Nitride*, Heli Seppänen, H. Lipsanen,* Department of Electronics and Nanoengineering, Aalto University, Finland

Aluminum nitride (AlN) is a material with a combination of piezoelectric lattice, high direct bandgap and high dielectric constant, which makes it interesting for a wide range of applications in modern technology [1, 2, 3, 4]. Thin films of AlN can be grown with atomic layer deposition (ALD) with both thermal and plasma-enhanced (PEALD) processes. Patterning the AlN film is often required to achieve the wanted structure, however wet etching of ALD AlN is not a well-studied topic. ALD AlN films commonly have a lower crystal quality in comparison with other deposition techniques, e.g. sputtering, and are thus easier to wet etch with safer chemicals [5]. As different process parameters affect the properties of the deposited film, the effect on etch rate is unknown.

In this study the effect of ion bombardment during the growth of the AlN film on the etching properties is investigated by comparing thermally grown AlN to PEALD grown AlN with different plasma times. The AlN films are characterized using spectroscopic ellipsometry and X-ray diffraction (XRD). The etchant is developer AZ 351B diluted in DIW, a solution commonly used in photolithography. The results show a difference in the etch rates between different plasma times; AlN film grown thermally is etched 1,9 nm/s whereas the etch rate of a film with a 15 s plasma exposure time is 0,9 nm/s and 0,6 nm/s with a film with a total 35 s plasma exposure time per cycle. This result is in accordance with previous study on the influence of plasma exposure time during growth of ALD film [6]. The decrease in the wet etch rate can also be predicted from the XRD scan, as the crystallinity is enhanced by the applied plasma time; the thermal sample is amorphous, and the crystallinity is enhanced by extended plasma exposure time.

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AF10-12 ALD of TiO2 using a Titanium Precursor with a Linked Amido-cyclopentadienyl Ligand: A Density Functional Theory Study*, Romel Hidayat, H. Kim, Y. Choi,* Sejong University, Korea (Republic of)*; J. Seok, J. Park,* Hansol Chemical, Korea (Republic of)*; W. Lee,* Sejong University, Korea (Republic of)

Titanium oxide (TiO_2) has been an attractive material with interest for various applications, including photocatalysts, optical coatings, and the high-permittivity dielectrics of DRAM capacitors. The atomic layer deposition (ALD) technique is used to deposit thin films with excellent step coverage, accurate thickness control, and excellent film quality. One of the most common precursors for the ALD of TiO_2 was tetrakis(dimethylamido) titanium (TDMAT). However, TDMAT showed low ALD temperatures because of its insufficient thermal stability. In general, the higher the deposition temperature, the better the physical and electrical properties of the dielectric film. Therefore, we need a Ti precursor with excellent thermal stability and reasonable reactivity to increase the ALD temperature. Thermal stability of the Ti precursor can be improved by introducing a cyclopentadienyl (C_5H_5, Cp) ligand, and tris(dimethylamido)cyclopentadienyl titanium ($CpTi(NMe_2)_3$) is more thermally stable than TDMAT [1]. We reported a Ti precursor, (2-(N-methylamido)1-methyl(ethyl-cyclopentadienyl))bis(dimethylamido) titanium (CMENT), designed to further improve the thermal stability of $CpTi(NMe_2)_3$ by linking a Cp ligand to an amido ligand [2]. In this study, we compared CMENT and $CpTi(NMe_2)_3$ by deposition experiments and density functional theory (DFT) calculations. CMENT showed higher ALD TiO_2 process temperature than $CpTi(NMe_2)_3$. The DFT simulation of thermolysis and hydrolysis of Ti precursors confirmed the better thermal stability and reactivity with hydroxyl groups of CMENT. The chemisorption of Ti precursors on a hydroxylated TiO_2 surface was also simulated. For CMENT, the linked ligand may remain on the surface after chemisorption. In contrast, after chemisorption of $CpTi(NMe_2)_3$, only a fraction of Cp would remain on the surface. Therefore, the introduction of a linked ligand enables the ALD process at higher temperatures compared to the introduction of a Cp ligand.

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AF10-13 Atomic Layer Deposition of Silicon Oxide Using a Silylamine Precursor and Ozone*, Heeju Son, Y. Choi, H. Han, H. Roh, Y. Kim, W. Lee,* Sejong University, Korea (Republic of)

To overcome the scaling limit of planar semiconductor devices, three-dimensional structures have been introduced, and new process technologies have been applied. The method of forming silicon oxide (SiO_2) thin film has been shifting from the conventional chemical vapor deposition (CVD) methods to atomic layer deposition (ALD) technologies for excellent step coverage and film characteristics at low process temperatures. Various silicon compounds have been studied as the precursor for the ALD of SiO_2, and the reported Si precursors can be categorized into chlorides and aminosilanes. Chloride precursors exhibit good film properties, but their low reactivity requires a large supply. Aminosilanes are more reactive than chlorides, but they have poor thermal stability and low growth rates. Silylamine compounds were investigated as the silicon precursor for the ALD of silicon nitride thin films, and superior film properties and step coverage were reported compared to aminosilane [1]. However, the study on the ALD SiO_2 using silylamine compounds was rare. In the present work, we studied the ALD SiO_2 using a silylamine compound, bis(dimethylaminomethylsilyl) trimethylsilyl amine (DTDN2-H2), as the silicon precursor. Ozone was used as the co-reactant. The maximum ALD temperature was 400°C and the growth rate of the thin film was 1.34Å/cycle at 400°C. The ALD SiO_2 films were stoichiometric pure SiO_2 and showed excellent step coverage. Raising the process temperature to 450°C improved the insulating properties of the deposited film but worsen the step coverage. The silylamine precursor could perform the ALD process with less supply at lower process temperatures than the chloride precursor. It also showed a higher growth thickness per cycle than the aminosilane precursor. We simulated the dissociative chemisorption of DTDN2-H2 on an OH-terminated SiO_2 surface by density functional theory (DFT) calculation. Surface species formed by the chemisorption may contain three silicon atoms or one silicon atom, resulting in a higher growth rate than aminosilane precursors.

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AF10-14 Reaction Mechanism and Film Characteristics of High-temperature ALD of Silicon Nitride*, **Tanzia Chowdhury**, H. Han, K. Jainuri, H. Son,* Sejong University, Korea (Republic of)*; J. Han, Y. Kim, J. Seok, J. Park,* Hansol Chemical, Korea (Republic of)*; W. Lee,* Sejong University, Korea (Republic of)

In modern semiconductor devices, silicon nitride is an essential dielectric material that has been utilized as gate spacers, etch stop layers, and diffusion barriers. Recently, it has been applied to the charge trapping layer and the sacrificial layers in three-dimensional vertical NAND flash memory devices. Atomic layer deposition (ALD) is required to deposit silicon nitride thin films with excellent conformality in high-aspect-ratio three-dimensional patterns. There have been several reports on silicon nitride ALD processes including both thermal and plasma-assisted schemes. As the deposition temperature increased, the physical and electrical properties of the deposited thin films were improved. However, thermal decomposition occurs above a certain temperature, resulting in poor thin film properties and step coverage [1]. To date, the maximum temperatures of the genuine ALD mode have been reported to be approximately 450–500°C, and ALD processes at higher temperatures have not been reported. In the present study, we investigated the high-temperature ALD of silicon nitride using thermally stable silicon precursors. Various silicon compounds were compared using NH_3 as the co-reactant. The reaction mechanism and the film characteristics were studied. The electrical characteristics of the films, such as leakage current, breakdown voltage, dielectric constant, and oxide trapped charge densities, were determined by I-V and C-V measurements. To study the ALD reaction mechanism, the chemisorption of the precursors on an NH_2/NH-terminated silicon nitride surface was modeled and simulated by density functional theory (DFT). The possible reaction pathways for each silicon precursor were compared to explain the properties of the deposited films using different silicon precursors.

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AF10-15 Atomic Layer Deposition of Nanometer Thick Tungsten Nitride Using Anhydrous Hydrazine for Potential X-Ray Optics Application*, **Dan N. Le**, A. Kondusamy, S. Hwang, A. Ravichandran, J. Mohan, Y. Jung,* University of Texas at Dallas*; D. Alvarez, J. Spiegelman,* RASIRC*; M. Markevitch,* NASA Goddard Space Flight Center*; J. Kim,* University of Texas at Dallas

In this study, we establish a low-temperature atomic layer deposition process of high-quality ultrathin WN_x films for applications like barrier layers of Cu metallization and X-Ray mirrors. Hydrazine has been extensively investigated as a nitrogen source at low temperature in place of conventionally used ammonia, due to its high reactivity.[1] Hydrazine along with Bis(tebutylimino)bis-(dimethylamino)tungsten (VI) (BTBMW) is investigated for thermal ALD of tungsten nitride. We confirm that high quality WN_x films, with a nano-crystalline structure, can be deposited at the low temperature window.

A home-built ALD chamber was employed to deposit WN_x films at a temperature range of 250–350°C. Deposited films are analyzed by using an ellipsometer, atomic force microscopy, X-Ray diffraction spectroscopy, X-Ray reflectivity spectroscopy, and cross-sectional transmission electron microscopy.

The GPC of the deposited WN_x films saturates with a short exposure time of hydrazine (0.1s). A GPC of 0.1 nm/cycle is observed at a temperature of 300°C, which is higher than the reported growth rate of WN_x films using NH_3 at the same temperature.[2] The AFM images demonstrate a smooth surface roughness (~0.23 nm) of films deposited in the temperature range of 250–350°C. XRR determines that film density is as high as 13.0 g/cm^3. An earlier report shows films deposited using NH_3 exhibit crystalline phase after a 30-minute annealing process at 700°C.[2] Interestingly, XRD measurements of films grown with hydrazine display crystallinity with highest intensity peak at 2θ value of 37.6°. It is suspected that, at low temperature, N_2H_4 provides an ideal condition for random distributed nucleation events to occur on the surface of the amorphous region per ALD cycle.[3] ALD cycles continue to add mass to the nuclei after the formation of a nucleus allowing crystallite to grow.[3] The resistivity of the deposited films ranges between 1.34x104–2.38x10^4 μΩ.cm. Based on the results of above, a stacking structure of WN_x and one other metal nitride thin film (WN_x and AlN_x) is deposited on a SiO_2 substrate. Such an alternating stack of nitride films with different densities could be applied as X-Ray mirrors. The experiment details and results will be presented.

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AF10-16 First-Principles Investigation of Atomic Layer Deposition of Silicon Nitride Using NH_3 Plasma*, **Tsung-Hsuan Yang**, G. Hwang,* University of Texas at Austin*; P. Ventzek, T. Iwao , K. Ishibashi ,* Tokyo Electron America

Plasma-enhanced atomic layer deposition (PEALD) has been demonstrated to be a promising technique for controlled growth of silicon nitride (SiN) thin films. The benefits of PEALD include excellent conformality, precise thickness control, and high quality at relatively low temperatures (<400°C). In this work, we focus on the mechanisms underlying the nitridation of Si-rich SiN surfaces with NH, NH_2, and H radicals generated from the NH_3 plasma. The surface reaction mechanisms have been examined using first-principles calculations based on density functional theory (DFT). Surface nitridation tends to proceed through the reaction of NH and NH_2 radicals with H-terminated Si-rich surfaces, leading to the formation of primary amines (Si-NH_2). H radicals are found to predominantly react with primary amines, if available, to form Si-NH_3 moieties; the NH_3 is likely to desorb from the surface rendering a Si dangling bond. It is also likely that H radicals abstract H from Si:H surface moieties creating Si dangling bonds. The Si dangling bond is predicted to be rather unreactive with both NH_3 and H_2 molecules. As such, the extent of nitridation appears to be a strong function of the flux ratio of H to NH/NH_2. The Si-N bond strength in Si-NH_2 is also found to be sensitive to the amine coverage, which in turn helps to achieve self-saturated nitridation reactions. The rate-determining steps in the nitridation process turn out to be bridging reactions (*i.e.*, Si-NH_2 + Si-NH_2–> Si-NH-Si + NH_3 or Si-H + Si-NH_2–> Si-NH-Si + H_2) depending on the primary amine coverage. Our work also predicts that the kinetics of the nitridation reactions is significantly affected by the amine surface coverage. Based on the calculation results, we will also discuss how the radical-surface chemistry would determine the deposition kinetics and the film quality.

AF10-19 Low Temperature ALD of Antimony Oxide*, J. Yang,* Leibniz Institute for Solid State and Materials Research, Germany*; S. He,* leibniz Institute for Solid State and Materials Research Dresden, Germany*; S. Lehmnann, **Amin Bahrami**, K. Nielsch,* Leibniz Institute for Solid State and Materials Research, Germany

Antimony oxide thin films can be used as etch stop layers, dopant source for ultra-shallow doping of silicon, as anode in various batteries, fire- and flame-retardant materials, etc. In this study we report the atomic layer deposition of Sb_xO_y coatings using $SbCl_5$, $Sb(NMe_2)_3$ as antimony reactants and H_2O and H_2O_2 as an oxidizer at low temperatures. Homogenous antimony oxide deposition can be achieved on flat silicon wafers. $SbCl_5$ can react with both oxidizers, while no deposition was found using $Sb(NMe_2)_3$ and H_2O. Uniform deposition growth was found at 80 °C deposition temperature for all the systems. X-ray photoelectron spectroscopy results confirm formation of Sb_2O_3 as the main phase with some minority of Sb_2O_5 phase. The ratio of Sb_2O_3 to Sb_2O_5 is affected by the type of precursor and deposition temperature.

AF10-22 Development of Fast Response Flow Controlled Vapour Delivery System for ALD/ALE Applications*, **Krunal Girase,*** HORIBA STEC, Co., Ltd., Japan*; H. Nishizato,* HORIBA STEC, Co., Ltd. , Japan*; T. Hayashi, M. Hotta,* HORIBA STEC, Co., Ltd., Japan*; P. Lowery P.E.,* HORIBA Reno Technology Centre*; P. Totten,* HORIBA Instruments Incorporated*; T. Hoke,* HORIBA Reno Technology Centre*; T. Freeman,* HORIBA Instruments Incorporated, Poland

Atomic layer processes, such as atomic layer deposition (ALD), atomic layer etch (ALE), and selective deposition/etch processes are becoming some of the predominant methods used to achieve new device geometry shrinks with smaller lithographic nodes. The chemical vapors used in ALD processes have to be delivered at a constant concentration per pulse. In the present study, a fast response flow-controlled vapor delivery system using a piezoelectric actuated electromechanical valve was developed and implemented for ALD application. This valve shows a response time of < 1 ms for ON/OFF pulsing and < 10 ms for flow control with the ability of programable waveform control. Due to fast flow control, this system reduces the waste of precursor by eliminating vent lines and increase the repeatability of vapor delivery per pulse. Both methods of vaporization: vapor drawer and bubbling method were demonstrated for vapor delivery to the ALD reactor and the results were found repeatable pulse to pulse. For the bubbling method of vaporization, an auto pressure regulator was used to control carrier gas pressure and hence to control the concentration of precursor vapor. A new self-contained, closed-loop design is being developed with piezoelectric-drive and an intuitive UI that will allow the end-user to be able to control variable pulse cycle for ALD/ALE applications.

AF10-25 Thermal Atomic Layer Deposition of Elemental Antimony at Room Temperature: Growth and Uniformity Studies*, **Majeda Al Hareri, D. Emslie,*** McMaster University, Canada

As feature sizes on devices continue to decrease, atomic layer deposition has become an invaluable tool for the fabrication of highly uniform and conformal thin films with nano-scale control of film thickness. Additionally, the utilization of low temperature thermal ALD techniques can aid in obtaining continuous films of low-melting metallic films that often observe issues with film continuity at low thicknesses as a result of agglomeration.[1,2] In 2011, the first elemental non-metal thermal ALD process was reported, which involved the use of tris(triethylsilyl)antimony ($Sb(SiEt_3)_3$) and antimony trichloride ($SbCl_3$) to produce thin films of elemental antimony through novel dehalosilylation surface chemistry.[3] Due to the fact that antimony has a low melting point, and is a common component in various micro- and nanomaterials,[4,5] reduction of the deposition temperature in this process may prove beneficial as a means to improve nucleation and prevent agglomeration.

Switching to the smaller and more volatile methyl derivative, $Sb(SiMe_3)_3$, allowed for a substantial decrease in the precursor delivery and deposition temperatures, as well as an improvement in nucleation on H-terminated silicon and SiO_2. We present the first report of room temperature thermal ALD of a pure element, and an investigation of the effects of substrate temperature and pulse durations on the uniformity of the deposited films at low thicknesses (< 10 nm).

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AF10-28 Impact of Different Intermediate Layers on the Morphology and Crystallinity of TiO_2 Grown on Carbon Nanotubes by Atomic Layer Deposition*, **Jiao Wang, Z. Yin, E. List-Kratochvil, N. Pinna,*** Humboldt-Universität zu Berlin, Germany

Nanocomposites of TiO_2 and carbon nanotubes (CNTs) have been extensively studied in photocatalysis, electrochemical sensing and energy storage over the last decade. The unique properties of these nanocomposites are greatly dependent on the morphology, crystallinity and homogeneity of the TiO_2 films. However, a fine control of the film microstructure is still challenging due to a lack of understanding of the early stages of the TiO_2 growth. The presence of an intermediate buffer layer can cause remarkable changes in the morphological and structural properties of the coatings. Here, TiO_2 films deposited by atomic layer deposition (ALD) on CNTs without and with different intermediate layers (Al_2O_3 and ZnO) have been systematically investigated. Compared to bare CNTs, it is suggested that these two intermediate layers with higher surface energy can lead to a delay of the TiO_2 crystallization, ultimately leading to the growth of conformal crystalline TiO_2 films. This study demonstrates a strategy to tailor the microstructure and the properties of thin-films via ALD by applying intermediate layers, and provides information about the role of surface energy of the substrate on crystallization and growth behavior of ALD thin films.

AF10-31 *Growth, Intermixing and Composition Control of Atomic Layer Deposited Zinc Tin Oxide* , *Poorani Gnanasambandan,* *R. Leturcq,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

Zinc tin oxide being abundant and non-toxic has varied applications from gas sensors, thin film transistors, to window and buffer layers in thin film solar cells, etc. The synthesis of zinc tin oxide (ZTO) by atomic layer deposition (ALD) has been widely studied with different Sn precursors and reactants [1][2]. Atomic layer deposition of ternary materials by mixing two binary ALD processes has its challenges [3]; the composition and growth rates of ternary materials deviate from that of the binary processes due to various factors, including the interaction between different precursors.

Previous studies aimed to understand deeper the ZTO ALD processes, by investigating the underlying surface chemistry of the precursors, influence of substrate temperature and constructing analytical models from observed deviations in the growth rate [4][5][6]. Still there remains a need for a consistent model that explains the nonidealities observed in the growth of ZTO by ALD under various processing conditions.

We study atomic layer deposited $Zn_{1-x}Sn_xO$ with x varying from 0.1 to 0.4 by optimizing the growth conditions with varying deposition temperatures and supercycle parameters such as pulse ratios and bilayer period. We analyze the deviation of growth rate and composition of ZTO from the respective binary ALD processes. We find that the composition of [Sn]/([Sn]+[Sn]) has a strong dependence on the deposition temperature in contradiction to Ref. [6]. We aim to achieve precise control over the composition and demonstrate the effect of doping on the band alignment, electrical and optical properties.

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AF10-34 Hollow Cathode Plasma Enhanced Atomic Layer Deposition of Vanadium Oxide Films: *in situ* Ellipsometric Monitoring of Film Growth with TEMAV and Oxygen Plasma*, **Adnan Mohammad, K. Joshi, S. Ilhom, . Shukla, B. Willis, B. Wells,*** Uconn*; A. Okyay,* Stanford University*; N. Biyikli,* Uconn

Vanadium dioxide is a bistate phase-change material that shows a low temperature phase transition from monoclinic to tetragonal rutile structure. The transition is called MIT (metal-insulator transition) which can be used in electrical and optical switching applications.There are several reports in the literature showing thermal atomic layer deposition (ALD) of vanadium oxide with TEMAV and VTIP precursors and water or ozone as co-reactant. The reported as-grown vanadium oxide films are mostly amorphous, which are typically annealed at high substrate temperatures (> 600 ℃) to achieve crystalline films. However, no significant report is yet found on VOx films grown by plasma ALD, where O2 plasma is used as the coreactant.

In this work we report on the low-temperature crystalline VOx deposition in a hollow cathode plasma reactor featuring in situ ellipsomteric monitoring, in which we utilized TEMAV and O2 plasma as the metal precursor and co-reactant, respectively. The parameters used for the plasma ALD experiments are 0.1 s of TEMAV pulse with 10 sccm of N2-carrier flow, 50 sccm Ar-purge for 10 sec, 50 sccm O2 plasma for 10 s, plasma power 50W-300W and finally another 10 s of Ar purge. In addition, the TEMAV precursor cylinder and line is heated at 110 °C to provide sufficient amount of precursor vapor into the growth chamber. We found a maximum growth per cycle (GPC) of 1.1 Å from in situ ellipsometry measurements. The x-ray diffraction (XRD) measurements revealed crystalline V2O5 phase for the as-deposited films and the ex situ ellipsometry showed a refractive index of 2.45. The next step is to anneal the as-grown films to achieve VO2 and to do temperature-dependent electrical and structural characterization of the VO2 samples to confirm the MIT character of the films.

AF10-37 Combined Fabrication and Testing System for Atomic Layer Deposition Microchannel Plates*, **Anil Mane**, J. Elam,* Argonne National Laboratory, USA

Microchannel plates (MCPs) are two dimensional solid-state electron multipliers consisting of a thin plate permeated with millions of parallel, micron-scale, high aspect ratio pores.Each pore acts independently to amplify electron signals incident on the front surface allowing MCPs to be utilized in imaging detectors for astronomy, high-energy physics, medical imaging (PET scanner), homeland security and the military (night vision devices).Over the last decade, we have researched and developed MCPs fabricated by depositing ALD nanostructured coatings on high aspect ratio (40-100), high porosity (>65%) glass microcapillary array (MCA) substrates. These ALD MCPs have many advantages over MCPs manufactured by conventional methods.This experience taught us that achieving uniform, precise coatings on these complex MCA substrates is challenging and time consuming. To streamline ALD MCP process development and to enable systematic studies of MCP structure and function, we constructed an integrated system which combines a viscous flow ALD reactor for coating high aspect ratio MCA substrates with a sample transfer chamber and high voltage MCP testing chamber, both of which are maintained under high vacuum. This combined system allows us to measure critical MCP metrics, such as gain and pulse height distribution, after each ALD precursor exposure to map out the MCP performance as a function of the ALD film thickness and composition.Critically, these measurements are performed without exposing the MCP to air which avoids the inadvertent formation of surface hydroxides, carbonates and other contaminants that can alter the materials properties such as the secondary electron emission (SEE) of the MCP surface.To our knowledge, this is the first integrated system combining ALD MCP fabrication and testing.Our initial tests used 33mm diameter borosilicate glass MCAs (Incom, Inc.) as MCP substrates that we first functionalized using an ALD nanocomposite tunable resistive coating.Next, we performed Al_2O_3 ALD using trimethyl aluminum and H_2O to deposit the SEE layer and measured the current-voltage characteristics as a function of the ALD Al_2O_3 film thickness. We used these measurements to extract the gain and SEE values which agree with previous measurements for ALD Al_2O_3 thin films. We believe this new system will reduce ALD MCP process development times by a factor of 10 and may be suitable for ALD process development in vertical interconnect access (VIA) substrates (e.g. TSV, TGV and TPV) for vertically integrated semiconductor microelectronics devices.

ALD Fundamentals

Room On Demand - Session AF2

Precursors and Chemistry: Simulation, Modeling, and Theory of ALD

AF2-1 Comparison of ALD Saturation Profiles Simulated With Two Theoretical Models*, **Jihong Yim**, E. Verkama, R. L. Puurunen,* Aalto University, Finland

Self-terminating chemistry of atomic layer deposition (ALD) process enables one to grow pinhole free conformal thin films on high-aspect-ratio (HAR) structures. ALD has attracted ever more attention in diverse applications, such as microelectronics and nanostructured catalyst preparation.[1] Yet, it is essential to optimize ALD process parameters for the conformal deposition especially on HARs. Our previous study investigated the effect of experimental parameters on conformality using saturation profiles of archetypical trimethylaluminum-water ALD processes in lateral HARs with an aspect ratio of typically 10000:1.[2]

The investigation on the effect of process parameters on ALD conformality is continued by simulating ALD saturation profiles with two modeling approaches: a MATLAB simulation based on a diffusion–reaction modeling (Model A)[3,4] and a Python simulation based on a ballistic transport modelling (Model B).[5,6] These simulated saturation profiles are compared to each other in approximately the same condition. While the main features of the simulated saturation profiles are similar, differences are found in the value of 50% thickness penetration depth ($PD_{50\%}$) and slope at $PD_{50\%}$, as well as the shape of the tail region.

Sticking coefficient of ALD reactants describes ALD growth kinetics. A recent study by Arts et al.[7] reported a method to back-extract the sticking coefficient value from the slope of saturation profile. By using this method, we back-extract the sticking coefficient values from the saturation profiles simulated by Models A and B and compare those values to the ones initially set for running the simulations. Interestingly, for both Models A and B, the sticking coefficient values set for the simulations differ somewhat from the ones back-extracted.

Acknowledgement

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AF2-2 Theoretical Prediction of the Adverse Effects of H^+/Cl^- Byproducts on SiN Atomic Layer Deposition with Dichlorosilane*, **Tsung-Hsuan Yang**, G. Hwang, E. Cheng,* University of Texas at Austin*; P. Ventzek, T. Iwao , K. Ishibashi ,* Tokyo Electron America

Plasma-enhanced atomic layer deposition (PEALD) has been demonstrated to be a promising technique for controlled growth of silicon nitride (SiN) thin films. The advantages of PEALD may include excellent conformality, precise thickness control, and high quality at relatively low temperatures. In this talk, we will present molecular mechanisms underlying the PEALD of SiN thin films using dichlorosilane (DCS) as the Si source and N_2/NH_3 plasma as the N source. The adsorption and decomposition of DCS have been found to be sensitive to the surface functional groups; especially, the presence of primary amines plays a critical role in the silicon deposition half cycle. According to our recent studies, the byproducts of DCS decomposition, $H^{\delta+}/Cl^{\delta-}$ pairs, may have a significant effect on the film quality and deposition temperature. First-principles calculations predict that $H^{\delta+}/Cl^{\delta-}$ pairs are strongly bound to the H-terminated N-rich surface by forming $-NH_3^+/Cl^-$ ionic complexes. Because of the sizable binding energy (~ 1 eV), it would be difficult to remove $H^{\delta+}/Cl^{\delta-}$ pairs from the surface unless the PEALD temperature is substantially high. This implies that the reaction of DCS with surface primary amines, and in turn SiN ALD, can be significantly suppressed by the presence of $H^{\delta+}/Cl^{\delta-}$ pairs at relatively low temperatures, which has been confirmed by very recent FTIR measurements at 200 °C. In this talk, we will also discuss a potential method to effectively remove $H^{\delta+}/Cl^{\delta-}$ pairs at low temperatures.

ALD Fundamentals
Room On Demand - Session AF3
Precursors and Chemistry: Mechanisms

AF3-1 Titanium Nitride ALD Process Using High Purity Hydrazine: N_2H_4 Reactivity in Gas Phase, ***Hayato Murata***, *H. Shimizu, K. Andachi,* TAIYO NIPPON SANSO Corporation, Japan*; D. Alvarez , J. Spiegelman,* RASIRC*; K. Suzuki,* TAIYO NIPPON SANSO Corporation, Japan

ALD titanium nitride (TiN) with lower resistivity has attracted an attention as DRAM device has higer-aspect-ratio capacitors with its scaling. We reported that ALD TiN films using $TiCl_4$ and hydrazine (Hy, N_2H_4) has higher GPC, smaller roughness, less chlorine (Cl) impurities, and lower resistivity [1]. Here, we delivered N_2H_4 employing BRUTE Hydrazine (RASIRC, Inc.) which enabled safe delivery of high-purity N_2H_4 gas[2]. In addition to safety and quality of N_2H_4, lab-to-fab scale-up could be efficiently achieved through understanding reaction mechanism of N_2H_4 in the ALD process. In this study, we investigated gas-phase reaction of N_2H_4 in the ALD process and an effect of gas-phase reaction on GPC (growth per cycle).

First, N_2H_4 decomposition was observed above 200°C at 133Pa by quadruple mass spectrometry installed at downstream of a hot-wall tubular reactor. When a gas mixture of 10 sccm N_2H_4 and 240 sccm N_2 flowed through the reactor at 300°C and 400°C (380 cm/s and 450 cm/s), 38% and 55% of N_2H_4 were respectively decomposed before reaching to a substrate (35 cm heated zone before the substrate). Thus, lower-concentration hydrazine is delivered to the substrate in ALD process at higher temperature.

Next, TiN ALD process using $TiCl_4/N_2H_4$ was performed at 250-400°C. GPCs in $TiCl_4/N_2H_4$ ALD were found to be 0.42-0.32 Å/cycle while those in $TiCl_4/NH_3$ ALD were 0.10-0.27 Å/cycle at 250-400°C. Interestingly, the GPC in $TiCl_4/N_2H_4$ ALD was lower at higher temperature, correlating to the hydrazine concentration estimated by the decomposition study. Further enhancement in throughput could be available by preventing the decomposition of N_2H_4 before reaching to the substrate.

In addition, ALD TiN film using $TiCl_4/N_2H_4$ likely had as good quality as sputtered TiN. Refractive index (R.I.) of $TiCl_4/N_2H_4$ film was about 1.68-1.73 at 250-300°C while R.I. of typical sputtered TiN was about 1.66. In contrast, R.I. of $TiCl_4/NH_3$ film formed at 250-300°C was larger than 2.00 likely due to the formation of titanium oxide whose R.I. is 2.4-2.5. The R.I. results indicate probably that higher-concentration hydrazine have an effect on TiN film quality at lower temperature.

Thus, since TiN ALD using $TiCl_4/N_2H_4$ has various advantages over that using $TiCl_4/NH_3$, N_2H_4 is expected to improve both throughput of ALD and quality of nitride ALD films.

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AF3-2 Mechanistic Insights into the Thermal ALD of Gold: Infrared, Mass Balance, Nucleation, and Epitaxy, *P. Liu,* Argonne National Laboratory*; A. Hock,* Illinois Institute of Technology*; **Alex Martinson**,* Argonne National Laboratory

An *in situ* microbalance and infrared spectroscopic study of alternating exposures to $Me_2Au(S_2CNEt_2)$ and ozone illuminates the organometallic chemistry that allows for the thermal atomic layer deposition (ALD) of gold. The synthetic yield of $Me_2Au(S_2CNEt_2)$ was also improved but remains well below 50%, leaving a significant room for improvement of the synthetic method and further motivating the search for related precursors. When we apply deposition conditions optimized for Au ALD growth on itself to oxide substrates the result is a long (300+ cycle) nucleation period, similar to other noble metal ALD processes. After steady-state growth is achieved, the final growth rate (0.14 nm/cycle) is measured to be significantly greater than previously estimated. *In situ* infrared spectroscopy informed by first-principles computation provides insight into the surface chemistry of the self-limiting half-reactions, which are consistent with an oxidized Au surface mechanism. The diethyldithiocarbamate ligand, or remnants thereof, is removed and volatilized by ozone, which is also required for activation of the growing Au surface to endow sufficient activity for reaction with the next Au precursor exposure. This reactivity is significantly reduced, even after ligand removal, upon exposure to a reducing CO atmosphere. X-ray diffraction of ALD-grown gold on silicon, silica, sapphire, and mica reveals consistent out-of-plane oriented crystalline film growth as well as epitaxially directed in-plane orientation on closely lattice-matched mica at a relatively low growth temperature of 180 °C. A more complete understanding of ALD gold nucleation, surface chemistry, and epitaxy will inform the next generation of low-temperature, nanoscale, textured depositions that are applicable to high surface area supports.

AF3-3 Oxygen Reservoirs in Metal Oxides: Mechanisms of Reactive Species Formation and Transport in Atomic Layer Deposition of Fe_2O_3 and NiO, ***Joel Schneider***, *C. de Paula, N. Richey, J. Baker, S. Bent,* Stanford University

The ability of atomic layer deposition (ALD) to deposit materials in a uniform, conformal, and controlled fashion hinges on the surface reactions being self-limiting. While this is often the case, not every ALD process is so well-behaved, and understanding and controlling growth mechanisms are critical given the increasing material demands of ALD. Previous work has shown that the ALD reactions of iron (III) oxide are not limited to the substrate surface but rather involve sub-surface mechanisms. This work uses *in situ* techniques to investigate these mechanisms of ALD growth and the role of active species transport through the film, using ozone-based ALD of Fe_2O_3 and NiO as comparative case studies.

Iron and nickel oxide thin films were deposited using metallocene precursors with ozone, and film thickness was monitored using ellipsometry. *Ex situ* angle-resolved X-ray photoelectron spectroscopy (XPS) and grazing-incidence wide-angle X-ray scattering (GIWAXS) revealed subsurface changes and in some cases the formation of a layer of superstoichiometric oxygen near the film surface that correlates with O_3 exposure. Quartz crystal microbalance and *in vacuo* XPS were then employed to probe the sub-surface storage of superstoichiometric oxygen. Oxygen is present in two different chemical states within Fe_2O_3, and it was found the introduction of superstoichiometric oxygen with O_3 and its consumption by TBF track most strongly with the lower binding energy state of oxygen. Comparisons to the behavior of the NiO process were also made, and through *in situ* quadrupole mass spectrometry to examine gaseous reaction byproducts, stored oxygen is observed to be in a reactive form that actively participates in ALD half-reactions.

The storage and transport of oxygen through the film was also investigated. GIWAXS measurements show sub-surface transport of oxygen correlates with the reorientation of the crystalline domains such that the lattice axis with most facile oxygen diffusion preferentially orients parallel to the direction of oxygen transport. Trends regarding the degree of crystallinity and domain orientation were also observed. These studies shed light on the fundamental chemical mechanisms behind reactive oxygen species in metal oxide ALD, with additional work suggesting these mechanisms can be leveraged in enhancing growth in both ternary ALD and catalytically activated ALD, posing implications for the broader class of ozone- and oxygen plasma-based ALD processes.

AF3-4 Nonaqueous Atomic Layer Deposition of Zinc Oxide Using Diethylzinc and Ethanol, ***Miso Kim***, *E. Shin, J. Hwang, B. Shong,* Hongik University, Korea (Republic of)

Zinc oxide (ZnO) is a transparent wide-band gap semiconductor that can be used in various fields such as thin film transistors (TFTs), gas sensors, and catalysts. Atomic layer deposition (ALD) of ZnO is widely applied due to the ability to form conformal high-quality thin films at the Angstrom level. Most previous studies on ZnO ALD utilized a few well-known precursors and reactants such as diethylzinc (DEZ), dimethylzinc (DMZ), H_2O and O_3. However, O_3 and H_2O oxidants have relatively strong reactivity, so that they are not suitable for substrates that are easily oxidized or reactive with water. Therefore, development of nonaqueous alternative ALD process for ZnO is desired. In this study, we introduce ALD of ZnO using ethanol as a nonaqueous oxidant. Density functional theory (DFT) results indicated that the β-H of the ethanol molecule is crucial in the reaction mechanism for removal of C moieties during the oxidant pulse. Using DEZ as Zn precursor, a typical ALD growth behavior and highly conformal films of ZnO were obtained between 100-300 °C. Compared to the ALD ZnO films deposited with H_2O, nonaqueous-ALD ZnO films showed similar C content, lower crystallinity, higher conductivity, and higher mobility.

ALD Fundamentals
Room On Demand - Session AF4
Growth and Characterization: Surface Science of ALD

AF4-1 Atomic Layer Deposition of Bimetallic Alloy and Work Function Modulation Using Discrete Feeding Method*, **Ji Won Han**, Y. Kim, J. Heo, T. Park,* Hanyang University, Korea

For the continuous scaling of semiconductor based nano-electronics, complementary metal oxide semiconductor (CMOS) field effect transistor (FET) also need to be scaled. 3D structures, such as FinFET, have been applied to suppress the short channel effect, and gate all around (GAA) structure which has all four side of channel is surrounded by the gate metal is anticipated as the next generation device structure. Atomic layer deposition (ALD) have been used as deposition technique since deposition of uniform and conformal film on complicated structure is essential and ALD is only way to successfully accomplish the requirements. Also, workfunction materials for both pMOS and nMOS are needed to developed. However, metals having a low work function suitable for nMOS have poor oxidation resistance and thermal stability due to low oxide formation energy. To overcome the limitation, ALD-based metal nitride and metal carbide are being studied as an alternative, but recent researches are still unsatisfactory.

In this work, we demonstrated deposition of bimetallic alloy film of n-type metal and p-type metal *via* ALD, and modulation of the ratio using discrete feeding method (DFM). DFM is an advanced ALD process that improves reaction efficiency, deposition behavior and overall properties of film by removing physisorbed precursors with cut-in purge introduced between subdivided precursor feeding.

It was confirmed that ratio of n-type metal in the film was able to be controlled in the range of 30~50 %, and detailed mechanism of composition modulation through DFM was elucidated based on change of deposition behavior. Resistivity of bimetallic alloy film was applicable to CMOS regardless of the process variation, while slightly changed depending on its composition. Also, effective workfunction of the film was decreased as ratio of n type metal increased, and since the effect from microstructure of the film is added, bimetallic alloy film having workfunction of 4.1 eV that is identical to conduction band minimum of Si was obtained.

AF4-2 Novel ALD Study of TiO_2 and ZrO_2 on Pmma Substrates as Separate and Mixed Oxide Thin Films for Enhanced Biomaterial Functionalization*, **Mina Shahmohammadi**,* University of Illinois - Chicago*; B. Nagay, V. Barão,* University of Campinas (UNICAMP), Brazil*; C. Sukotjo, C. Takoudis,* University of Illinois - Chicago

Titanium(IV) oxide (TiO_2) and zirconium oxide (ZrO_2) are well-known materials due to their biocompatibility, hydrophilicity, antimicrobial activity, excellent corrosion resistance, and low cost. Polymethyl methacrylate (PMMA), on the other hand, is a promising polymer with a huge range of applications such as denture base materials. However, its poor surface properties lead to fracture and deformation.The mainline inquiry that is to be explored through this work is how functionalization of PMMA surface would make this polymer more stable and robust in the aggressive oral environment and reduce biofilm formation when used in dental applications. Here, low-temperature Atomic Layer Deposition (ALD) was used to systematically deposit TiO_2 and ZrO_2 as separate and mixed oxide thin films on PMMA substrates. Five groups are deposited and characterized: 1. Non-deposited PMMA (control); 2. TiO_2 deposited PMMA; 3. ZrO_2 deposited PMMA; 4. Mixed TiO_2 and ZrO_2 film with 1:1 thickness ratio of TiO_2:ZrO_2 (TZO1); 5. Mixed TiO_2 and ZrO_2 film with 3:1 thickness ratio of TiO_2:ZrO_2 (TZO3). Tetrakis(dimethylamido)titanium (TDMAT) and tetrakis(dimethylamido)zirconium (TDMAZ) precursors were used to deposit TiO_2 and ZrO_2 thin films, respectively and ozone was used as the oxidizer. The reactor temperature for all the depositions was kept at 120ºC and the precursor bubblers of TDMAT and TDMAZ were both kept at 70ºC. Spectroscopic ellipsometry was used to measure the metal oxide film thickness on PMMA substrates. The wettability, composition, and surface roughness of each group were examined with water contact angle measurements, x-ray photoelectron spectroscopy (XPS), and Atomic Force Microscopy (AFM), respectively. A systematic ALD study was successfully performed on PMMA to improve its properties for dental applications. The coatings increased the wettability of PMMA surface by over 30%,which is a necessary characteristic for dental applications since a hydrophilic surface has less potential for bacterial attachment. AFM revealed not a significant change in the surface roughness of PMMA after ALD, which corroborates conformal deposition of the thin films across the substrate. XPS confirmed the presence of each oxide on the surface of PMMA for single oxide films and more importantly, the presence of both oxides for the mixture. The antibacterial activity of each group as well as the studies on the surface roughness and hardness of each group before and after thermal aging will be discussed.

AF4-3 Advanced Atomic Layer Deposition of Metal Oxide Films With Discrete Feeding Method*, **Jae Chan Park**,* Hanyang University, Korea*; S. Lee, S. Yoo, J. Lee, K. Dae, J. Jang,* Korea Basic Science Institute, Korea (Republic of)*; W. Kim, T. Park,* Hanyang University, Korea

HfO_2, the most widely used gate dielectric layer for semiconductor devices, was grown via atomic layer deposition with discrete feeding method (DFM), and its physical, chemical and electrical properties were studied. In a typical ALD process, all the substrate surface sites hardly react with precursor or reactant molecules, even in adsorption saturated condition, because physisorbed precursor and byproduct molecules screen the subjacent surface sites. The DFM process consists of multiple steps of feeding and purging precursor molecules prior to the reactant feeding/purging step, which can efficiently remove the physisorbed precursor molecules and byproducts.

The assorted properties of HfO_2 thin film were improved with DFM process in various ways; i) increased film density, ii) decreased thickness of the HfO_2/Si interfacial layer, and iii) decreased impurity level in the film, which are crucial for the electrical properties of the high-k dielectrics. These are associated with increased adsorption and filling efficiency of precursor molecules on the substrate surface during initial stage of ALD. The detailed experimental results will be presented.

AF4-4 Study of SiO_2 Growth Mechanism Between a Single SiO_2 and $(HfO_2)/(SiO_2)$ Nanolaminate Formation by ALD Using TDMAS and H_2O Gas*, **Toshihide Nabatame**,* WPI-MANA, National Institute for Materials Science, Japan*; M. Inoue, E. Maeda, T. Onaya, M. Hirose, R. Kobayashi,* National Institute for Materials Science, Japan*; A. Ohi,* WPI-MANA, National Institute for Materials Science, Japan*; N. Ikeda,* National Institute for Materials Science, Japan*; K. Tsukagoshi,* WPI-MANA, National Institute for Materials Science, Japan

Recently, Hafnium silicate ($HfSiO_x$) material has been investigated as dielectrics for AlGaN/GaN high-electron-mobility transistors. To form $HfSiO_x$, A HfO_2 and SiO_2 $(HfO_2)/(SiO_2)$ nanolaminate film was generally deposited by plasma-enhanced atomic layer deposition (PE-ALD) using tetrakis(dimethylamino)hafnium (TDMAHf) and tris(dimethylamino)silane (TDMAS) and O_2 plasma [1]. This is because the SiO_2 film could not deposit by ALD using TDMAS precursor and H_2O gas. The water gas supply process during ALD sequence is a key point to understand this mechanism of no SiO_2 deposition. In this paper, we study the $(HfO_2)/(SiO_2)$ nanolaminate growth by ALD at 300°C using TDMAHf and TDMAS precursors and H_2O gas. We also discuss about SiO_2 growth mechanism based on data of a single SiO_2 and $(HfO_2)/(SiO_2)$ nanolaminate films.

The growth per cycle (GPC) values of HfO_2 films on p-Si/SiO_2 substrate by ALD with H_2O gas and PE-ALD with O_2 plasma at 300°C using TDMAHf were 0.085 and 0.082 nm/cycle, respectively. On the other hand, the GPC value of SiO_2 film by ALD at 300°C using TDMAS and H_2O gas was ~0 nm/cycle while the GPC value by PE-ALD was 0.043 nm/cycle. Furthermore, the $(HfO_2)/(SiO_2)$ nanolaminate film was deposited by ALD using TDMAHf and TDMAS and H_2O gas. The numbers of ALD cycles (2 and 1) used to deposit the HfO_2 and SiO_2 layers. The GPC of the $(HfO_2)/(SiO_2)$ (2/1) nanolaminate film was found to be 0.25 nm/cycle. This GPC value was closely same as that of the PE-ALD. The Hf:Si ratios in the $(HfO_2)/(SiO_2)$ nanolaminate film were estimated to be 0.59:0.41 and 0.57:0.43 by ALD and PE-ALD, respectively, based on XPS and EDS analysis. In our previous research, we found that the adsorption of the TDMAS precursor strongly depends on the difference in the electronegativities between metal and oxygen of the Metal-O underlayer [2]. Here, we discuss the SiO_2 growth mechanism by ALD using TDMAS and H_2O gas. In the $(HfO_2)/(SiO_2)$ nanolaminate deposition, the TDMAS precursors adsorb on the Hf-O and Si-O areas of the underlayer. Next, the adsorbed TDMAS on the Hf-O area easily react with H_2O gas but no reaction on Si-O area during H_2O gas supply process. This is because TDMAS precursor was partially decomposed on the Hf-O and activated. As a result, the SiO_2 film could be selectively formed on Hf-O area by the oxidation reaction between activated TDMAS precursor and H_2O gas.

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AF4-5 Discovery of Crystalline Anatase on Fluorine-Rich Carbon Substrates During Low Temperature ALD of Ultra-Thin TiO2, *Brian Butkus, S. Dabas, C. Feit, J. Ganesan, Z. Parsons, X. Feng, P. Banerjee,* University of Central Florida

We discover crystalline anatase phase in atomic layer deposition (ALD) of $TiO_2$when deposited on a fluorine-rich carbon substrate using titanium(IV) isopropoxide (TTIP) and O2 plasma. Highly crystalline anatase phase has been detected in films deposited at temperatures as low as 100 ºC and with thickness of only ~ 4 nm. On the other hand, TiO_2 films deposited on other forms of carbon substrates, glass and silicon, consistently produce amorphous films under these conditions. This talk will highlight the unique substrate-driven crystallization of ALD TiO_2 and lays the ground rules for selective crystallization using surfaces with suitable initiation chemistries.

TiO_2 was deposited on hydrophobic, polytetrafluoroethylene (PTFE) coated carbon substrates (AvCarb GDS2230 from Fuel Cell Store) using a Veeco® Fiji Gen2 ALDsystem. ALD temperatures were varied from 100 ºC to 200 ºC and O_2 plasma (300 W) and H_2O were used as oxidants. Target film thickness varied from 4 nm to 22 nm. Raman, Fourier transform infrared spectroscopy (FTIR) and x-ray photoelectron spectroscopy (XPS) were used to characterize the films. Raman spectroscopy data indicated that anatase TiO_2 was observed on all AvCarb GDS2230 substrates using O_2 plasma as an oxidant, including films as thin as 4 nm and, deposited at temperatures as low as 100 ºC. When the oxidant is switched to H_2O, the anatase phase is still found, though significantly weaker. An interfacial layer of ALD Al_2O_3suppresses the growth of anatase phase. XPS data indicates that in films that show anatase TiO_2, Ti-F bond formation occurs at the preliminary deposition stages. This structurally differentiates the amorphous TiO_2on non-fluorinated substrates which do not show the presence of the Ti-F bond. The presence of fluorine on the surface of the carbon paper acts as a 'structure directing agent' [1-5] where the resulting flourolysis reaction between TTIP with PTFE drives the TiO_2 crystallizing into anatase film.

Fluorine doped crystallization in Ti-O systems have been reported in sol-gel and hydrothermal approaches to synthesize TiO_2 powders.[6, 7] Here, we report the first gas-phase analog of the above reaction mechanism to synthesize crystalline anatase TiO_2 films. The approach highlighted here can lead to area selective and in situ crystallization of films using suitable surface initiation chemistries.

AF4-6 Thin Films Island Structure Analysis Using X-Ray Photoelectron Spectroscopy Methodology, *V. Afanas'ev, **Daniil Selyakov**,* Moscow Power Engineering Institute, Russian Federation

Overlayer thickness determination is an important application of X-ray Photoelectron Spectroscopy (XPS). The methodology is based on measurement of substrate and film peak intensities and assumes the presence of a plane-parallel film located on a semi-infinite flat substrate. We will analyze how the XPS signal intensity changes if the film is not a flat homogeneous layer but constitute an island (cluster) structure, which may be energetically favorable for the atoms of the film. Such structures are typical of gold in submonolayer configurations. XPS spectra were measured for three samples (gold films of different thicknesses located on top of silicon substrates) at five different angles and have been interpreted by the straight line approximation model, developed within XPS framework. The effect of a decrease in the value of the effective average coating thickness (d) with a detecting angle increase was observed, when signal is interpreted within flat homogeneous layer coating model. Considering the configuration of an island surface coverage (the simplest model when the half of the silicon surface is covered with plane-parallel islands with a thickness of 2d we can compare the behavior of the theoretical curves showing the dependence of the signal intensity ratio for island and uniform coverage and see that if the flux of photoelectrons is detected at grazing angles, the curves will coincide. The value of the critical angle at which curves coincidence will be determined by the shape of the islands. The presence of an island surface coating can be confirmed by XPS measurements with an angular resolution and will be accompanied by a decrease in the layer thickness values determined by traditional XPS methodology as the detecting angles approach the grazing angle. The average value of the film thickness (the thickness of an equivalent homogeneous layer) is determined by detecting the XPS signal at angles exceeding the critical angle determined by the island morphology. The simplest model of an island coating makes it possible to qualitatively interpret the effect of a decrease of the effective average coating thickness observed in XPS experiments with an angular resolution.

AF4-9 Thermal and Plasma Enhanced Atomic Layer Deposition of Tio_2 from Amide and Alkoxide Precursors: Growth Characteristics and Photoelectrochemical Performance, ***Shane O'Donnell**, F. Jose, K. Shiel, M. Snelgrove, C. McFeely, R. O'Connor ,* Dublin City University, Ireland

Due to its low cost and suitable band edge positions, Si has been under investigation as a photoanode material for water oxidation for some time[1]. However, as a result of poor stability in the oxidative environment, Si is unsuitable for extended use without a protective layer to prevent surface oxidation. Ultra-thin titanium dioxide (TiO_2) films deposited by atomic layer deposition (ALD) have been used as protective coatings and are shown to enhance Si photoanode lifetimeby distancing the oxidation reaction from the photoanode surface[2].

This study details the nucleation, growth chemistry, and photoelectrochemical performance of 2 nm TiO_2 thin films on Si prepared via atomic layer deposition (ALD). We investigate in detail the growth characteristics of films by plasma enhanced and thermal ALD using x-ray photoelectron spectroscopy (XPS), without breaking vacuum. Growth and charactersiation takes place in a custom designed system with a commercial ALD reactor (Oxford Instruments FlexAl) coupled in vacuum via fast transfer robotic handler allowing for analysis of the nucleation and growth chemistry with half-cycle resolution.

The precursors investigated in this study are titanium isopropoxide (TTIP) and Tetrakis(dimethylamido)titanium (TDMAT). Each precursor material was employed to grow TiO_2 using thermal (H_2O co-reactant) and plasma enhanced (O_2 plasma co-reactant) ALD using the manufacturer's optimised recipes, and the effect of post deposition treatments in reducing and oxidising ambients was also investigated. The photoelectrochemical performance was monitored to link the impact of precursor and co-reactant choice on surface chemistry and the measured photocurrent.

TiO_2 grown by plasma enhanced ALD results in cleaner films with reduced carbon incorporation from the precursor ligands and titanium exclusively in the 4+ oxidation state. However, despite carbon conentrations of up to 15%, thermally grown films show improved photocurrent. This increased photocurrent is correlated with presence of titanium suboxides observed in the Ti 2p peak of these films. This suggests that oxygen vacancies improve the charge transport through the films. Post deposition annealing in a H_2 ambient is shown to further improve photocurrent in all cases. Thermal annealing in atmosphere leads to even higher photocurrent, enhanced photocurrent stability, and uniform chemistry across all films

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ALD Fundamentals
Room On Demand - Session AF5
Growth and Characterization: High Aspect Ratio/High Surface Area/Powder ALD

AF5-1 Conformal Atomic Layer Deposition of Ultra-Thin Conductive Silver Films, *S. Wack, P. Lunca Popa, N. Adjeroud, C. Vergne, **Renaud Leturcq**,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

In the fabrication of microelectronic devices, which include DRAM capacitors, transistors, and back-end-of line (BEOL) interconnects, silver (Ag) is of particular interest due to its low electrical resistivity and low residual stress compared to Cu, and allows downscaling to less than 100 nm without a considerable increase in resistivity [1]. While the deposition of highly uniform and conformal conductive ultra-thin Ag films is of great interest due to the miniaturization and three-dimensional architecture of semiconductor devices [2,3], there is currently no reliable Ag deposition method providing conformal ultra-thin conductive films, mainly due to the island deposition mode of standard non line-of-sight deposition methods, including atomic layer deposition (ALD) [3,4].

We have investigated the conformal deposition of silver films by plasma-enhanced atomic layer deposition (PEALD) using large horizontal aspect ratio (LHAR) structures from Pillarhall®, including a new process in two steps allowing the conformal deposition of ultra-thin conductive silver films [5]. While the standard PEALD process shows an exponential decrease of the deposited material in the LHAR structure, presumably limited by the recombination of plasma radicals on the walls, our new approach demonstrates high conformality of the deposited film on complex lateral high aspect ratio structures (up to 100). Moreover the obtained layer remains continuous inside the structure.

This new processing approach opens a very promising route for the use of ultra-thin silver films for electronic and optoelectronic applications, and could be extended to other metals deposited from metal-organic precursors, in particular copper and gold, for which the deposition using chemical vapor based methods is a very active field.

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AF5-2 Toolbox for ALD Process Development on High Surface Area Powders

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Atomic layer deposition (ALD) is an industrially applied technique for thin film deposition with its origin in microelectronics.[1] Over the course of the past 50 years a wide variety of elements and combinations thereof were deposited *via* ALD.[2] However, the vast majority of processes targets flat substrates rather than powders. For ALD on powders, different reaction conditions are required and need to be identified for ALD to be applicable to high surface area powders. This work shows two setups in detail, which enhance the ALD process development for powders.[3] The first setup is capable of directly measuring the vapor pressure of a given precursor to pre-select promising precursors and their ideal saturation temperature. Afterwards, the second setup, consisting of four parallel reactors with individual temperature zones, is used to screen the optimal ALD temperature window in a time efficient way. Identifying the precursor saturation temperature beforehand and subsequently performing the first ALD half cycle in the parallel setup at four different reactor temperatures simultaneously will drastically reduce process development times. Validation of both setups is shown for the well-known ALD precursors trimethylaluminum to deposit aluminum oxide and diethyl zinc to deposit zinc oxide, both on amorphous silica powder. It can be shown that ALD on high surface area powders requires lower reactor temperatures than ALD on flat substrates. Furthermore, vapor pressures measurements of metal acetylacetonates revealed the need for elevated precursor temperatures for sufficient vapor pressures. There, to achieve reasonable vapor pressures of >10 mbar saturation temperatures of 100 °C are often needed.

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AF5-3 Tunable ALD Infiltration into Ultra-High-Aspect-Ratio Aerogels Enabled by Process Modeling for High-Temperature Solar Thermal Applications

Andrew J. Gayle, *Z. Berquist,* University of Michigan, Ann Arbor*; Y. Chen,* University of Michigan*; A. Hill, J. Hoffman, A. Bielinski, A. Lenert, N. Dasgupta,* University of Michigan, Ann Arbor

ALD provides a unique opportunity to impart conformal surface functionalization onto ultra-high-aspect-ratio structures, but depositions are complicated by precursor diffusion and dosing limitations. ALD modifications on substrates such as aerogels helps enable their use in fields such as concentrated solar thermal (CST), catalysis, and filtration. In particular, SiO_2 aerogels possess a unique combination of desirable properties for CST applications, including high optical transparency and low thermal conductivity, but they suffer from poor stability at elevated temperatures. In this work, we investigate the ALD conditions needed to conformally coat SiO_2 aerogel monoliths (AMs) with aspect ratios >60,000:1 [1]. In order to minimize precursor waste during the long diffusion times necessary to conformally coat the AMs, we implemented a multi-dose-quasi-static-mode (multi-dose-QSM) deposition procedure. In standard QSM recipes, reactor pumping is halted during an "exposure step", allowing precursor to diffuse into a structure without being purged. In the multi-dose-QSM technique, multiple doses and exposure steps of a single precursor are implemented prior to dosing the counter reactant. This was necessary due to the large surface area of the AMs.

To enable tunable ALD infiltration depths into the AMs, we developed a model of the multi-dose-QSM deposition process. Building on previous work by Gordon [2] and Yanguas-Gil [3], our model accounts for precursor depletion in the ALD chamber during an exposure step and the effect of multiple precursor doses. This model also allowed for the optimization of the ALD coating process, including precursor usage efficiency and total process time.

SEM-EDS was used to quantify the ALD infiltration depth to validate the model. ALD saturation was further confirmed using mass gain measurements. After deposition, the AMs showed enhanced infrared light absorption while maintaining high visible light transparency after only one cycle of ALD Al_2O_3. The ALD-coated AM also showed improved resistance to structural degradation at elevated temperatures, likely due to stabilization of the SiO_2 nanoparticle surface. These changes may be due to the formation of a ternary Al-Si-O phase at the interface between the SiO_2 backbone and deposited Al_2O_3 film, as shown using XPS measurements. This combination of properties makes the ALD-coated AMs a promising transparent insulating material (TIM) for CST applications.

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AF5-4 Enhanced Throughput of High-Aspect-Ratio Atomic Layer Deposition Using Trimethylaluminum and Hydrogen Peroxide

Hideharu Shimizu, *T. Mizuno,* Taiyo Nippon Sanso, Japan*; D. Alvarez, J. Spiegelman,* RASIRC

Aluminum oxide (Al_2O_3) ALD has been studied and used for the mass production of devices. However, its long process time for high-aspect-ratio (HAR) structures is a critical drawback [1]. In this study, the reaction mechanism of Al_2O_3 ALD using trimethylaluminum (TMA) and H_2O_2/H_2O mixture [2] or H_2O was investigated; our results indicate that H_2O_2 could be purged more quickly than other reactants. Here, we used RASIRC's Peroxidizer™ to deliver the H_2O_2/H_2O mixture at a reproducible concentration. We demonstrated that the H_2O_2/H_2O mixture can shorten the purge period after a reactant feeding, leading to higher-throughput Al_2O_3 ALD for a HAR structure.

First, quantum chemical calculations and an exhaust gas analysis based on quadruple mass spectrometry were employed to study the reaction mechanism of ALD using the H_2O_2/H_2O mixture. A surface reaction between H_2O_2 and adsorbed TMA is expected to generate CH_3OH, which is thermodynamically favorable since the calculated reaction energy (ΔH) is -256 kJ/mol (Fig. 1). In addition, a surface reaction between H_2O and adsorbed TMA is expected to generate CH_4, for which the calculated ΔH is estimated to be -40 kJ/mol. In fact, using H_2O_2/H_2O, the exhaust gas analysis identified CH_3OH during reactant feeding step in ALD (Fig. 2a). CH_4, but not methanol, was observed in ALD using H_2O (Fig. 2b). These results indicate that the surface reaction in ALD using H_2O_2/H_2O is irreversible, while that using H_2O can be reversed to regenerate H_2O during the subsequent purge period.

Next, Al_2O_3 ALD was performed on a HAR structure (A/R ~100) using H_2O_2/H_2O mixture, H_2O, or O_3 with different purge periods and a reactant feed period of 10 s (Fig. 3a). Under these conditions, the conformality of the ALD was controlled by TMA diffusion. Conformality is generally worsened with a shorter purge period due to the formation of a reactive intermediate during precursor feeding [3]. In fact, when H_2O or O_3 was used as a reactant, ALD with the shorter purge period provided films with poorer conformality (Fig. 3b, c). However, using the H_2O_2/H_2O mixture with ALD reduced the purge period from 10 to 5 s without reducing conformality (Fig. 3d). This likely occurred because the irreversible reaction noted above prevented regeneration of H_2O_2/H_2O during the purge period. Thus, H_2O_2/H_2O is a promising reactant to enhance the throughput of ALD processes.

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ALD Fundamentals
Room On Demand - Session AF6
Growth and Characterization: Plasma Enhanced ALD

AF6-1 Plasma-Enhanced Atomic Layer Deposition: Correlating O_2 Plasma Parameters and Species to Blister Formation and Conformal Film Growth*, **Andreas Werbrouck**, K. Van De Kerckhove, J. Dendooven, C. Detavernier,* Ghent University, Belgium

Plasma-enhanced ALD is now an essential part of the nanomanufacturing toolbox. Lots of processes have been reported and are used in production. Nevertheless, what happens in the plasma often remains a black box. Hence, it would be useful to have a basic insight in how plasma parameters affect the properties of the plasma and the resulting depositions. This way, partial pressure of active species can be increased, while possible damage to the films could be limited.

In this work, the effect of plasma parameters (power, pressure and flow) on the creation of plasma species was studied in a remote, inductively coupled oxygen plasma. In the plasma source region the O and O_2^+ production was characterized with optical emission spectroscopy (OES). In the remote region, near the substrate position we used an electrostatic quadrupole analyser (EQP) to measure energies and relative concentrations of O_2^+, O^+, O_2^- and O^-. Finally, a series of depositions with different plasma parameters was used to link these observations to growth and damage in actual ALD films.

An analysis of OES spectra (300-1000 nm) showed that a higher power linearly correlates with the concentration of created species. The O/O_2^+ ratio is determined by the flow and the power, and not so much by the pressure. The higher the flow, the higher the O/O_2^+ ratio. This is of relevance if we want to maximize the amount of radicals (for growth) or ions (for physically altering the film).

The EQP measurements at the substrate position show that the pressure is the determining factor for ions to reach the surface. The lower the pressure, the more ions can reach the surface. This may result in additional damage to the films. The influence of pressure on ions was dramatically illustrated with a series of depositions at different pressures with the gas coming from the side.

Finally, we deposited Al_2O_3 in lateral high aspect ratio structures with TMA and oxygen plasma at different powers and pulse times. The higher the partial pressure of reactive species near the entrance of the feature, the quicker the feature will be coated. We used a Markov chain simulation approach to quantify this. Simulated and fitted deposition profiles allowed us to estimate the partial pressure of active species in the plasma as a function of power and pressure. This analysis confirmed that higher plasma powers result in a higher partial pressure of reactive species.

With this research, we show that plasma parameters used in an PEALD process may strongly influence the growth and physical quality of the resulting film, especially on more challenging substrates.

AF6-2 Plasma-Enhanced ALD of TiN: Effect of the N-Source on the Growth and Quality of the Thin Films*, **Clémence Badie**,* CINaM , France*; T. Defforge,* GREMAN, France*; G. Gautier,* GREMAN , France*; L. Santinacci,* CINaM, France

The thermal ALD of TiN is well documented in literature. Various parameters of the process such as temperature or precursor pulse and purge durations have been deeply studied. The common precursor combination is TDMAT/NH_3, for thermal and for plasma-enhanced ALD. The PE-ALD recipe found in the literature [1] exhibits a longer cycle duration associated to a slower GPC regarding to thermal ALD. This can be detrimental for industrial production. In addition to NH_3, PE-ALD offers the possibility to use other N-sources: N_2, H_2 and N_2/H_2. The aim of this work is therefore to compare PE-ALD of TiN using two different N-sources to assess their effect on the final properties of the films and to shorten the deposition duration. The processes using NH_3 and N_2 combined with Ar are thus investigated in details and their growth rate is optimized. The influence of a set of parameters on the deposition process has been monitored by in situ characterizations (ellipsometry, OES) and the morphology, the composition, the crystalline structure and the electric properties of the films have been studied by ex situ techniques (TEM/SEM/AFM, XPS, DRX, 4-probes measurements).

To optimize the initial plasma-based recipe, the pulse and purge durations are investigated as well as additional parameters such as dilution of the N-sources within Ar and the plasma power. Those parameters are adjusted to limit the recombinations of the reactive species generated between the remote plasma source to the substrate. A large Ar dilution of both N_2 and NH_3 limits the film growth, a gas ratio of 1:1 for N-source and Ar flow is set to the optimal values. The pulse duration is shortened, 2 and 5 s for NH_3- and N_2-based plasmas, respectively. Saturation is assessed adjusting the purge duration optimum. The applied power (50 to 300 W) has no significant effect on the GPC with NH_3 plasma while, for N_2-based plasma, the GPC is maximum at the highest power. This is consistent with the expected low reactivity of N_2 (inert without plasma activation) as compared to highly reactive NH_3. Those results indicate that producing less active species facilitate their transport by limiting the recombinations. The films grown from both N-sources have a similar roughness, composition and morphology. However, the conductivity, conformality on high aspect ratio substrates and the growth rate are better using NH_3-based plasma. The N_2 plasma process exhibits an acceptable film quality and it should be considered as since it uses a non-harmful gas.

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AF6-3 Plasma Treatment to Tailor Growth and Photoelectric Performance of Plasma Enhanced Atomic Layer Deposition SnOx Transparent Conductive Thin Films*, **Liangge Xu**,* Harbin Institute of Technology, China

Transparent conducting oxides (TCOs) are widely used materials with high optical transparency and electrical conductivity. SnO_2 is an n-type semiconductor material with high carrier concentration and low resistivity. Currently, further development and application of tin-doped indium oxide is limited by the high cost and rarity of indium. Alternatively, Tin dioxide (SnO_2), which is a low-cost, non-toxic, and abundant material, has been extensively studied for its optical and electrical properties, which are comparable to those of indium oxide. More recently, SnO2-based materials, such as ATO (Sb-doped SnO_2) and FTO (F-doped SnO_2), have attracted considerable attention in theoretical and experimental studies. Improved crystallinity by mild plasma bombardment of surface molecular structure is practical. Crystallization by plasma treatment is advantageous in that it can be implemented in-situ, does not need an elevated temperature, and reduces preparation time.Low ion density and nondestructive crystallization of films make remote plasma ALD a promising process for future use.

The performance of atomic layer deposition films is mainly limited by precursor residues, low crystallinity, and densities due to low deposition temperatures. Here, we used atomic layer deposition to deposit tin oxide thin films at a relatively low temperature of 250 °C. At this temperature, the change in the valence of Sn due to precursor residue is eliminated by layer-by-layer Ar plasma treatment, and the crystallinity of the films is improved. The effects of Ar plasma treatment power and Ar treatment time on the structural and optoelectronic properties were investigated. It was found that Ar plasma treatment time more significantly affects the surface morphology and the optical and electrical properties of the film. The film is transparent to both visible and near infrared light over a wide range of wavelengths from 400 nm to at least 5000 nm. The film resistivity can be as low as $1.117\times10^{-3}\Omega\cdot$cm. The film has a relatively low level of residual stress due to the fact that there is no need to improve the crystallinity of the film by conventional high temperature annealing. On the basis of the high transparency and high conductivity of the SnOx films with layer by layer Ar plasma treatment in situ, the films can be applied as electromagnetic shielding windows for photodetectors.

AF6-4 Plasma-Induced Local Crystallization of ALD TiO_2 Films*, **DOHYUN GO**, J. SHIN, . LEE, J. AN,* Seoul National University of Science and Technology, Korea (Republic of)

Titanium oxide (TiO_2) films get much attention in various fields because of their unique properties including high permittivity, chemical stability, non-toxicity, and low cost. Interestingly, crystallinity and phases affect the properties of TiO_2 films. For instance, the dielectric constant of amorphous TiO_2 is lower than 30, but anatase and rutile show a much higher dielectric constant (anatase: 30-75 and rutile: 90-170). Simultaneously, the grain boundary formation of crystalline TiO_2 can also be an electron conduction path leading to high leakage. Atomic layer deposition (ALD) is known to form the thin-film at much lower temperature regime (<300℃) than chemical vapor deposition (CVD). Lowering the deposition temperature can increase the types of available substrates such as polymer and organic substrates, but may hamper the crystallization of thin-films. In this regard, additional processes are necessary for crystallizing thin-film and modifying the electrical/optical properties. Annealing (e.g., rapid thermal annealing (RTA)) and seed-layering (e.g., deposition on the crystalline seed) are representative methods. However, high process temperature (>500℃) and material selection are limits of those methods.

Recently, thin-film crystallization using plasma treatment has been actively researched in plasma-enhanced ALD (PEALD). Plasma-induced crystallization proceeds by ion bombardment of highly reactive ions and radicals inside the plasma and transferring kinetic energy through the thin-film surface. Plasma-induced crystallization can minimize thermal damage and be free of material selection. However, the relatively high oxidation power of plasma compared to the oxidant typically used in thermal ALD (e.g., H_2O, O_2) can develop the unwanted interfacial layer, which decreases the device performance, especially when the interface property between film and substrate is important.

In this study, we precisely modulate the film properties (physical, optical, and electrical) by controlling the crystallinity of TiO_2 thin-film along the thickness direction. We stack the amorphous TiO_2 and crystalline TiO_2 with varying ratios (so-called vertical phase-gradient film). The thickness ratios of amorphous TiO_2 and crystalline TiO_2 are accurately adjusted using extremely-localized plasma-induced crystallization by *per-cycle* plasma exposure. The physical and optical properties are precisely modulated depending on the ratio. Furthermore, we figure out the optimal ratio of amorphous TiO_2 and crystalline TiO_2 for the high dielectric constant and low leakage current.

AF6-7 In-situ Photoemission Study on the Growth of Cobalt Nitride through PE-ALD*, **Matthew Snelgrove**, K. Shiel, E. McGlynn, R. O'Connor,* Dublin City University, Ireland

This work provides new insights into the nucleation and growth characteristics of thin cobalt nitride films deposited by plasma enhanced ALD. The material has applications in CMOS processing for promoting Cu interconnect adhesion and in renewable energy fields as a metallic electrocatalyst.[1,2]Cobalt Nitride, while successfully grown via PE-ALD using several Co-based precursors and co-reactant gases, has presented interesting results where the deposited film can contain large amounts of carbon impurities.[3] Additionally, the effect of deposition temperature has been reported to have a drastic impact on the stoichiometry of the resulting films.[4]

By using an integrated XPS/ALD system, which allows for rapid photoemission analysis during an ALD process without the need to leave high vacuum, the growth characteristics of CoN using the precursor Cobaltocene ($CoCP_2$) with ammonia plasma as co-reactant is studied without complication of the results by atmospheric carbon and oxygen contamination. We examine the impact of the temperature and plasma pulse duration on the film composition and show that rather than displaying saturation, longer plasma pulses severely inhibit the growth rate at all temperatures. The optimum plasma pulse duration for maximum growth per cycle is shown to reduce with increasing temperature. The *in-situ* approach combined with high-energy synchrotron-based photoemission studies of the resulting films enables understanding of the bulk properties without need for physical removal of matter by sputtering. Our results provide an insight into optimising PE-ALD processes for deposition of cobalt nitrides and strategies for minimizing carbon incorporation from the $CoCP_2$ precursor ligands.

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AF6-10 Atomic Layer Doping of β-Ga_2O_3 Films via Plasma Processing*, **Saidjafarzoda Ilhom**, A. Mohammad, D. Shukla, J. Grasso, B. Willis, A. Okyay, N. Biyikli,* University of Connecticut

Gallium oxide (Ga_2O_3) is an emerging ultrawide-bandgap (UWBG) semiconductor attracting significant interest for high-power and high-frequency electronics that features comparable electrical properties (larger bandgap ~4.9 eV, high dielectric constant 6-8 MV/cm) to wide-bandgap GaN and SiC. However, growing device level high-quality (Ga_2O_3) films have been mainly possible using high-temperature requiring harsh environments (700 – 1000 °C), which substantially limit its application space. In this work, we report on the low-temperature deposition of β-Ga_2O_3 films on Si, sapphire, Kapton, and glass substrates coupled with *in situ* atomic layer doping using hollow-cathode plasma-enhanced ALD. The films were deposited using triethylgallium (TEG) and Ar/O_2plasma as metal precursor and oxygen co-reactant, respectively, whereas tris-dimethylaminosilane (3DMAS) was utilized as the n-type dopant precursor. Growth experiments have been performed at 200 – 240 °C substrate temperatures and 50 W rf-power level. The doping process was carried out via both co-dosing (where the dopant is pulsed together with the metal precursor) and super-cycle (ABC-type ALD-cycle) methods. Additionally, each unit ALD-cycle was followed by an *in-situ* Ar-plasma annealing treatment, which consisted of Ar-plasma exposure for 20 seconds at 250 W rf-power. Both *in-situ* and *ex-situ* ellipsometry were employed to measure the thickness and optical properties of the films. The samples grown without Ar-plasma annealing step exhibited amorphous character with a growth-per-cycle (GPC) of 0.69 Å/cycle. However, with the incorporation of the *in situ* Ar-plasma annealing process crystalline films showing monoclinic β-Ga_2O_3 phase were achieved showing a GPC of ~1.04 Å/cycle. X-ray photoelectron spectroscopy (XPS) measurement of the β-Ga_2O_3 sample grown under optimal *in situ* plasma annealing power (250 W) revealed near-ideal film stoichiometry (O/Ga of ~1.44) with relatively low carbon content (~5% at.). Our results demonstrate the effectiveness of *in situ* Ar-plasma annealing process to transform amorphous wide bandgap oxide semiconductors into crystalline films without needing high-temperature post-deposition annealing treatment. Further outcomes from our ongoing atomic layer doping experiments featuring co-dosing and super-cycle techniques followed by additional structural, optical, and electrical characterizations will be discussed as well, which provide additional insight to overcome the challenges in achieving device quality β-Ga_2O_3 layers on low-temperature compatible substrates.

AF6-13 Electron Enhanced Atomic Layer Deposition of Aluminum Phosphide with Trimethylaluminum and Tritertbutylphosphine*, **SeongUk Yun**, A. Kummel, S. Ueda, V. Wang, C. Kuo, H. Kashyap, A. Mcleod,* University of California, San Diego, USA

Aluminum phosphide (AlP) is an interesting wide bandgap III-V semiconductor with applications in optoelectronics, small lattice-mismatch regarding GaP/Si, and potential use as X-ray multi-layer mirror[1]. Most AlP films have been deposited using the chemical vapor deposition processes (CVD) with PH_3. High-quality AlP films require the high partial pressure of PH_3, which is highly toxic. Terada et al. investigated the 500°C CVD AlP with trimethylaluminum (TMA) and Tritertbutylphosphine (TBP), which is safer than PH_3[2]. Gudovskikh et al. reported that nanocrystalline GaP was grown at 380°C using plasma-enhanced atomic layer deposition (PE-ALD) with trimethylgallium and PH_3 in an H_2 purge[3]. However, AlP deposition using ALD process has rarely been investigated yet since it is highly reactive toward moisture and difficult to crystallize.

The major challenge in TMA + TBP ALD process is the low reactivity of the TBP precursor. High process temperature (>500°C) and substrate atomic H bombardment have been shown to improve reactivity, but ALD of related compounds shows there may be alternatives. For example, Sprenger et al. reported that electron enhanced ALD (EE-ALD) improved the growth rate of GaN film at below 100 °C.

The low-temperature (≤ 400°C) ALD of AlP on III-V semiconductors was investigated using three techniques: thermal ALD, atomic layer annealing (ALA), and EE-ALD [4]. TMA and Tri(dimethylamido)aluminum(III) (TDMAA) were employed as Al precursor and TBP was employed as the phosphorus precursor. The films were characterized with in-situ Auger and ex-situ atomic force microscopy (AFM).

Table 1 summarized the atomic composition in the AlP films from in-situ Auger analysis of the AlP ALD and AlP ALA at 300°C with TDMAA and TMA, respectively. Si composition in AlP in ALA was lower compared to that in AlP ALD, suggesting improved AlP growth rate with ALA process. Figure 1 (a) showed that P/Al atomic ratio increased up to 0.8 in AlP EE-ALD process. This suggested AlP films with high P/Al=0.8 were prepared using EE-ALD with TBP precursor at 300°C. The atomic compositions of AlP EE-ALD process at different temperatures are shown in Figure 1 (b). Large size (≥ 15 nm) of islands of AlP film in Figure 2 (a) and low P/Al=0.5 indicated the formation of AlPOx nanoparticle of AlP ALD due to the insufficient nucleation of TBP at 210°C. AlP films at 300°C and 400°C showed high P/Al = 0.8. While Figure 2(b) showed the amorphous AlP film at 300°C, the high-quality (~P/Al=0.8) and nano-crystallized (RMS=0.9 nm) AlP films were successfully deposited by EE-ALA at low temperature (≤ 400°C) using TBP precursor.

AF6-16 Tuning the Structural Properties of Low-Temperature Grown GaN Films via *in Situ* Ar-Plasma Annealing During Hollow-Cathode Atomic Layer Deposition, ***DEEPA SHUKLA***, *N. Biyikli,* University of Connecticut

Future energy efficient devices and will feature wide bandgap semiconductors allowing greater power efficiency, smaller size, lighter weight, lower overall cost. GaN among the other wide bandgap materials, has a large bandgap (3.4 eV) and when compared to the conventional electronics material of choice Si, the critical breakdown field is an order of magnitude higher and the achievable electron mobility (2DEG mobility in AlGaN/GaN HEMT structures) is nearly double. Both the output charge and gate charge are ten times lower than with Si, and the reverse recovery charge is almost zero which is key for high frequency operations. Owing to these attractive properties and features, GaN is used in a variety of microwave power applications due to their superior electron transport properties.

In this work, we report on the low-temperature, as-grown crystalline GaN films on various substrates via a hollow-cathode plasma-ALD system. The purpose of this work is to see the effect of different plasma gas mixture on the growth of GaN films at substrate temperatures less than 250oC and tune the crystallinity via in situ Ar-plasma annealing.

Plasma assisted atomic layer deposition of GaN thin films is carried out in a hollow cathode plasma-ALD chamber. Si (100), Si (111), glass, and sapphire films have been used as the substrate. The growth temperature is kept between 120 to 240 °C, 10 sccm of N2 flow is used as a carrier gas and Ar-purging gas flow at 50 sccm. Triethylgallium is used as Ga precursor and various nitrogen plasma chemistries including different compositions of N2, H2, and Ar gases are studied. The optimized growth condition is determined from the saturation studies, where the growth-per-cycle (GPC) parameter is noted for different precursor pulse time (30, 45, 60 and 90 ms), rf-plasma power (100 W to 200 W) and plasma-gas chemistries at different plasma compositions have been studied at (i) Ar/N2 at 50/50 sccm; (ii) N2-only at 50 sccm; and (iii) N2/H2 at 50/10 sccm. We observed the crystalline nature of GaN films through XRD analysis. The as-grown films were compared with films grown with an additional Ar-plasma annealing step within the unit-ALD cycle. As we recently reported for Ga2O3 films, our main goal is to achieve improvement in crystalline properties with the surface heating effect of the in situ Ar-plasma annealing treatment. The XRD measurements of these in situ Ar-plasma annealed samples will be presented along with the spectroscopic ellipsometer, x-ray reflectivity (XRR), and x-ray photoelectron spectroscopy (XPS) studies. The impact of the reactor ambient during plasma annealing under different plasma gas mixtures will be presented as well.

AF6-19 Optimization of AlN Film Purity Using Atomic Layer Annealing, ***Markus Bosund***, *E. Salmi, K. Väyrynen, M. Söderlund,* Beneq, Finland*; P. Rabinzohn,* Beneq, France*; M. Heikkilä,* (2) University of Helsinki, Department of Chemistry, Finland*; J. Julin,* (3) University of Jyväskylä, Department of Physics, Finland*; T. Sajavaara,* University of Jyväskylä, Department of Physics, Finland

Aluminum nitride (AlN) combines a high band-gap with good thermal conductivity making it an excellent material for several applications. AlN films are being considered as passivation and dielectric layers for power devices and other compound semiconductor devices such as RF, VCSEL, LED, and Light Sensor. Both bulk film and boundary impurities affect the device performance. This study presents observations of Atomic Layer Annealing (ALA) on PEALD AlN film and interface impurities. Less examined hydrogen impurity level was also measured from the films.

Atomic layer annealing is a method where additional thermal energy is introduced after each ALD cycle. In this work the ALA step was done using an additional plasma pulse. Earlier studies indicate that epitaxial growth can be reached with plasma ALA step **[1-3].** Although this method has been demonstrated earlier, the effect of ALA step on atomic concentrations and especially film hydrogen concentrations and especially film hydrogen concentration are published for the first time.

This research work also presents a slightly different simplified process using only N_2 gas in the ALA step instead of Ar or Ar/N_2 mixture. The difference of AlN films deposited with and without ALA steps were investigated using X-ray diffraction (XRD) and Time-of-flight elastic recoil detection analysis (TOF-ERDA) spectrometer for elemental analysis.

AlN purity variation within wafer was also investigated. Atomic concentrations were measured from 200 mm wafers. Three measurement points were taken at precursor flow direction.

Beneq TFS 200 and Transform^{TM} reactors equipped with direct CCP plasma were used in this work. Plasma frequency was 13.56 MHz. Ammonia plasma was used in ALD step but ALA step was done using N_2 as presented in Fig. 1. (supplemental file). Various plasma times and reactor temperatures were investigated.

ALA step had clear effect on the crystalline structure of the AlN film. All films were polycrystalline hexagonal wurtzite aluminum nitride layers but the films deposited with ALA step had stronger (002) preferential orientation.[1,3]

TOF-ERDA elemental analysis indicated that the atomic concentration of hydrogen decreased from 12 to 7 at.-% with ALA step. This difference was obtained from the bulk of the film. Oxygen impurity was optimized below 0.5 at.-% and carbon impurity always lower than 1.2 at.-%

AF6-22 Understanding the Influence of Plasma-Enhanced Atomic Layer Deposition of SiN on GeSbTe, ***Hamid Razavi,*** University of California, Los Angeles*; M. Shen, J. Hoang, T. Lill,* Lam Research Corporation*; J. Chang,* University of California, Los Angeles

Keeping the composition of $Ge_xSb_yTe_z$ (GST) materials constant during the encapsulation process is a challenging problem mostly due to the volatility of Ge products during the deposition processes particularly at higher temperatures between 100 and 150^{o}C.

This work studies the effect of the Ge, a constituent element of GST, as a model substrate on the nucleation and growth behavior of SiN capping layer deposited by plasma-enhanced atomic layer deposition (PE-ALD) method using Bis(t-butylamino)silane (BTBAS) with the molecular formula of $[NH(C_4H_9)]_2SiH_2$ as the Si precursor. Atomic nitrogen generated by a 2.45 GHz coaxial waveguide microwave plasma source was used as a nitridizing agent of the precursor.

The deposition of PEALD SiN was assessed by examining the effect of substrate temperature (25 to 150^{o}C), microwave plasma power (25 to 75 W), and the pre-deposition plasma surface treatment. The in-situ N_2 plasma was effective for substrate cleaning by reducing O concentration from the Ge native oxide layer. The nucleation and the growth of deposited SiN on the substrates was studied using an in-situ x-ray photoelectron spectroscopy and ex-situ scanning electron microscopy (SEM). The relative concentration of nitrogen atoms was quantified as a function of plasma processing parameters by optical emission spectroscopy as it dictates the surface reaction with the precursor to form SiN. XPS results confirmed the nucleation of Si_xN_y with the ratio of x/y=1/2 on Ge/GeO_2. Pre-deposition N_2 plasma surface treatment resulted in nitridation of Ge and a significant reduction of the oxygen and carbon content, making the interface a higher quality one

AF6-25 Low-Temperature Plasma Enhanced Atomic Layer Deposition of WO_x using a novel Tungsten Precursor, ***Kamesh Mullapudi***, *K. Holden, J. Peterson,* Oregon State University*; R. Kanjolia, D. Moser, C. Dezelah,* EMD Performance Materials*; J. Conley,* Oregon State University

Tungsten oxide (WO_3) has garnered interest lately for its use in smart windows,[1] forming-less resistive memories,[2] and as a potential candidate for emerging neuromorphic memories.[3] Microelectronics applications require films of high electrical quality with excellent conformality, uniformity, and thickness control for which ALD is the method of choice. Early thermal ALD reports of WO_3 films employed the use of halide-based precursors which resulted in self-etching due to reaction byproducts.[4,5] More recent work has focused on metal-organic chemistries and plasma-enhanced ALD (PEALD), which provides benefits such as lower deposition temperatures. Recent PEALD work includes $WH_2(iPrCp)_2$ and $W(tBuN)_2(Me_2N)_2$ with a direct O_2 plasma source which required temperatures in the range of 300-400°C for a constant GPC window.[6,7] Another recent study used $WH_2(Cp)_2$ with a remote O_2 plasma and reported a constant GPC ALD window between 200-300°C and that O-content could be controlled with H_2 plasma in an ABC type process.[8]

In this work we report PEALD of WO_3 using a novel metal-organic tungsten precursor [bis(tert-butylimido)bis(trimethylsilylmethyl)tungsten(VI), $W(CH_2Si(CH_3)_3)_2(CN(CH_3)_3)_2$ or WSN-4] with remote O_2 plasma as a co-reactant using a Picosun R200 reactor. A plot of film growth per cycle (GPC), using a 2/15/40/30 s WSN-4/N_2/O_2 plasma/N-$_2$ pulse sequence, shows growth decreasing from 1.0 to 0.44 Å/cycle as the growth temperature increases from 150 to 350^{o}C, accompanied by an increase in optical refractive index from (Fig. 1). Pulse saturating behavior for both the WSN-4 (Fig. 2) and O_2 plasma (Fig. 3) half-cycles, indicates that film growth is self-limited at 250^{o}C. Grazing angle x-ray diffraction (GI-XRD) reveals that an as-deposited 12 nm thick film was amorphous, while post-deposition isochronal (60 min) O_2 annealing produced crystallization at 600^{o}C into the triclinic phase of WO_3, with an estimated grain size of ~30 nm (Fig. 4 and SEM image inset).

Further details on WSN-4 properties, nucleation behavior on BEOL metals such as TiN and TaN, film density, stoichiometry, band gap, and electrical properties of ALD WO_3 will be discussed at the meeting.

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ALD Fundamentals
Room On Demand - Session AF7
Growth and Characterization: Low Temperature ALD

AF7-1 Neutral Beam Enhanced Atomic Layer Deposition at Room Temperature for Si Dielectric Film, ***Ge Beibei,*** Tohoku University, Japan, China*; C. Hua Hsuan,* National Yang Ming Chiao Tung University , Taiwan*; O. Daisuke, O. Takuya, S. Seiji,* Tohoku University, Japan

Atomic layer deposition (ALD) is a synthesis thin film technique based on sequential, self-limiting reactions which has developed significantly in recent years [1]. Silicon dielectric films such as silicon dioxide (SiO_2) films and silicon nitride (SiN) films can be deposited using several ALD techniques, such as thermal ALD and plasma-enhanced ALD. The high deposition temperature and high thermal budgets have become a problem of traditional thermal ALD, the deposited films show low quality and poor step coverage [2]. PEALD could deposit at lower temperature, but inherent problems in plasma process such as plasma irradiation and charge accumulation will cause defects on films [3]. In previous report by Samukawa et al, using O_2 neutral beam could synthesize the very high quality SiO_2 film on the Si substrate at room temperature [4]. In this work, we demonstrated growth of Si dielectric thin films by neutral beam enhanced atomic layer deposition (NBEALD) at room temperature.

Thin SiO_2 and SiN films were deposited on Si substrate at 30°C using bis(diethylamino)silane (BDEAS) as Si precursor, O_2 or N_2 as the neutral beam gases. The NBEALD cycle was composed as follows: precursor absorption, purge, reactive gases injection, neutral beam irradiation and purge. In this process, neutral beam instead of plasma was used in irradiation step of ALD for providing energy on surface reactions. The thickness of NBEALD Si dielectric films was measured by spectrum ellipsometer. Film quality was investigated by X-ray photoelectron spectroscopy (XPS) to analyze the element composition. The density of the Si dielectric films was studied by x-ray reflectivity (XRR). The surface roughness of the deposited films was investigated by atomic-force microscope (AFM).

SiO_2 films with high quality in terms of chemical composition, surface roughness and mass density are equivalent to that of thermal oxidation films. For the growth of SiN film, the growth per cycle of the feed time was saturated over the 2 sec. The deposition rate was 0.32 Å/cycle. For the XPS results, SiN film showed the strong $N\text{-}Si_3$ peak at 397.5 eV. On the other hand, weak $C\text{-}NH_2$ peak at 399.7 eV, and C=O peak at 531.5 eV were observed. As a result, it suggests that the carbon contamination was amide group that comes from precursor. It can be solved to optimize the NB source power and bias power condition. Hence, N_2 neutral beam with BDEAS achieved the SiN film growth at room temperature.

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ALD Fundamentals
Room On Demand - Session AF8
Growth and Characterization: *In-situ* Monitoring and Analysis

AF8-1 Optimization of Quadrupole Mass Spectrometers for In-situ Monitoring of Atomic Layer Deposition Processing, ***Chenglong Yang****, J. Blessing,* MKS Instruments, Inc.*; U. Meissner,* MKS Instruments, Inc., Germany*; A. Wallace ,* MKS Instruments, Inc., UK

Quadrupole Mass Spectrometers (QMS) have been used widely in atomic layer deposition (ALD) for process optimization and troubleshooting. Unfortunately, QMS has had little application for in-situ process monitoring owing to its short lifetime and less persuasive value of process monitoring. This study is to improve the QMS sampling system design for ALD processes, which includes the ALD gas sampling and delivery, inlet valve design, and the range and control of the sampling system temperature. In addition, the QMS hardware and operating methods are also upgraded to improve the sensitivity and its lifetime for ALD processes. This QMS system has been applied to ALD processes for in-situ monitoring of chamber base vacuum, ALD precursors, process reaction by-products, and chamber contamination.

AF8-2 Quantitative Calorimetry of ALD: Design, Model, and Calibrate, ***Ashley Bielinski,*** *A. Martinson,* Argonne National Laboratory

Pyroelectric calorimetry presents a new approach for the *in situ* study of the thermodynamics and kinetics of ALD reactions with unmatched thermal sensitivity and temporal resolution. Complementary techniques such as quartz crystal microgravimetry, spectroscopic ellipsometry, and mass spectrometry are limited by sampling times that are typically on the order of 50ms – 1s. We demonstrate response times down to 50ns and sensitivities of < 1μJ/cm^2, which corresponds to less than 1% of the heat generated by some ALD half reactions.

Large temperature changes, >10°C, as a result of ALD surface reactions have been observed on high surface area substrates. However, attempts to quantitatively measure reaction heats on planar substrates, ≪1°C, using thermocouples or pyroelectric detectors have previously been limited by hardware with insufficient thermal and temporal resolution, difficulties accounting for heat lost to cooling, and challenges with external calibration. To overcome these issues we designed and built pyroelectric calorimeters compatible with ALD systems, modeled the transient thermal and electric response, and quantitatively calibrated the system using a laser to provide precise heat generation.

This work was inspired by the techniques used in pyroelectric adsorption calorimetry, but the approaches used in this field resulted in unacceptable tradeoffs in responsivity in order to achieve the temporal resolution needed for ALD. A new calorimeter design was implemented to suspend the pyroelectric crystal with minimal physical contact. This reduced conductive cooling, enabling improved temperature sensitivity and faster responsivity.

Previously, ALD reaction energies have been computationally predicted, but not experimentally measured. ALD calorimetry contributes a new experimental technique with a wide range of applications including the study of fundamental reaction thermodynamics, the impact of non-ideal surfaces on nucleation, selective defect passivation, and growth inhibition.

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AF8-3 Atomic Layer Deposition of Hafnium Oxide on InAs: Insight from Time-Resolved *in Situ* Studies, ***Giulio D'Acunto,*** Lund University, Synchrotron Radiation Research, Department of Physics, and NanoLund, Sweden*; A. Troian,* Lund University, Dept. of Electrical and Information Technology, and MAX IV laboratory, Sweden*; E. Kokkonen,* MAX IV Laboratory, Lund University, Sweden*; F. Rehman,* Lund University, Synchrotron Radiation Research, Department of Physics, and NanoLund, Sweden*; J. Schnadt,* Lund University, Synchrotron Radiation Research, Department of Physics, and NanoLund and MAX IV laboratory, Sweden*; R. Timm,* Lund University, Synchrotron Radiation Research, Department of Physics, and NanoLund, Sweden

Despite the numerous applications of atomic layer deposition (ALD), used e.g. in the semiconductors industry to produce thin films with thickness control at the Ångström level and tunable composition, only limited knowledge exists about the kinetics of the surface chemical reaction, the reaction mechanism, and the role of the substrate. ALD-grown thin high-k oxide films, such as HfO_2 or Al_2O_3, help to significantly improve device performance of III-V semiconductor-based MOSFETs. Those materials, such as InAs, come along with an electron mobility 20 times larger than that of silicon, but unfortunately with a high defect density at the interface with its oxide. It has been demonstrated that so-called "self-cleaning" occurs during the early stage of the high-k ALD, in which the growing high-κ oxide substitutes the unwanted native oxide. However, in spite of all progress, the III-V/oxide interface still suffers from incomplete self-cleaning and too high defect levels.

In this work, we present a time-resolved study of the self-cleaning effect during the first ALD half cycle. We performed ALD of HfO_2 on InAs in the reaction cell of a synchrotron-based ambient pressure X-ray photoemission spectroscopy (APXPS) setup. Tetrakis(dimethylamido)-hafnium (TDMA-Hf) is used as the metallorganic precursor, and we followed in real time all relevant core levels to monitor the surface species during the deposition. Our findings challenge the established view of the ALD process based on the ligand exchange model and the surface's passive role. In fact, we establish a two-step reaction based on molecular adsorption followed by ligand exchange and the immediate formation of HfO_x, in which the native oxide acts as the oxygen source. In more detail, we find evidence for an As-In-O-Hf bonding configuration at the semiconductor/high-k interface.

Hence, time-resolved APXPS enables us to further understand the surface chemical process in ALD and how the III-V semiconductor/high-k interface can further be improved by optimizing ALD, promising superior device performance.

ALD Fundamentals
Room On Demand - Session AF9
Growth and Characterization: Characterization of ALD Films

AF9-1 Smoothing Surface Roughness Using Al_2O_3 Atomic Layer Deposition*, Tyler Myers,* University of Colorado Boulder*; J. Throckmorton, R. Borrelli, M. O'Sullivan, T. Hatwar,* L3Harris*; S. George,* University of Colorado Boulder

Surface roughness can affect many areas such as optical scattering, friction, adhesion and semiconductor device performance. There are various methods for smoothing surfaces including chemical mechanical polishing (CMP) and chemical etching. However, these methods are abrasive and corrosive and can be detrimental. Atomic layer deposition (ALD) deposits conformal films that can “pinch off” surface roughness by filling in the gaps between surface asperities. In this study, Al_2O_3 ALD was used to smooth rough silicon wafers and improve the optical reflectivity of Ag mirrors deposited on the silicon wafers.

Al_2O_3 ALD was performed on rough, pre-CMP silicon wafers. Al_2O_3 was deposited at 200°C using trimethylaluminum (TMA) and water (H_2O) as the reactants. Al_2O_3 ALD films of various thicknesses were grown on the silicon wafers using up to 4000 Al_2O_3 ALD cycles. The RMS roughness was measured using atomic force microscopy (AFM). AFM showed that the original rough, pre-CMP silicon wafers had an RMS roughness of 3.5 nm. AFM line scans measured an average lateral spacing between the surface asperities of 400 nm (Figure 1a). After 3000 Al_2O_3 ALD cycles, the RMS roughness of the wafers was reduced to 1.5 nm and the average lateral spacing between the surface asperities increased to 700 nm (Figure 1b).

The RMS roughness decreased progressively with number of Al_2O_3 ALD cycles (Figure 2). The minimum surface roughness of 1.5 nm was reached after 3000 cycles. Additional Al_2O_3 ALD cycles then produced little change in the RMS roughness. The smoothing is believed to limit when the lateral distance between the surface asperities is much larger than the Al_2O_3 ALD film thickness. Power spectral density (PSD) analysis revealed that the ALD smoothing was most effective for surface topographical features with lateral spacings in the range of 10s to 100s of nanometers. The PSD analysis showed that most of the smoothing occurs during the first 1000 Al_2O_3 ALD cycles. Reflectivity studies of Ag mirrors deposited on the silicon wafers demonstrated that Al_2O_3 ALD smoothing improves the optical performance of reflective mirrors.

AF9-2 Effect of Oxidant on Film Properties of HfO_2 grown via Atomic Layer Deposition using Newly Synthesized Cp-based Hf Precursors*, Seonyeong Park,* *H. Yoon, Y. Lee, S. Lee, H. Lee, S. Chung, H. Kim,* Yonsei University, Korea

With the scaling down of semiconductor devices, SiO_2 was replaced by high-k materials due to increased leakage current. Among the various high-k materials, HfO_2 has been widely used owing to its high dielectric constant (~25) and suitable band offset with Si (~1.4 eV).[1] For ultrathin high quality HfO_2, atomic layer deposition (ALD) has been used. Through ALD technology, atomic layer controlled HfO_2 film with high conformality and high uniformity can be obtained. For HfO_2 ALD technology, various precursors such as halides, alkoxides, alkylamides, and β-diketonates have been applied. Using halide precursor, HfO_2 films do not have C impurities. However, corrosive byproducts such as HCl can degrade the film quality.[2] Furthermore, halide precursors have low volatility which means that high temperature is needed to get HfO_2 films.[2] Alkoxides have strong metal-O bonds, so that they require high temperature for deposition process. In addition, β-diketonates are not proper precursors for ALD, because they have bulky ligands which leads to steric hindrance and have low volatility.[1] β-hydride elimination causes hydrolytic decomposition of β-diketonates, which leads to the non-saturated growth characteristics. Since alkylamides have weak metal-N bonds, they are highly reactive at low temperature. Although alkylamides are widely used for ALD process, they are easily decomposed at high temperature.[1] Therefore, there can be a lot of impurities on thin films deposited with ALD. By employing cyclopentadienyl (Cp) ligand as functional ligand group of heteroleptic precursor, thermal stability and volatility of alkylamide precursors are improved.[1] Research has been conducted to increase thermal stability of precursors by increasing the number of Cp ligands. However, even that has now reached its thermal stability limit, requiring a precursor available at higher temperatures. We newly synthesized the Hf precursor which is stable at higher temperature. We investigated the effect of oxidants on film properties of HfO_2 using newly synthesized Cp-based alkylamide Hf precursor.

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AF9-3 Advanced Wafer Scale Uniformity Characterization Method for Conformal 3D Thin Films*, Mikko Utriainen,* *P. Hyttinen, F. Gao,* Chipmetrics Ltd, Finland*; A. Bider, K. Saastamoinen, H. Rekola,* University of Eastern Finland, Institute of Photonics, Finland*; R. Puurunen,* Aalto University, School of Chemical Engineering, Finland*; O. Ylivaara,* VTT Technical Research Centre of Finland

Atomic layer deposition (ALD) enables uniform thin film coating over large substrate areas. Besides thickness uniformity, today’s memory and MEMS applications with three-dimensional structures require good conformality over high aspect ratio (HAR) structures. The state-of-art method to define wafer scale uniformity is film thickness mapping. Easy wafer level conformality characterization from 3D HAR structured wafers is hardly accessible due to challenging high-resolution cross-sectional measurements. PillarHall® Lateral High Aspect Ratio (LHAR) silicon test chip has already proven its value in conformality metrology and even in the characterization of the thin film properties inside deep cavity walls [1,2,3] without cross-sectioning. The purpose here is to study further the consistency, sensitivity and accuracy of the wafer level uniformity and conformality analysis using PillarHall® LHAR4 test chip (Chipmetrics Ltd) on 150 and 200 mm silicon carrier wafers. Chips were placed evenly over the studied substrate area. An analysis was made using simple optical measurement tools such as optical modelling software, optical microscopy with image analysis, and reference reflectometry measurements. Experimental work consisted of several thermal ALD processes (Al_2O_3, SiO_2, TiO_2 and TiN). ALD reactors were Picosun R-150 and Beneq TFS-200. Optical microscope image analysis was used to assess conformality analysis accuracy using ALD Al_2O_3 on LHAR samples from various positions of the wafer area. The results show good accuracy and are in line with optical modelling outcome and in agreement with reflectometry data. Optical modelling also enables predictions of the method compatibility and limitations with various other thin-film materials. When comparing the ALD Al_2O_3 data to the simultaneous flat substrate thickness mapping, it is shown that PillarHall® method is a sensitive measure for wafer-level uniformity and conformality mapping. The presented method is widely compatible to ALD and related 3D thin film processes and can accelerate their industrial applications.

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AF9-4 Thermal Atomic Layer Deposition of Silicon Nitride Using Anhydrous Hydrazine and Ammonia

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In this study, a thermal atomic layer deposition (t-ALD) for silicon nitride (SiN_x) is established at the temperature window of 320–600°C. Hexachlorodisilane (HCDS) and high purity anhydrous hydrazine (N_2H_4) are utilized as the precursors for silicon and nitrogen, respectively. The characteristics of deposited films are analyzed by the growth per cycle (GPC), refractive index (R.I.), wet-etch rate (WER), and chemical composition. The electrical properties of SiN_x deposited using N_2H_4 are also studied using "metal-insulator-metal (MIS)" structure. -*in-situ* FTIR technique is employed to examine the bonding information.

At 480°C, the GPC of silicon nitride gradually increases with an increase in the N_2H_4 pulse time (0.2, 0.5, 1.0, and 2.5 s). SiN_x exhibits a growth rate of 0.031 nm/cycle with 0.5-second N_2H_4 exposure time at the working pressure of 150 mTorr. At the same deposition temperature (480°C) and hydrazine exposure time (0.5 s), the GPC at 500 mTorr is 0.048 nm/cycle. Within the temperature range of 390–520°C, the growth per cycle is nearly constant, with the approximate value of 0.049 nm/cycle. Furthermore, silicon nitride thin films are also grown using ammonia (NH_3) as references. Under identical deposition conditions (exposure time, temperature, and working pressure), ammonia delivers a lower growth rate (~0.019 nm/cycle) than hydrazine. As the deposition temperature increases, the refractive index of SiN_x grown with hydrazine increases (as high as 1.99), while the WER significantly decreases with the etch rate as low as 0.37 nm/min in 200:1 HF diluted solution. At 480°C, silicon nitride grown using hydrazine and ammonia has a density of 2.73 and 2.69 g/cm^3, respectively. The R.I. and WER values are 1.86 and 2.24 nm/min for hydrazine, while 1.96 and 7.48 nm/min for NH_3. The chemical composition of SiN_x grown with N_2H_4 is 54±1.0 [Si] at.%, 44±1.0 [N] at.%, 2±1.0 [O] at.%, and <1.0 at.% [Cl] (under the detection limit). The deposited silicon nitride has a leakage current density as low as approximately 12.0±0.2 nA/cm^2 and a break down field as high as 12.8±0.2 MV/cm.

Ovanesyan *et al*. and Meng et al. suggested that HCDS reacts with $–NH_2$ groups on the surface and leaves –NH– groups as the primary form of hydrogen bonds in SiN_x.[1,2]*in-situ* FTIR is used to investigate the different surface reaction pathways between N_2H_3 and NH_3. Experimental details and results will be presented.

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AF9-5 Importance of XPS Investigations of ALD Grown 2D Materials

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The success of graphene opened a door for a new class of semiconducting 2D transition metal chalcogenide materials (TMDs) displaying unique properties [1]. ALD MoS_2, as TMDs benchmark, has been widely studied for several applications. In parallel, 2D selenide and telluride analogues, i.e. $MoSe_2$ and $MoTe_2$, have also attracted important interest due to intriguing properties, such as a higher electrical conductivity than that of MoS_2 among others [2, 3].

Recently, we have demonstrated the ALD synthesis of both 2D $MoSe_2$ [4-7] and 2D $MoTe_2$ [8] (using an in-house synthesized precursors), as well as their outstanding performances in different applications. XPS turned a key tool to provide detailed chemical composition analysis of as-deposited 2D Mo TMDs family on different nature substrates. Besides, the post-performance XPS characterization was appealing since the applications of the aforementioned 2D materials involved chemical and/or electronic processes on the surface and it enabled to identify potential chemical composition changes and physicochemical photo-electro stability of the 2D TMDs. This presentation will thus focus on the XPS as key tool for assessment of chemical composition of both as-deposited and post-performance 2D Mo TMDs family, recent experimental results as well as the description of some inherent drawbacks that XPS must face during the analysis of the 2D materials.

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AF9-6 Microstructure and Mechanical Properties of Atomic Layer Deposited Alumina Doped Zirconia

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ZrO_2 metastable polymorphs possess higher hardness and elastic modulus compared to the monoclinic phase that could increase the mechanical endurance of the material [1-2]. Metastable phases of ZrO_2 could be obtained at ambient conditions with a low film thickness or by doping with foreign metal oxides [3-4]. Atomic layer deposited ZrO_2 thin films with high mechanical resilience could be applied as protective coatings.

In the present study, Al_2O_3-doped ZrO_2 films were atomic layer deposited on TiN/Si substrate at 300°C with $ZrCl_4$, $Al(CH_3)_3$ and H_2O. One $Al(CH_3)_3$ + H_2O cycle was performed between every 2, 4, 9, 14 and 19 consecutive cycles of $ZrCl_4$ + H_2O. The thickness of the films neared 100 nm.

Grazing incidence X-ray diffraction revealed that the film grown using ZrO_2: Al_2O_3 cycle ratio of 19:1 was crystallized in its tetragonal polymorph (Fig. 1). Increasing the Al_2O_3 content with cycle ratios of 14:1 and 9:1 stabilized the cubic polymorph. The films with higher Al_2O_3 contents remained amorphous and the reference ZrO_2 films was monoclinic. All the crystalline films possessed a preferential grain orientation to different extent beneath the surface and in the vicinity of the substrate.

Nanoindentation was used to determine the hardness and elastic modulus averaged over 30 indents in each film (Fig. 2). The most rigid films with hardness up to 15 GPa and elastic modulus above 167 GPa were obtained with cubic ZrO_2 stabilized with Al_2O_3. In general, the hardness and elastic modulus increased in the vicinity of the substrate even though the substrate possessed lower values of hardness (12 GPa) and elastic modulus (147 GPa). The texture in thin films had an effect on the mechanical properties.

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AF9-7 Friction and Wear Properties of Low-Temperature Metal Oxides*, Oili Ylivaara*, *L. Kilpi,* VTT Technical Research Centre of Finland*; R. Ritasalo,* Picosun Oy, Finland*; H. Ronkainen,* VTT Technical Research Centre of Finland

In microelectromechanical system (MEMS) devices, thin film made by atomic layer deposition (ALD) can be used as a functional material or as a protective coating due to its ability to coat high-topology surfaces with good conformality. In MEMS devices, there are moving parts involved and during its lifetime, device might be exposed to internal friction causing wear, and long-term reliability issues. Here, we studied low-temperature thin films made by ALD in a system where a silicon counterpart is sliding against ALD coating. Thin films were grown in a temperature range from 85 to 200 °C with a target thickness of 100 nm. Studied materials were Al_2O_3, TiO_2, Ta_2O_5, SiO_2, and some of their nanolaminates. Friction and wear properties of ALD coatings were evaluated with reciprocating sliding test using Anton Paar Tritec Pin-On-Disc tribometer. The load and sliding speed were kept constant during the testing, at 0.3 N and 0.01 m/s, respectively. Sliding distance was up to 20 meters using 10 mm back and forth movement. For each material, friction coefficient was measured during the testing, and after the testing wear surfaces on both the ALD coated silicon sample and silicon pin were analysed, and wear rate was calculated. On most coatings, friction coefficients were on the same level as with reference silicon. In case of the Al_2O_3 and TiO_2 visible tribolayer was formed in the wear surface. In the case of Ta_2O_5, besides tribolayer formation, coating was worn during the testing revealing silicon substrate. For SiO_2 both coating was worn and tribolayer was formed on the surface. Friction and wear results presented here give interesting options for low-temperature protection of the wear surfaces.

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AF9-8 Cryo-ePDF to Measure the Atomic Structure of Amorphous ALD Interfaces*, Matthias Young*, *N. Paranamana, X. He, T. White,* University of Missouri-Columbia

Atomic layer deposition (ALD) provides uniform and conformal thin films that are of interest for a range of applications. To better understand the properties of amorphous ALD films and ALD-modified interfaces, we need improved understanding of their local atomic structure. Previous work demonstrated measurement of how the local atomic structure of ALD-grown aluminum oxide (AlO_x) evolves in operando during growth by employing synchrotron high energy X-ray diffraction (HE-XRD). In this work, we report on efforts to employ electron diffraction pair distribution function (ePDF) measurements using more broadly available transmission electron microscope (TEM) instrumentation to study the atomic structure of amorphous ALD-AlO_x and ALD-modified interfaces. We observe electron beam damage in ALD-coated samples during ePDF at ambient temperature and successfully mitigate this beam damage using ePDF at cryogenic temperatures (cryo-ePDF). We examine both wide-area electron diffraction over a ~200 nm spot size, as well as local diffraction over a <2 nm spot size using cryo-ePDF. The smaller spot size (achieved using convergent electron diffraction with a small convergence angle) allows for local electron diffraction, for example at multiple positions along the cross-section of a 10 nm thick ALD film, and enables characterization of the interfacial atomic structure of the ALD film relative to the bulk structure. We employ Reverse Monte Carlo (RMC) modeling to obtain structural models from the cryo-ePDF data. From these model structures, we derive structural metrics including stoichiometry, pair distances, and coordination environments in the ALD films and ALD-modified interfaces. The cryo-ePDF technique can be used for routine measurement of atomic structure with high spatial resolution to improve understanding of ALD materials, establish structure-property relationships, and help accelerate the timescale for the application of ALD to address technological needs.

AF9-11 Growth and Characterization of Sodium Fluoride Thin Films Deposited by Atomic Layer Deposition*, Sara Kuraitis*, Boise State University*; D. Kang, A. Mane, H. Zhou,* Argonne National Laboratory*; J. Soares,* Boise State University*; J. Elam,* Argonne National Laboratory*; E. Graugnard,* Boise State University

Control over the interface between electrolytes and electrodes is key to improving the performance of lithium and sodium ion batteries. Atomic layer deposition (ALD) has attracted interest as a promising approach to the deposition of conformal, pinhole-free thin films on anodes and cathodes in rechargeable battery systems. Such coatings must be stable, prevent dendrite formation, allow for ion conduction, and, ideally, extend cyclability and lifetime. ALD of LiF has shown promise for Li-ion battery systems, and here we report an ALD process for sodium fluoride (NaF) thin films using a similar chemistry. NaF growth experiments were carried out using sodium *tert*-butoxide and HF-pyridine temperatures between 175 and 250 °C. The resulting cubic polycrystalline NaF films exhibited nearly stoichiometric composition (Na:F = 1:1.05), low roughness (Rq ≈ 1.6 nm for ~8.5 nm thick films), and a growth per cycle value of 0.85 Å/cycle on SiO_2 substrates and 3.2 Å/cycle on Al_2O_3. Application of conformal ALD NaF films to battery electrodes may hold promise for improved performance in rechargeable battery systems.

AF9-14 Advanced Applications of Noncontact Electrical Metrology for ALD Films and Interfaces*, Marshall Wilson*, *D. Marinskiy, J. Lagowski,* Semilab SDI

The noncontact charge-based metrology adopted from the silicon industry enables wafer level, very precise electrical characterization without fabrication of any test devices or contaminating contacts. The key advantages are the low cost and rapid feedback that shall benefit the novel implementations of ALD films.

Two different, new applications presently discussed include: 1. characterization of Al_2O_3 and AlN films on wide bandgap AlGaN and GaN structures for HEMT technology; and 2. a unique charge-induced, noncontact ferroelectric poling and characterization of ALD HfO_2 on silicon.

Noncontact metrology employs precise dosing of charge, ΔQ_C, on ALD film surface, performed with a corona discharge in air.The surface charge provides an electrical bias in analogy to gate bias. The response is monitored as a change of the surface voltage, ΔV, measured with a noncontact Kelvin probe. The differential capacitance $C=\Delta Q_C/\Delta V$ is determined, and corresponding C-V and C-Q characteristics provide a means for extraction of parameters characterizing ALD films, and the film/substrate interfaces, including 2DEG. Results are presented for a skew of thermal ALD AlN films with varying ALD cycles on standard, normally on AlGaN/GaN HEMT structures.

The metrology also includes high charge, time resolved SASS voltage technique for direct determination of a dielectric film thickness. For the AlN skew a linear thickness dependence is seen above 50 cycles. However, the growth is slower for 20 cycles. The latter may be an indication of the growth incubation effect analogous to thermal ALD AlN on silicon substrates. ALD films in the HEMT multi-layer structure may be difficult to model in ellipsometry measurements. The direct SASS technique offers an advantage.

For noncontact measurement of ferroelectric Si doped HfO_2, it is critical that the high charge density SASS pulses provide a noncontact means for poling of the film. A subsequent small charge incremental capacitance measurement gives hysteresis characteristics and “butterfly” permittivity curve. In recently introduced metrology, the ferroelectric poling-measuring sequence is fully automated. As demonstrated by results for 4% Si doped ALD HfO_2, such measurement gives the ferroelectric characteristics and the ferroelectric parameters that also includes the maximum capacitance and polarization charge.

The wafer testing includes initial surface voltage mapping. This high speed, 2 min per wafer screening, is a powerful means for evaluation of wafer uniformity after ALD growth.

AF9-17 Assessing the Quality of 3D-printed ALD Films by Low Energy Ion Scattering*, Philipp Brüner*, IONTOF GmbH, Germany*; I. Kundatra, M. Plakhotnyuk,* ATLANT 3D Nanosystems, Denmark*; J. Bachmann,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany*; T. Grehl,* IONTOF GmbH, Germany

Miniaturizing a spatial ALD reactor for integration into a small print head enables 3D-printing of ALD films in arbitrary patterns on large areas of many cm² by lateral movement of the substrate. The lateral resolution, or line size, of 400 µm is given by the size of the print head, while the vertical resolution is determined by the ALD process employed, ideally reaching atomic layer resolution [1].

In this study, we use Low Energy Ion Scattering (LEIS) to assess the quality and the properties of the deposited films. With its high surface sensitivity of just a single monolayer, the ability to measure film thickness, and the quantitative determination of the elemental composition, LEIS elucidates the lateral homogeneity of the printing process with regards to film thickness, surface coverage, and film composition. The selectivity of the deposition is another important aspect. Naturally, any printed pattern comprises growth areas and non-growth areas, and the print head must be designed in a way to provide maximum selectivity between these areas. Good detection limits in combination with the high surface sensitivity allow

LEIS to pick up trace amounts of deposited material on the non-desired areas, such that the selectivity is determined quantitatively.

The samples analyzed include line patterns for testing purposes, consisting of Pt and TiO_2 films, and the ATLANT 3D company logo printed with Pt (fig. 1). While LEIS is normally used as an averaging technique, with analysis areas of a few mm², this type of sample requires a pixel-resolved analysis by scanning the analysis ion beam. We show how the data obtained is evaluated to address the analytical questions outlined above. The LEIS surface scattering signal shows that the Pt film only reaches full coverage in the thicker parts of the film (fig. 1), which is an indication for the growth of individual particles instead of flat films. Excellent selectivity for the deposition of Pt is found, with a lower bound of at least 100,000 (ratio of material deposited on growth area vs. non-growth area).

Analyzing the sub-surface LEIS signal originating from ion scattering processes below the surface allows determining film thickness up to a few nm in a laterally resolved way. We also show how LEIS distinguishes between different film compositions, in this case pure Pt and PtO_x films.

AF9-20 Resistive Switching Performance of Mixed Al_2O_3 and ZrO_2 Thin Films*, **Joonas Merisalu**, T. Jõgiaas, A. Kasikov, A. Tamm, J. Aarik, K. Kukli,*
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In the search for resistive switching (RS) media, mixing dielectric materials is widely practiced, taking advantage of versatile possibilities of atomic layer deposition (ALD). There are some studies on RS of ZrO_2 as the host dielectric oxide [1,2], and few papers have reported RS of ALD-grown ZrO_2:Al_2O_3 mixtures [3] or nanolaminates [4]. In the present study, ZrO_2:Al_2O_3 films were grown on TiN bottom electrodes to thicknesses 10–15 nm by ALD using $Al(CH_3)_3$, $ZrCl_4$ and H_2O as precursors at 300 °C, whereas earlier $AlCl_3$, as a precursor less prone to thermal decomposition has been applied in the processes [3,4]. In the present study, the ZrO_2:Al_2O_3 cycle ratios ranged from 24:1 to 4:1 yielding Al:Zr cation ratios 0.04–0.4. The RS structures with Ti-Au top electrodes demonstrated multiple clockwise bipolar RS with low to high resistivity window over 5 orders of magnitude in the conductivity scale (Fig. 1), clearly exceeding that observed earlier [3,4], while some samples demonstrated multilevel RS (Fig. 1). The forming voltage, though, was rather high ranging from 4 to 6 V. Interestingly the forming took place under positive voltage applied to Ti-Au electrode which is more common for counterclockwise RS. The effects of cycle ratios and sequencing on the crystalline structure, switching polarity and low to high resistivity ratios will be discussed.

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Author Index

Bold page numbers indicate presenter

Author Index