ALD Fundamentals
Room Jan & Hubert Van Eyck - Session AF3-MoA
ALD Growth and Surface Chemistry

Moderators: Christian Dussarat, Air Liquide Laboratories, Simon D. Elliott, Schrödinger

4:00pm **AF3-MoA-11 As Deposited Epitaxial Functional Complex Oxides - Enabling Novel Technology**, ***Henrik H. Sønsteby,*** University of Oslo, Norway **INVITED**

Low temperature direct epitaxy of functional complex oxides is attracting increased attention in novel device integration. Traditional techniques for depositing epitaxial films of complex oxides with sharp interfaces and high structural integrity, such as MBE and PLD, require high vacuum and high temperature. In addition, upscaling for device manufacturing is not straightforward due to limitations in deposition area. Techniques like CVD and sputtering are also employed, but the resulting films are often in need of post-deposition annealing to facilitate solid phase epitaxy.

This has usually also been considered true for ALD, however recent development has led to ALD emerging as a viable technique for epitaxy of a range of complex oxides at low temperatures. Careful selection of precursors, deposition conditions, substrates and pulsing recipes are key to enabling direct epitaxy.

In this talk, I will use complex nickelates and ferrites as examples to emphasize how ALD can solve key issues in complex oxide device fabrication. I will discuss strategies for direct epitaxy via ALD, and show how the resulting films have functionality that can compete with films deposited by more traditional physical techniques. Some surprising features related to epitaxial quality with respect to pulsing recipes will be discussed. I will show results on possibilities of doping such materials to enhance functionality, and how this affects epitaxy. Examples of extremely sharp as deposited interfaces will be used as highlights on what ALD can achieve in the world of complex oxides.

Finally, I will propose architectures for all-ALD complex oxide electronic devices that may offer fundamentally different behavior as compared to traditional silicon technology (that is currently close to reaching inherent physical limitations). This will highlight how ALD can enable new technology under deposition conditions that are viable for monolithic device integration.

4:45pm **AF3-MoA-14 RT Atomic Layer Deposition of Aluminum Silicate and its Application to Ion Sorption Surfaces**, *Y Mori, T Saito, K Saito, K Yoshida, M Miura, K Kanomata, B Ahmmad, S Kubota,* ***Fumihiko Hirose***, Yamagata University, Japan

Aluminum-silicate is a main material of zeolite minerals, used as an ion sorption surface in the field of water purification. In the zeolite minerals, Al atoms are negatively charged in the aluminum-silicate framework, which causes the ion sorption in the mineral in an aqueous solution. In our laboratory, we have been developing the RT atomic layer deposition of aluminum silicate to offer the ion sensing function in flexible electronics. Conventionally, the plasm enhanced aluminum silicate ALD was reported where the minimum growth temperature was 150̊C. In this study, we designed the RT ALD with a successive adsorption process of tris [dimethylamino] silane (TDMAS) and trimethylaluminum (TMA) using an oxidizer of plasma excited humidified Ar.

N-type Si (100) samples and PEN films were used as substrates. Before the ALD process, all the samples were treated with plasma excited humidified argon for a prolonged time to remove the surface contaminants from the air. In the precursor adsorption step, TDMAS was first introduced to the sample surface with an exposure of 2×10^5 L Then TMA was introduced to the TDMAS saturated oxide surface with exposures ranging from 4×10^3 to 1×10^5 L. After the TMA exposure, the chamber was evacuated for 70 s to remove the residual gas there. In the oxidizing step, the plasma excited humidified argon was introduced to the chamber for 300 s. After the oxidizing step, the chamber was evacuated for 30 s.

Fig. 1 shows the XPS narrow scan spectra of Al 2p and Si 2p obtained from the RT deposited aluminum silicate on Si substrate. The Si to Al atomic ratio in the deposited film was estimated as 1.01. Fig.2 indicates that the aluminum silicate dipped in a NaCl solution absorb Na ion from the solution and the adsorbed Na is exchanged with K in a KCl solution. This suggests that the RT deposited aluminum silicate works like the conventional zeolite mineral. In the conference, we shall discuss the growth mechanism of aluminum silicate and ion sorption mechanisms.

5:00pm **AF3-MoA-15 Nucleation and Growth of Thermal ALD Au Films - Towards Coalescence of Ultrathin Films**, ***Virginia Wheeler****, B Greenberg, N Nepal, J Avila, B Feigelson,* U.S. Naval Research Laboratory

Gold (Au) is the metal of choice in many electronic and optoelectronic applications due the beneficial combination of high electrical and thermal conductivity with excellent resistance to corrosion. For this reason, significant efforts have been made to develop ALD Au precursors, resulting in two possible options - $Me_3Au(PMe_3)$ and $Me_2Au(S_2CNEt_2)$[1,2]. The latter is particularly interesting due to its ability to thermally deposit films with near bulk resistivities[2]. However, to obtain fully coalesced films required relatively thick (>20nm) and thus limits their use as transparent metal films in applications such as neutral beam splitters, transparent electrodes, and thermal insulating and solar control coatings. In this work, we focus on understanding the nucleation and growth mechanisms of thermal ALD Au films and the influence of substrate and deposition parameters on the ability to reduce the thickness at which fully coalesced films can be attained.

ALD Au films were deposited in a Veeco Savannah 200 reactor using $Me_2Au(S_2CNEt_2)$ and ozone at temperatures (T_g) from 125-200° C. The Au precursor was held at 110° C and delivered using a vapor boosted process. Initial films were deposited on a variety of substrates with different chemical inertness, wettability, and roughness including sapphire, Si, ALD TiN, Au, and others. SEM images reveal that growth proceeds similar to other CVD Au processes on all substrates with nucleation and growth of individual islands, which then form elongated structures that lead to percolation and eventual coalesced films. This type of growth makes it difficult to define thickness with traditional methods such as ellipsometry. Thus, we use a combination of XRR, ellipsometry, and XPS to evaluate the films and define ALD windows. For instance, at 200 cycles, film thickness constant at ~24 nm from 150-200° C but the density and total coverage increases with temperature.

Initial results at 150° C also show that the percolation threshold (t_c) is dependent on substrate with t_c on Au < sapphire < Si < ALD TiN, suggesting that thinner films can be obtained on more inert surfaces. Thick films (50-60nm) show resistivities of 3-4.8 μΩ cm depending on substrate and pinhole density. At low T_g here, the kinetic freezing model can be used to describe the crossover from island growth to coalescence[3]. This suggests that t_c is influenced by growth temperature, surface diffusion constant, and surface energy. We will discuss our approach to decouple these aspects and their resulting effect on reducing t_c.

[1] Griffiths, et al. *Chem. Mat.* 2016, 28, 44-46

[2] Makela, et al. *Chem Mat.* 2017, 29, 6130-6136

[3] Jeffers, et al. *JAP* 1994, 75, 5016-5020

5:15pm **AF3-MoA-16 ABC-Type Pulsing for Improved ALD of Group 13 Nitrides using Trialkyl Metal Precursors**, ***Henrik Pedersen****, P Rouf, P Deminskyi,* Linköping University, Sweden*; T Törndahl,* Uppsala University, Sweden*; L Ojamäe,* Linköping University, Sweden

The group 13 nitrides (13-Ns) are essential electronic device materials for present and future technologies. Deposition of AlN and GaN are well explored by CVD at high temperatures (800-1000 °C). This aids epitaxial growth and ligand removal, rendering high crystalline quality films with low impurity levels. As 13-N CVD almost exclusively uses the trimethyl complexes of the group 13 metals, carbon is the major unwanted impurity with concentrations in the 10^{17} cm^{-3} range by SIMS.

ALD is less explored for the 13-Ns but could potentially open routes to low deposition temperatures and allow topographically more advanced 13-N structures. However, the low deposition temperatures used in ALD compared to CVD hampers the removal of ligands from the surface leading to an increase in impurity levels, mainly carbon, to the several atomic percentage levels.

We explore the possibility to improve ALD of 13-Ns with the standard trialkyl metal precursors by developing the time-resolved precursor supply further by adding an additional pulse between the metal and nitrogen precursor pulses to an ABC-type pulsing ALD. The role of the additional B-pulse is to aid the ligand removal from the surface and thereby reduce the impurity levels in the film that additionally allows higher degree of 13-N atoms rearrangement leading to higher film crystallinity.

ABC-type pulsing allowed thermal ALD of AlN from $AlMe_3$ and NH_3 at 480 °C, which is 150 °C above the decomposition temperature for $AlMe_3$. A B-

pulse of H_2, N_2 or Ar between the $AlMe_3$ and NH_3 pulses was shown by XPS measurements to reduce the carbon content in AlN from about 3 at. % to below the 1 at. % detection limit of C by XPS. We show by mass spectrometry combined with kinetic- and quantum chemical modeling that the B-pulse lowers the carbon content by enhancing desorption and preventing re-adsorption of methyl ligands from the surface. The surface methyl groups desorb as CH_3, CH_4 and C_2H_x. Addition of a B-pulse also increases the crystallinity of the AlN, as seen from the GIXRD peak intensity.

ABC-type pulsing also aided to improve the deposition of GaN with plasma ALD from $GaEt_3$ and NH_3 plasma. B-pulses of H_2 gas, Ar plasma and H_2 plasma where explored and all found to increase the growth per cycle compared to AB-pulsing ALD. The highest increase was found for H_2 plasma. We speculate that the growth per cycle increase can be explained by enhanced surface chemical mechanisms for removal of the relatively bulky ethyl groups from the surface where Ar-plasma enhanced the β-elimination of ethyl groups, H_2 allows for elimination as ethane and H_2 plasma allows both mechanisms.

5:30pm **AF3-MoA-17 Atomic Layer Deposition of Metal Thin Film using Discrete Feeding Method (DFM) and Electric Field/Potential Assisted-Atomic Layer Deposition (EA-ALD)***, **Ji Won Han**, T Park,* Hanyang University, Republic of Korea*; H Jin,* SK Hynix Inc, Republic of Korea*; Y Kim,* Hanyang University, Republic of Korea

Ruthenium (Ru) has been considered as a promising electrode material for next generation semiconductor devices due to its low resistivity (~ 7 μΩ·cm), high oxidation resistance, and its conductive oxide phase, RuO2 (~ 30 μΩ·cm). As a complicated 3-dimensional integration scheme has been developed recently to improve the degree of device integration, ultrathin (< 5 nm) and uniform Ru metal electrode is required. Even though atomic layer deposition (ALD) of Ru film was employed, it is difficult to achieve ultrathin and continuous film due to island growth at the initial stage of growth. Therefore, we proposed advanced ALD processes, discrete feeding method (DFM) and electric field/potential assisted ALD (EA-ALD).

DFM is composed of subdivided precursor feeding and purge which enables instant removal of physisorbed precursor molecules screening functional group on substrate, hence chemical adsorption efficiency and surface coverage can be improved. EA-ALD also improves chemical adsorption and surface coverage by applying bias voltage on substrate during precursor/reactant injection. Electric field formed across ALD reactor increases impingement of precursor and modulated surface potential changes activation energy of ALD reaction on surface. Nucleation at initial stage of deposition improved by advanced ALD method and thus critical thickness for coalescence of Ru islands is reduced. Microstructure, density and resistivity of Ru film are improved consequently. While physical properties are improved, chemical composition and binding state of Ru were also changed, resulting change in effective work function of Ru film.

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