

ALD Fundamentals

Room 113-115 - Session AF1-WeA

In-situ Monitoring and Analysis

Moderators: Christophe Detavernier, Ghent University, Belgium, Christian Dussarrat, Air Liquide

1:30pm AF1-WeA-1 In Situ IR Spectroscopic Investigation of Thermal and Plasma-Enhanced ALD of Pt: Temperature Dependency of the Growth Rate, Michiel Van Daele, C Detavernier, J Dendooven, Ghent University, Belgium

The O₂-based processes of Pt using the MeCpPtMe₃ precursor have become a model system for oxidative noble metal ALD processes. The thermal process is characterized by a narrow temperature window (250-300°C; below this temperature range the growth rate quickly diminishes), while PE-ALD process has a much larger temperature window. An intriguing question is why the growth diminishes below 250°C for the thermal process. It has been suggested in literature that the precursor ligands dehydrogenate on the catalytic Pt surface and form a carbonaceous layer causing surface poisoning. However, direct identification of the surface species to support this hypothesis is missing. This is mainly because IR light is absorbed by metals, which complicates in-situ IR spectroscopy studies in transmission. In this work, in situ reflection IR spectroscopy is used during O₂ and O₂ plasma based ALD processes at different deposition temperatures to shed light on the reactions that take place on the surface during the processes.

The ALD setup used for this work is shown in Fig. 1. It concerns a pump type ALD chamber that is connected to a Bruker Vertex 70v IR spectrometer. To ensure steady state growth conditions, a sputtered Pt film is used as the substrate. Substrate temperatures of 100, 200, and 300°C are used. FTIR spectra are taken after every precursor and reactant pulse. Consecutive spectra are subtracted, giving difference spectra for each half cycle. Positive (negative) features in Fig. 2 are due to added (removed) surface groups.

We have found evidence that CH₃ and C=C containing species are present on the surface after precursor exposure at low substrate temperatures (<150°C), poisoning the surface during thermal ALD. These species are removed by O₂ plasma which enables PE-ALD below 150°C through combustion reactions. Above 150°C, no CH₃ groups were detected and the C=C vibrations diminished for both the thermal and PE-ALD process which indicates dehydrogenation reactions and ligand restructuring. Both processes show the presence of CO combustion products after precursor exposure. In addition, the PE-ALD FTIR spectra indicate the presence of ether and ester combustion products after precursor exposure, likely due to a higher amount of surface oxygen for the PE-ALD process compared to the thermal process. We conclude that the restructuring and dehydrogenation of the precursor ligands is necessary to allow the dissociation of molecular O₂ on the Pt surface, explaining the need for high substrate temperatures for the thermal Pt process.

1:45pm AF1-WeA-2 Growth Mechanisms and Diffusion Behavior of Molecular Layer Deposition Films Deposited by Cyclic Azasilanes, Maleic Anhydride, and Water, Ling Ju, N Strandwitz, Lehigh University

Molecular layer deposition (MLD) using N-(2-aminoethyl)-2,2,4-trimethyl-1-aza-2-silacyclopentane (AZ), maleic anhydride (MA), and H₂O is used to grow hybrid organic-inorganic films.¹ The growth rate (~ 90 Å/cycle in the steady state at 100 °C) is much larger than for MLD/ALD chemistries that involve exclusively surface reactions, indicating that precursor diffusion into the MLD film plays a key role in the large growth rate.¹

In-situ quartz crystal microbalance (QCM) measurement monitors the mass gains during individual reactions, and provides detailed information of precursor diffusion behavior by varying the precursor sequence, substrate temperature, and purging time. The mass profiles during the AZ and MA reactions are consistent with these two precursors diffusion into and out of the MLD films. The growth also displays a strong dependence on the substrate temperature and purge times of AZ and MA, that is consistent with the effects of the sub surface reactions. Diffusion coefficient and diffusion depth of different precursors were quantified. These studies provide better understanding of the structures and growth behavior of the MLD films, and avenues for basic studies of the effects of specific chemical functionalities on growth.

1 L. Ju, B. Bao, S. W. King and N. C. Strandwitz, J. Vac. Sci. Technol. A **35**, (2017).

2:00pm AF1-WeA-3 In-situ RAIRS Investigation of the Oxidation and Reduction of Cu using UV/O₃ and Ethanol, Luis Fabián Peña, The University of Texas at Dallas; M Todd, Versum Material, Inc; Y Chabal, The University of Texas at Dallas

Copper is the most widely used material in semiconductor interconnect technology because of its superior conductivity and resistance to electromigration. Although several methods to deposit copper oxide on nanostructured surfaces with high aspect ratio have been developed using ALD,^{1,2} a reduction step is required to convert the deposited copper oxide film into metallic copper. Promising results have been demonstrated using ethanol as the reduction agent but little experimental data is available on the reduction pathways; the reaction mechanisms and surface chemistry are poorly understood.

In this work we use *in-situ* reflection absorption infrared spectroscopy (RAIRS) to investigate each step of the oxidation (UV/O₃) and reduction (ethanol (EtOH)) process to achieve an ideal Cu metal surface in an ALD environment.

To understand the reduction of copper oxide thin films with ethanol, we investigate the role of ethanol partial pressure on the oxide reduction rate by monitoring the surface species after each dose. To illustrate, the IR spectra in Fig. 1 shows that the initial reaction begins by reducing the concentration of surficial C≡O species (2209 cm⁻¹) and this frequency is red shifted to (2175 cm⁻¹) as the extent of dipole coupling is reduced after subsequent ethanol exposures. At the same time, the reduction of CO₂ (2337 cm⁻¹) takes place after the 2nd EtOH exposure at which point the reduction of Cu₂O also begins to take place (636 cm⁻¹). Eventually, 4 consecutive EtOH exposures are enough to reduce the oxide on Cu (632 cm⁻¹). Having established an understanding on the reactions taking place on the surface, the process is optimized to reduce by-product re-deposition using an ALD-like binary process with EtOH and nitrogen.

References

- [1] Alnes, M. E., Chem. Vap. Deposition, 18: 173–178
- [2] Waechter, T., J. Electrochem. Soc. 2009 156(6):H453-H459

2:15pm AF1-WeA-4 Real Time GISAXS Study of the Effects of Plasma Gas Chemistry on Growth of InN Films by Atomic Layer Epitaxy, Neeraj Nepal, U.S. Naval Research Laboratory; V Anderson, The American Society for Engineering Education; S Johnson, U.S. Naval Research Laboratory; S Rosenberg, J Woodward, A Kozen, The American Society for Engineering Education; C Wagenbach, Boston University; D Meyer, B Downey, J Hite, V Wheeler, U.S. Naval Research Laboratory; Z Robinson, SUNY College at Brockport; D Boris, S Walton, U.S. Naval Research Laboratory; K Ludwig, Boston University; C Eddy, Jr., U.S. Naval Research Laboratory

III-N semiconductors have found application in a variety of technologies, however, the requisite heteroepitaxy on foreign substrates, miscibility gaps, substrate versatility and low strain heterojunctions challenge material developments. Among III-Ns, InN has the lowest growth temperature, which represents a significant challenge to epitaxial growth of single phase In containing layers. To address this, the growth temperature has to be reduced. Plasma assisted atomic layer epitaxy (ALEp) offers a new low temperature growth approach to achieve epitaxial thin films [1]. At reduced growth temperatures, plasma driven non-thermal equilibrium kinetics on nucleation and growth process is critical for improved material quality. As conventional, ultra-high vacuum growth monitoring methods generally difficult to employ, we have shown that using high intensity x-rays to monitor the evolution of grazing incidence small angle x-ray scattering (GISAXS) features directly correlate with the surface roughness, impurities, and electrical properties of the thin film [2].

In this paper, we present real time GISAXS Study of plasma gas chemistry and its effect properties on growth in the synthesis of high quality InN films by ALEp on a-plane sapphire substrate at 250°C. The total gas flow through the plasma source (N₂ + Ar = 275 sccm) was kept constant while the N₂ flow was varied from 15 to 95 sccm. During the initial cycles of InN growth on a-plane sapphire, the specular peak broadens and the correlated length scale (CLS) start to evolve along the native wing with different correlated length scales (CLSs). At N₂= 95 sccm surface scattering is higher and it appears to increase with N₂ flow fraction. During growth CLS remains constant at 11.56 nm for 94 sccm N₂ while it increases from 9.72 to 12.56 nm for 15 sccm of N₂. Separation between the diffuse scattering rod and CP is smaller for lower N₂ flow at the end of the growth. Lower N₂ flow through plasma increases reactive nitrogen species on the growth surface, which initiate

Wednesday Afternoon, August 1, 2018

coarsening by converging nucleation islands. Consistent with *in situ* GISAXS, post-growth atomic force microscopy shows that surface roughness decreases from 0.35 nm to 0.12nm by decreasing N₂ flow fraction from 34% to 5%. Post-growth x-ray photoelectron spectroscopy indicates shows no carbon for all films. In this paper we present plasma characterization results to understand the influence of relative gas flow on species production and their effect on growth besides structural, morphological, and electrical properties of ALEp grown InN films.

[1] Nepal et al., Cryst. Growth and Des. **13**, 1485 (2013).

[2] Nepal et al., J. Vac. Sci. Technol. A **35**, 031504 (2017).

2:30pm **AF1-WeA-5 Low-Temperature Plasma-Enhanced Atomic Layer Deposition of Cobalt Thin Films using Cyclopentadienylcobalt-dicarbonyl and N₂-H₂ Plasma, Pouyan Motamedi, K Bosnick**, National Research Council Canada, Canada; *K Cadien, J Hagan*, University of Alberta, Canada

The field of thin and ultrathin metallic thin films has attracted a great amount of attention, owing to their various applications, including microelectronics, enhanced solar absorbers, and catalysts for growth of carbon nanotubes. In most cases, achieving the capacity to deposit a conformal thin film on a three-dimensional structure is an important factor. Plasma-enhanced atomic layer deposition (ALD) offers potential for growth of conformal thin films with a precise control over the thickness, and its capability for deposition at relatively low temperatures. A survey of the literature reveals that the field of growing metallic thin films via ALD is relatively under-studied. Specifically, cobalt has several applications as a magnetic material, and is being increasingly considered to be used as an interconnect in nanofabrication. Unfortunately, the amount of research available on ALD of cobalt thin films is extremely limited. Here, we demonstrate that, using an organometallic precursor and nitrogen plasma, cobalt thin films can be deposited at temperatures as low as 240°C. The deposited films show no sign of carbon and oxygen impurities. A comprehensive characterization analysis was performed on the films, in order to study their composition, physical properties, surface properties, and crystal structure. In addition, *in-situ* spectroscopic ellipsometry was utilized to observe and analyze the growth rate and optical properties of the films, as a function of growth cycles. All these analyses were performed for the growth temperature range of 120-500°C. The general conclusion was that the specific combination of the precursors and the recipe was very successful in deposition of smooth, crystalline, and chemically pure cobalt thin films with resistivity and optical properties close to those of the bulk material. A wealth of useful information was gathered about the growth mechanism of metals using ALD, which can be potentially applied to other metallic thin films.

2:45pm **AF1-WeA-6 A Surface Science Toolbox for Understanding Atomic Layer Epitaxy, Charles R. Eddy, Jr., S Rosenberg, J Woodward**, U.S. Naval Research Laboratory; *D Pennachio, C Palmstrøm*, University of California, Santa Barbara; *N Nepal*, U.S. Naval Research Laboratory; *V Anderson*, Kennesaw State University; *S Johnson*, U.S. Naval Research Laboratory; *C Wagenbach, K Ludwig*, Boston University; *A Kozen, S Walton, D Boris, V Wheeler*, U.S. Naval Research Laboratory

Atomic Layer Epitaxy (ALEp) is a promising subset of atomic layer processes (ALPs) which has the potential to open a new realm of non-equilibrium semiconductor growth. In ALEp, the objective is to grow crystalline, epitaxial layers on a crystalline substrate for active regions of electronic and optoelectronic devices. This requires expansion of the ALD processing space to higher temperatures and adds constraints of crystallinity and purity (electronic grade requires impurity concentrations less than ppm). While ALEp has been shown to maintain the self-limiting nature of ALD at temperatures up to 500°C, the additional materials quality criterion requires a more complete understanding of the ALEp process if it is to be fully successful. In this regard, it is essential to develop a set of surface science tools that can be employed either *in situ* or *in vacuo* to ensure that atmospheric exposure does not influence or interfere with observed process mechanisms.

In this work, we highlight the development and early application of a suite of *in situ* or *in vacuo* characterization techniques aimed at providing surface and near-surface structure assessments [reflection high energy electron diffraction/low energy electron diffraction (RHEED/LEED) and grazing incidence small angle x-ray scattering (GISAXS)] as well as surface chemistry assessments [(x-ray photoelectron spectroscopy (XPS), resonant ion trap mass spectrometry (RIT-MS) and reflection-absorption infrared spectroscopy (RAIRS)]. We present select results from these characterizations during efforts to develop ALPs for GaN surface preparation for epitaxy and for early ALEp growth of heteroepitaxial AlN

and InN films on GaN and Al₂O₃ substrates as a function of plasma pulse conditions. As an example, GISAXS measurements have revealed a distinction in the growth mode of InN on sapphire vs. GaN substrates for an otherwise identical ALEp process, with the former proceeding by correlated island growth with short range order and the latter by long range order evolution on properly prepared surfaces. Further, the duration of the plasma pulse is shown to influence the growth mode between a bimodal distribution of islands for short pulses to a single mode distribution for intermediate pulses to etching for the longest pulses. Changes in plasma chemistry are also found to affect growth mode and film quality. These changes are correlated to independent measurements of plasma properties in an effort to establish plasma process – film property relationships. A combination of RAIRS and RIT-MS will be presented to further illustrate the role of plasma chemistry.

3:00pm **AF1-WeA-7 Investigation of the Temperature Dependence of Plasma-assisted Atomic Layer Epitaxy Growth of InN on GaN using *in situ* Grazing Incidence Small-angle X-ray Scattering, Jeffrey M. Woodward, S Rosenberg**, The American Society for Engineering Education; *N Nepal, S Johnson*, U.S. Naval Research Laboratory; *C Wagenbach*, Boston University; *A Kozen*, The American Society for Engineering Education; *Z Robinson*, SUNY College at Brockport; *K Ludwig*, Boston University; *C Eddy, Jr.*, U.S. Naval Research Laboratory

Plasma-assisted atomic layer epitaxy (ALEp), a variant of atomic layer deposition in which relatively higher temperatures are utilized to promote surface diffusion for epitaxial growth, offers several potential advantages over conventional methods such as metalorganic chemical vapor epitaxy and molecular beam epitaxy for the growth of III-N materials and device structures. These advantages include significantly lower growth temperatures and highly controlled layer thicknesses, the latter of which is the result of the sequential pairs of self-terminating and self-limiting reactions that constitute the growth process. However, plasma-assisted ALEp is a relatively new method for III-N growth, and significant efforts will be required to better understand the nucleation and growth kinetics. To this end, grazing incidence small-angle X-ray scattering (GISAXS) has been previously utilized for the study of surface morphology during the plasma-assisted ALEp growth of InN¹ and AlN² on a-plane Al₂O₃ substrates. GISAXS is a non-destructive technique that can probe electron density fluctuations of length scales ranging from approximately 1 nm to 250 nm in an integral manner, making it well-suited to the study of epitaxial growth. The resulting intensity distribution from a collection of scattering objects is related to the form factor and structure factor, which are the Fourier transforms of functions describing the object shape and spatial arrangement, respectively.

In this work, we present *in situ* GISAXS studies performed at the Cornell High Energy Synchrotron Source during the plasma-assisted ALEp growth of InN on bulk GaN substrates, using 180°C, 250°C, and 320°C growth temperatures. We analyze the intensity distributions in order to extract information about the evolving morphologies. The data indicates that the InN islands are cylindrical, with mean inter-island spacings that scale with temperature. While deposition on GaN at 180°C was found to yield comparable inter-island spacings to those previously reported for deposition on a-plane Al₂O₃ at low temperatures¹, deposition on GaN at 250°C produced islands with increased spacing compared to a-plane Al₂O₃ at the same temperature. The inter-island spacing at 180°C was approximately constant throughout the growth process, which may indicate that such temperatures are insufficient for island coalescence. In contrast, the inter-island spacings at 250°C and 320°C were found to increase with growth time.

[1] N. Nepal et al., J. Vac. Sci. Technol. A **35**,031504 (2017)

[2] V. R. Anderson et al., J. Vac. Sci. Technol. A **35**, 031508 (2017)

3:15pm **AF1-WeA-8 In situ Investigations on the Crystal Structure Dependent ALD Film Growth of TiO₂, Martin Knaut, M Albert, J Bartha**, Technische Universität Dresden, Germany

The ALD of TiO₂ from titanium tetraisopropoxide (TTIP) and water or ozone is a widely known and well-reviewed ALD process.¹⁻³ Nevertheless, there are papers reporting inhomogeneous film growth or non-ideal surface reactions which might cause CVD effects.³⁻⁶ Additional, Kim et al. published an impact of the crystal structure of TiO₂ films on the density of surface hydroxyl groups and thus on the amount of chemisorbing TTIP molecules correlating with the film growth per cycle.⁷ In this paper we present detailed *in situ* based investigations on the TiO₂ film growth and its interaction with process parameters and film properties. Quartz crystal microbalances were used to monitor the TiO₂ deposition at temperatures

Wednesday Afternoon, August 1, 2018

between 200 and 300°C showing a spontaneous thickness and substrate temperature dependent change in GPC (marked by black dots in figure 1). This change in GPC corresponds to the crystallization of amorphous TiO₂ films into an anatase phase which was confirmed by atomic force microscopy and Raman spectroscopy measurements. A detailed analysis of the mass changes during single ALD cycles revealed an impact of the crystal structure on the amount of chemisorbing precursor molecules and so on the growth per cycle. While Kim et al. addressed this effect to a higher density of surface hydroxyl groups this work shows that the change in film growth is also related to an enhanced thermal decomposition of TTIP molecules on an anatase film resulting in a non-saturating CVD-like film growth once the film crystallizes. To enable linear and reproducible processes Al₂O₃ buffer layers have been applied to suppress film crystallization even at elevated temperatures and thicknesses. This approach allows to deposit thick amorphous TiO₂ films with a constant growth per cycle (see figure 2).

1. Rahtu, A. & Ritala, M., Chem. Vap. Depos. 8, 21–28 (2002).
2. Aarik, J., Aidla, A., Uustare, T., Ritala, M. & Leskelä, M., Appl. Surf. Sci. 161, 385–395 (2000).
3. Ritala, M., Leskela, M., Niinisto, L. & Haussalo, P., Chem. Mater. 5, 1174–1181 (1993).
4. Cleveland, E. R., Henn-Lecordier, L. & Rubloff, G. W., J. Vac. Sci. Technol. Vac. Surf. Films 30, 01A150 (2012).
5. Kim, W. D. et al., J. Electrochem. Soc. 152, C552 (2005).
6. Yanguas-Gil, A. & Elam, J. W., J. Vac. Sci. Technol. Vac. Surf. Films 30, 01A159 (2012).
7. Kim, S. K., Hoffmann-Eifert, S., Reiners, M. & Waser, R., Thin Films. J. Electrochem. Soc. 158, D6 (2011).

Author Index

Bold page numbers indicate presenter

— A —

Albert, M: AF1-WeA-8, 2

Anderson, V: AF1-WeA-4, 1; AF1-WeA-6, 2

— B —

Bartha, J: AF1-WeA-8, 2

Boris, D: AF1-WeA-4, 1; AF1-WeA-6, 2

Bosnick, K: AF1-WeA-5, 2

— C —

Cadien, K: AF1-WeA-5, 2

Chabal, Y: AF1-WeA-3, 1

— D —

Dendooven, J: AF1-WeA-1, 1

Detavernier, C: AF1-WeA-1, 1

Downey, B: AF1-WeA-4, 1

— E —

Eddy, Jr., C: AF1-WeA-4, 1; AF1-WeA-6, **2**;
AF1-WeA-7, 2

— H —

Hite, J: AF1-WeA-4, 1

Hogan, J: AF1-WeA-5, 2

— J —

Johnson, S: AF1-WeA-4, 1; AF1-WeA-6, 2;

AF1-WeA-7, 2

Ju, L: AF1-WeA-2, **1**

— K —

Knaut, M: AF1-WeA-8, **2**

Kozen, A: AF1-WeA-4, 1; AF1-WeA-6, 2; AF1-
WeA-7, 2

— L —

Ludwig, K: AF1-WeA-4, 1; AF1-WeA-6, 2;

AF1-WeA-7, 2

— M —

Meyer, D: AF1-WeA-4, 1

Motamedi, P: AF1-WeA-5, **2**

— N —

Nepal, N: AF1-WeA-4, **1**; AF1-WeA-6, 2; AF1-
WeA-7, 2

— P —

Palmstrøm, C: AF1-WeA-6, 2

Peña, L: AF1-WeA-3, **1**

Pennachio, D: AF1-WeA-6, 2

— R —

Robinson, Z: AF1-WeA-4, 1; AF1-WeA-7, 2

Rosenberg, S: AF1-WeA-4, 1; AF1-WeA-6, 2;
AF1-WeA-7, 2

— S —

Strandwitz, N: AF1-WeA-2, 1

— T —

Todd, M: AF1-WeA-3, 1

— V —

Van Daele, M: AF1-WeA-1, **1**

— W —

Wagenbach, C: AF1-WeA-4, 1; AF1-WeA-6, 2;
AF1-WeA-7, 2

Walton, S: AF1-WeA-4, 1; AF1-WeA-6, 2

Wheeler, V: AF1-WeA-4, 1; AF1-WeA-6, 2

Woodward, J: AF1-WeA-4, 1; AF1-WeA-6, 2;
AF1-WeA-7, 2