Tuesday Afternoon, July 31, 2018

ALD Fundamentals
Room 116-118 - Session AF1-TuA
Characterization

Moderators: Sean Barry, Carleton University, Canada, HyeongTag Jeon, Hanyang University, Korea

1:30pm **AF1-TuA-1 Studying Metal ALD Processes through X-ray Based in situ Characterization***, J Dendooven,* Ghent University, Belgium*; E Solano,* ALBA Synchrotron Light Source, Spain*; R Ramachandran, M Minjauw,* Ghent University, Belgium*; G Portale,* University of Groningen, Netherlands*; D Hermida-Merino,* ESRF, France*; A Coati,* SOLEIL, France*; **Christophe Detavernier,*** Ghent University, Belgium **INVITED**

Initial nucleation is particularly important during metal ALD. Using three different case studies, we aim to demonstrate that x-ray based characterization techniques such as x-ray fluorescence (XRF), grazing incidence x-ray scattering (GISAXS) and x-ray diffraction (XRD) can offer unique insights in metal ALD processes, offering approaches towards the conformal deposition of metal nanoparticles with carefully controlled loading, size and composition, as required for e.g. applications in catalysis and plasmonics.

A first case study concerns Ag ALD. We recently reported that combining the Ag(fod)(PEt_3) precursor with NH_3 plasma results in a six-fold increase of the steady growth rate (0.24 ± 0.03 nm/cycle) when compared to H_2-plasma as reactant (0.04 ± 0.02 nm/cycle). The film morphology was investigated by electron microscopy and GISAXS, and it was found that films grown with the NH_3-plasma process exhibit a much higher particle areal density and smaller particle sizes on oxide substrates compared to those deposited using the H_2-plasma process (Chem. Mater. 29, 7114 (2017)).

A second case that will be discussed concerns initial nucleation during Pt ALD. The Me_3(MeCp)Pt precursor was combined with different reactants (O_2, O_2 plasma, O_3 and N_2 plasma), and in situ XRF and GISAXS measurements provided detailed information about the evolution of Pt loading, average particle dimensions, and mean center-to-center particle distance during the initial stages of ALD, revealing that the choice of reactant had a significant impact on the nucleation and growth of the Pt nanoparticles. In the case of oxidizing reactants, there was a clear impact of the mobility of Pt surface species on the evolution of island morphology. The particle areal density could be controlled by tailoring the number of ALD cycles using oxygen as reactant, while subsequent growth using the same Pt precursor in combination with nitrogen plasma as reactant allowed for tuning of the particle size at the atomic level (Nat. Comm. 8, 1074 (2017)).

A third case concerns a recently reported ALD-based synthesis of bimetallic Pt-In nanoparticles. First, a Pt/In_2O_3 bilayer is deposited by ALD, where the thickness control inherent to ALD enables an accurate control of the Pt/In composition ratio. After ALD, annealing in H_2 ambient results in a reduction of the In_2O_3 and the controlled agglomeration of the bilayer structure into a film of bimetallic nanoparticles. In situ XRD and GISAXS were used to study the annealing process, and illustrate the accurate phase and size control that is offered by this two-step approach (ACS Nano 10, 8770 (2016)).

2:00pm **AF1-TuA-3 Stresses in ALD Films: Aiming for Zero Stress Thin Films***, R Ritasalo,* Picosun Oy, Finland*; O Ylivaara,* VTT Technical Research Centre of Finland, Finland*; **Tero Pilvi**, T Suni,* Picosun Oy, Finland

When grown films by atomic layer deposition (ALD) both intrinsic and thermal stresses are formed into the film; latter due to the mismatch in the thermal expansion coefficient of the substrate and the grown film. Films under high residual stress may cause problems for further processing, and for device performance and reliability. High residual stress can induce film delamination or buckling; bend released structures or the materials where the films are attached. Especially in microelectromechanical system (MEMS) manufacturing, zero or well-controlled residual stress is desired, as the stress effect is more prominent on released structures. Here, the residual stress measured from most common metal oxides deposited by thermal ALD processes on silicon substrates are presented. The thermal processes have an advantage that those can be scaled up to batch processing to achieve through-put and cost efficiency required for volume production. By varying the process parameters (e.g. temperature, chemicals) we aim for zero stress films or film stacks as well as for comprehensive stress data set to help for example MEMS designers and process integrators choosing proper thin film material, and ALD process chemistry and process conditions.

All films were grown in Picosun™ R-200 advanced reactors using thermal ALD processes. Deposited materials were HfO_2, TiO_2, SiO_2, Al_2O_3 and Ta_2O_5 and combinations of these. The ALD temperature was varied between 150°C and 300°C. The substrates used were 150 mm diameter double side polished silicon wafers, which have been pre-measured for stresses before the ALD. For stress measurement we used TOHO FLX-2320-S wafer curvature measurement tool and the measurements were carried out at room temperature. Deposited film thicknesses were measured with Semilab SE-2000 ellipsometer.

Residual stress data from most common metal oxides are presented. For some of the films there is also comparison for the same film material made with different precursors. In Figure 1 the residual stress data for the HfO_2 film grown at varying temperature is presented. The stress changes from compressive to tensile as the ALD temperature was increased from 150°C to 200°C.

Acknowledgements: This work has been done in the ECSEL Joint Undertaking project InForMed (An integrated pilot line for micro-fabricated medical devices) coordinated by Philips Electronics Netherlands BV.

2:15pm **AF1-TuA-4 High-throughput Screening of Atomic Arrangements of Surface and Interfacial Structures of ALD-deposited Thin Films***, **Orlando Trejo**, N Dasgupta,* University of Michigan

Atomically-precise engineering of surfaces and interfaces is critical for the development of PV technology. To address such atomic-scale engineering challenges, it is necessary to exploit advances in atomic-scale synthesis and characterization techniques by leveraging advances in corresponding theoretical understanding, modeling algorithms, and computational performance. However, there is a lack of software and modeling platforms to enable user-friendly and systematic investigation of surface and interfacial structure/disorder. Therefore, in this work we are developing a computational procedure for high-throughput screening of atomic arrangements of surface and interfacial structures.

Atomic structures of interfaces are typically a few Angstroms thick, not well-defined, multi-phase, non- periodic, and have intermixing of chemical species. Techniques like X-ray absorption near edge structure (XANES) and electron energy less spectroscopy (EELS) are promising to characterize interfacial structure as they capture element-specific geometric and electronic information [1]. However, identifying viable atomic configurations to simulate XANES spectra with density functional theory (DFT) is challenging due to computational time limitations. In my previous work [2,3], no more than 40 atomic arrangements were explored due to computational time limitations.

A statistical screening method for empirical fitting of experimental XANES spectra with simulated spectra is performed by a regression on critical geometric descriptors (e.g. space groups, unit cell parameters, and fractional coordinates). This process narrows down the range of atomic arrangements that produce simulated XANES spectra that resemble the experimental spectra. To determine the fit quality, the coefficient of determination (R2) is calculated between normalized experimental and simulated spectra over a defined X-ray energy range. The atomic arrangements yielding the best-matched XANES spectra are ran in DFT packages in order to determine their relative energetic stability and likelihood of representing the actual surface or interfacial structure.

Billinge, S. J. L. & Levin, I. The Problem with Determining Atomic Structure at the Nanoscale. *Science* 316,

561–565 (2007).

Trejo, O. *et al.* Quantifying geometric strain at the PbS QD-TiO2 anode interface and its effect on electronic

structures. *Nano Lett.* 15, 7829–7836 (2015).

Dadlani, A. L., Acharya, S., Trejo, O., Prinz, F. B. & Torgersen, J. ALD Zn(O,S) Thin Films' Interfacial

Chemical and Structural Configuration Probed by XAS. *ACS Appl. Mater. Interfaces* 8, 14323–14327

(2016).

Tuesday Afternoon, July 31, 2018

2:30pm **AF1-TuA-5 Application of Low Energy Ion Scattering for Characterization of Modern ALD Films of Industrial Relevance***, Philipp Brüner, T Grehl,* ION-TOF GmbH, Germany*; G Saheli, Y Uritsky, Y Xu, Y Lei, Y Yang, W Tang,* Applied Materials

ALD has become an essential part of the semiconductor manufacturing process. More and more materials are deposited using this technique, and its application will become even more relevant in the future. It is therefore of high importance to also expand the means of characterization of the films during and after growth, supporting both process development and quality control.

One technique that is well suited for this purpose is Low Energy Ion Scattering (LEIS). Noble gas ions of a few keV are scattered back from the surface; by measuring the energy spectrum of these ions, the composition of the outer atomic layer is determined in a quantitative way. Even more, LEIS determines information about the depth distribution of the elements over the first few nm of the film. In this way, the film can be monitored from nucleation to film closure and beyond. While the surface coverage is measured directly, information of the thickness distribution can be deducted from the tails in the spectrum. The combination of surface coverage and thickness distribution allows determining the growth mode. The minimal continuous thickness can be identified either by looking for the film reaching a coverage of 100%, or by the substrate signal disappearing. Depending on the masses of the elements involved, one of the two approaches is more sensitive. Also diffusion and surface segregation can be studied, and contaminations monitoring is possible.

Due to the ultimate surface sensitivity, the focus of LEIS studies is usually the nucleation phase, from the first cycle to formation of a closed film. In this presentation, a range of samples systems are studied to demonstrate the application of LEIS in the industrial R&D context. These examples include W on SiO_2 substrate for contact application with a thickness range of 0 – 1.5 nm. These films were grown under two different conditions and the effect of these conditions is shown. Another set of samples – again under two different growth conditions – includes 0.2 – 1.7 nm TaN on 1.5 nm TiN for barrier and work function applications. Time permitting, one or two other examples will be shown to illustrate the range of information that can be deducted from the LEIS results.

2:45pm **AF1-TuA-6 Characteristic Evaluation of ZrO_2 Thin Films by PEALD to Semiconductor and Display using Cp-Zr Precursor***, Sang-Yong Jeon, G Park, S Lee, W Chae, S Yim, J Park, S Lee, M Kim,* DNF Co. Ltd, Republic of Korea

ZrO_2 has been widely used for high-k material and studied in various fields such as hardmask, thin film transistor (TFT), and encapsulation layer of Organic light-emitting diodes (OLEDs) due to its low dry etch characteristics and low moisture permeability.

In this study, we used $CpZr(DMA)_3$ as a precursor to evaluate characteristics of ZrO_2 by PEALD method and confirmed high applicability to high-k, hardmask, encapsulation, and TFT due to its electrical characteristics, dry etch rate, and WVTR characteristics.

ZrO_2 grown on Si substrate showed ALD window up to 280℃, which is relatively high temperature as shown in Fig. 1, and self-limited reaction was observed in linearity evaluation as shown in Fig. 2. The deposition rate was 29Å/min, which is relatively fast. The XPS results showed that the films were free of N and, C, and pure films with an O/Zr ratio of about 1.9. The dielectric constant and leakage current density of the ZrO_2 thin films were about 23 and 5E-8A/cm^2, respectively. In addition, it was confirmed to be HT-ACL of less than 40% of that of HT-ACL in a dry etch atmosphere based on C4F8 gas.

The WVTR of ZrO_2 deposited on PEN film at low temperature (<100℃) for OLED application was 10 times better than SiO_2 of the same thickness as shown in Fig. 3.

As can be seen from the above results, it was confirmed that the ZrO_2 thin film deposited with PEALD can be applied to various areas such as high-k, hardmask, TFT and encapsulation.

3:00pm **AF1-TuA-7 Hybrid Electronically Tailorable Dielectric Thin Films and Substrate Effects on Electrical and Chemical Properties of ALD Al_2O_3***, Jessica Kopatz,* Pennsylvania State University*; J Daubert, W Xie,* North Carolina State University*; A Meddeb, Z Ounaies, M Lanagan,* Pennsylvania State University*; G Parsons,* North Carolina State University

Our study is focused on the fundamental understanding of electronic transport and reliability of dielectric interfaces resulting from both MLD and ALD-grown thin films on two technologically important substrates: silicon and polymers. Based upon the deposition sequence and deposition time, the hybrid film possesses a range of properties incorporating both inorganic and organic natures. The organic alucone is grown via ethylene glycol and trimethylaluminum (TMA) precursors, while the use of water and TMA enables the growth of Al_2O_3. By capping 80 nm of MLD alucone with 20 nm ALD Al_2O_3, the permittivity was found to exceed the permittivity of Al_2O_3 itself, while the low loss remained in the same order of magnitude. This was unexpected because organic materials generally have a lower polarizability compared to inorganic metal oxides, thus causing lower permittivity values. The focus was then directed towards investigating the capacitive behavior and the nature of charge transport at the substrate-ALD interface by depositing Al_2O_3 onto different types of substrates. Herein, we examine the effect of substrate interface on the electrical and chemical properties of atomic layer deposited 100 nm Al_2O_3 thin films at deposition temperatures ranging from 100-300°C. Our substrates included platinized silicon (1500 Å) and low-resistivity (0.001-0.005 Ω*cm) p-type and n-type silicon. Electrical measurements consisted of utilizing current-voltage sweeps, dielectric spectroscopy, and capacitance-voltage sweeps. The use of platinized silicon was found to have a significant improvement on the dielectric permittivity of the deposited Al_2O_3 compared to the highly doped silicon substrates with values of 9 as opposed to 7.5, respectively. Capacitance-voltage measurements will help determine trapped states present within the highly doped silicon substrates. Chemical measurements regarding the refractive index of the deposited films were obtained using a Woollam Ellipsometer and Cauchy model. According to Ellipsometry, the refractive index of all Al_2O_3 films deposited at 300 °C was 1.66. This similarity demonstrates the difference in permittivity values must result from the interfacial reactions and not from film quality. At 300°C, the growth rate of 0.80 Å/cycle was calculated. Atomic force microscopy images of the Al_2O_3 films will offer insight on the relationship between surface roughness, deposited thickness, and deposition temperature.

3:15pm **AF1-TuA-8 Atomic Layer Deposition of Pyrite FeS_2, CoS_2, and NiS_2***, Xinwei Wang,* Peking University, China

The pyrite-type transition-metal disulfides (MS_2, M = Fe, Co, Ni) form a series of compounds that are highly interesting in many aspects. These compounds share the same cubic pyrite crystal structure but differ in the progressive increase of an anti-bonding *d* electron in the conduction band, and as a result, the metal pyrites exhibit very diverse and intriguing electrical magnetic properties from diamagnetic semiconductive to itinerant-electron ferromagnetic and to antiferromagnetic semiconductive. This diversity of the material properties has not only offered a model system platform for fundamental science studies but also enabled tremendous engineering possibilities for practical applications, such as solar cells, lithium/sodium-ion batteries, and electrocatalytic hydrogen evolution, oxygen evolution, and oxygen reduction.

In this presentation, we will show our latest progress on the development of atomic layer deposition processes for the metal pyrites of FeS_2, CoS_2, and NiS_2 (*Angew. Chem.Int. Ed.* 2018, doi:10.1002/anie.201803092). We use the metal amidinate compounds as the precursors for the metals and H_2S plasma as the sulfur source, and we will show that the deposition processes for FeS_2, CoS_2, and NiS_2 all follow ideal layer-by-layer ALD growth behavior over a wide temperature range to produce fairly pure, smooth, pyrite-structure metal disulfide films. We will further show that the ALD FeS_2, CoS_2, and NiS_2 films can be conformally deposited into deep narrow trenches with aspect ratios as high as 10:1, which thereby highlights the broad and promising applicability of these ALD processes for conformal film coatings on complex high-aspect-ratio 3D architectures in general.

Author Index

Bold page numbers indicate presenter