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

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

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

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

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

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

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

In this study, the exchange between Zn and Al is explored during the initial reaction of trimethylaluminum (TMA) on ZnO films during Al_2O_3 ALD at temperatures from 100-225°C. The exchange is evident from a variety of experimental measurements. Fourier transform infrared (FTIR) investigations detect absorbance changes consistent with ZnO loss and Al_2O_3 gain after the TMA reaction on ZnO ALD films. Quadrupole mass spectrometry (QMS) measurements also observe $Zn(CH_3)_2$ reaction products as expected from the conversion reaction: $3ZnO + 2Al(CH_3)_3 \rightarrow Al_2O_3 + 3Zn(CH_3)_2$. In addition, studies of the effect of TMA exposures on ZnO nanoparticles with a diameter of ~10 nm measured the conversion of ZnO to Al_2O_3. The conversion produces a large mass loss that is consistent with the formation of an Al_2O_3 surface layer. The ZnO to Al_2O_3 conversion is also self-limiting as a function of TMA exposure.

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

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

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

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

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

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

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

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

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

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

Linear growth with no nucleation delay was observed for WpO process, and the growth rate was about 0.09 nm/cycle. Since nucleation delay was not observed for all other processes (WO, pOW, pO, O, and W), it is probable that EtCpIn well adsorbs onto surface oxygen. For WO process, linear growth was also observed, and the growth rate was about 0.11 nm/cycle, significantly larger than that of WpO process. These results support the prospected reactions at oxidation step in WpO process; substitution of

hydroxyl groups for ethylcyclopentadienyl ligands by water and subsequent sufficient surface oxidation by plasma oxygen. In WO process, the oxygen without plasma activation does not oxidize surface hydroxyl groups, and the remaining hydroxyl groups cause additional adsorption at the EtCpIn adsorbing step. The additional adsorption increases the growth rate of WO process. For the other processes (pOW, pO, O, and W), the growth rates were markedly small due to incomplete reactions in oxidation step.

Reference

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

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

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

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