ALD Fundamentals
Room Evergreen Ballroom & Foyer - Session AF5-MoP
Characterization of ALD Films Poster Session

AF5-MoP-1 Film Thickness and Trace Metal Analysis of Compound Semiconductor Stacks through Direct Film Stripping (DFS) followed by ICP-MS/OES, ***Vijay (Jaya) Chowdhury****, J Huang,* ChemTrace*; P Sun,* UCT - ChemTrace*; E Appiah,* ChemTrace

Advances in the deposition of thin film and heterojunctions have revolutionized the photonics and LED markets. Promising gate dielectric deposition techniques such as atomic layer deposition (ALD) on compound semiconductors such as Sapphire and Gallium Nitride (GaN) have accelerated the scalability and high yield manufacturability. Deposition of high quality and scalable thin films through ALD involve some sequential use of gaseous precursors introduced to the substrate surface within a reaction chamber. In order to achieve ultra-high purity products, essentially free from trace metals and organic impurities, the film precursors need to be fully qualified and the deposited films require full characterization for process optimization to eliminate device critical contaminants in the mature process. Several techniques are available for the analysis of film thicknesses and impurity levels on the surface and bulk of the stacks keeping in view the precision and accuracy requirements. One of the technical challenges for in-film trace metal contamination analysis is the lack of selective film stripping sample preparation methods.

In this paper, we will discuss the direct film stripping (DFS) technique developed for top metal oxide film analysis on Sapphire/GaN substrates with minimal etching of the substrate. Using the optimized direct film stripping sample preparation method followed by ICP-MS/OES, trace metals in a single film layer can be analyzed with minimum etching of the substrate below. Efficient film removal selectivity and satisfactory method detection limits are achieved. We will also share a film depth study done on HfO_2/Al_2O_3 stack on silicon wafers using ICP-OES. The study results provided an excellent stoichiometric quantification of the Al and Hf elements and good correlation with a beam based technique, Rutherford Backscattering (RBS). A combination of the two techniques can be useful for the study of thin film analysis. The direct film stripping technique developed in this study can be expanded for trace metal analyses of other films stacks.

Keywords: *Direct film stripping (DFS), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), trace metals, Gallium Nitride (GaN)*

AF5-MoP-2 Overview of Doctoral Theses on Atomic Layer Deposition Worldwide - Outcome of the Virtual Project on the History of ALD, *J Aarik,* University of Tartu, Estonia*; J Aav, E Ahvenniemi,* Aalto University, Finland*; A Akbashev,* Stanford University*; S Ali,* Aalto University, Finland*; M Bechelany,* Institut Européen des Membranes, France*; M Berdova,* Aalto University, Finland*; I Bodalyov,* St. Petersburg State Institute of Technology, Russian Federation*; S Boyadjiev,* Bulgarian Academy of Sciences, Bulgaria*; D Cameron,* Masaryk University, Czech Republic*; N Chekurov,* Oxford Instruments Analytical Oy, Finland*; R Cheng,* Huazhong University of Science and Technology, China*; M Chubarov,* The Pennsylvania State University*; V Cremers,* Ghent University, Belgium*; A Devi,* Ruhr University Bochum, Germany*; V Drozd,* St. Petersburg State Institute of Technology, Russian Federation*; L Elnikova,* Institute for Theoretical and Experimental Physics, Russian Federation*; G Gottardi,* Fondazione Bruno Kessler, Center for Materials and Microsystems, Italy*;* ***J. Ruud van Ommen****,* Delft University of Technology, Netherlands*; R Puurunen,* Aalto University, Finland

Atomic Layer Deposition (ALD) is a materials growth technique that has become globally important during the past decades. In 2018 the Finnish inventor of ALD, Tuomo Suntola, received the Millennium Technology Prize.

ALD has been discovered independently twice, under the names Molecular Layering (ML) in the 1960s in the USSR and Atomic Layer Epitaxy (ALE) in 1974 in Finland. The Virtual Project on the History of ALD (VPHA) is a volunteer-based Open Science effort set up in 2013 [2] to clarify the early days of ALD. Especially the ML path has remained poorly known and acknowledged until recently. The core activity of VPHA is to overview early ALD publications up to 1986. VPHA has already resulted in four scientific journal articles [2-5] and several presentations at international conferences.

This poster will overview doctoral theses worldwide related to ALD up to year 2018. The doctoral thesis list has been built by combining the lists of Ref. 4 and the exhibition material 40 Years of ALD in Finland - Photos, Stories (FinALD40) [6], and allowing volunteers to enter missing information (open list in http://vph-ald.com/VPHAopenfiles.html). At the time of writing the abstract, the doctoral thesis collection contains close to 500 entries. The list is likely not yet complete and more entries are welcome. More volunteers are also still welcome to join and contribute in the VPHA.

Acknowledgements: R.L.P. thanks Tuomo Suntola for his support during the VPHA. Aziz Abdulagatov and Annina Titoff are acknowledged for significant help during the initiation of VPHA. The authors are grateful for all volunteers, who in addition to the current authors have shared at least one comment in the ALD-history-evolving-file during VPHA (as of Feb. 11, 2019): S.D. Elliott, D.C. Smith. The author list is intentionally in alphabetical order.

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AF5-MoP-3 Nanoscale Chemical Characterization of Ultrathin Films via PiFM, ***Sung Park****, D Nowak, W Morrison,* Molecular Vista

Chemical analysis of ultrathin films with nanometer scale lateral spatial resolution remains a challenge for the nanotechnology community. In this poster, we introduce a new nanoscale and non-destructive chemical imaging technique called photo-induced force microscopy (PiFM) where the dipole-dipole force due to optical response of the sample is measured by an atomic force microscope (AFM) along with the standard AFM topography [1]. This dipole-dipole optical force interaction between the AFM tip and the sample is strongly enhanced at the apex of the metal-coated tip due to the antenna effect and leads to a routine spatial resolution that is better than 10 nm. Since both the optical excitation and detection are accomplished in near-field, the optical information can be acquired without the far-field background interference, making the technique easy-to-use compared to other near-field techniques. PiFM can be coupled with a tunable infrared (IR) light sources to probe the IR absorption of various organic and inorganic materials for identification of molecular materials and their relationship to local topography. PiFM is surface sensitive due to the short interaction range of the measured dipole-dipole force and can detect monolayer of materials with good sensitivity, making it an ideal tool for characterizing ultrathin films.

PiFM works equally well with both organic and inorganic materials and lends itself as an excellent analytical to characterize ALD, molecular layer deposition, and organic-inorganic hybrid materials.

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AF5-MoP-4 The Effect of Impurities on Film Properties in the $Y(MeCp)_3/O_3$ Process, *J Kalliomäki, T Lehto, M Kääriä, T Sarnet,* ***Jani Kivioja****,* Picosun Oy, Finland

Y_2O_3 thin films are utilized as insulating materials in electronic devices, hydrophobic layers and corrosion inhibiting coatings. Several different yttrium ALD precursors have been demonstrated in the literature, from β-diketonates to heteroleptic cyclopentadienyls. When the deposition temperature is below 300 °C, authors usually report deterioration of film properties, such as crystallinity and density, with increasing impurity levels. [1,2] Nevertheless, further studies on the impurities are often outside the scope of the research found in literature.

The cyclopentadienyl-based ligands are commonly used in rare earth metal precursors, and the reaction mechanisms for them are proposed in literature. [3] However, the effect of deposition temperature over the full available range is not as widely researched.

This work focuses on the effects the reaction mechanism of the $Y(MeCp)_3/O_3$ process has on the type of carbon-based impurity species that result in the deposition temperature range 150-425 °C. The change in coordination/bonding of the impurities, and associated effect on film properties, is considered.

The experiments were made with a PICOSUN™ R-200 Advanced hot-wall ALD system. Si wafers with native oxide layers were used as substrates.

According to the results, the deposition temperature range can be divided into three regions that produce films with notably different materials properties (Figures 1-2). Each region is categorized by its distinct type of carbon-based impurity content, and the effect on optical, structural and electrical film properties will be discussed.

Understanding the underlying mechanism of growth, and how it can change and shape the process and the properties of the resulting films, is one key factor to widen the effective deposition temperature range of known oxide processes. Knowing the impact of the reaction mechanisms on the film properties allows more accurate process controls for specific applications and ultimately will help to create more high-quality end products.

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AF5-MoP-6 Internal Photoemission Spectroscopy Measurement of Barrier Heights between ALD Ru and Al_2O_3*, Melanie Jenkins**, M Hayes, K Holden, J Conley, Jr.,* Oregon State University

ALD metals are of growing interest for applications that require conformal, pinhole free conductive films, particularly for high aspect-ratio structures. Ru, due to relatively low bulk resistivity, high work-function, a conductive oxide (RuO_2), and ease of etching, is of interest as a gate electrode for MOS transistors, metal-insulator-metal (MIM) capacitors, RRAM, and tunnel diodes, and well as a conductive Cu diffusion barrier/liner for Cu interconnects. A recent ALD process for Ru using $Ru(DMBD)(CO)_3$ and O_2 shows near zero nucleation, low roughness, and low resistivity.[1] The electrode performance depends strongly on the effective work function ($\Phi_{M,eff}$) or barrier height (ϕ_{Bn}) of the metal in direct contact with an insulator. Although capacitance-voltage (C-V) measurements may be used to estimate $\Phi_{Ru,eff}$ using MOS devices with a series of insulator thicknesses, this procedure is not possible in MIM devices. Internal photoemission (IPE) spectroscopy is the only analytical technique capable of directly determining metal-insulator ϕ_{Bn} in device structures.[2-5] To date, little IPE work has been reported on ALD metals. In this work, we use IPE to directly measure the ϕ_{Bn} between ALD dielectrics and ALD Ru.

10 nm ALD Al_2O_3 was deposited at 300 °C using TMA and H_2O in a Picosun Sunale R-200, immediately followed by 12 nm of ALD Ru at 260 °C using $Ru(DMBD)(CO)_3$ and O_2.[1,2] TaN and TiN were used for bottom metal electrodes in MIM devices. For direct comparison to C-V extracted Φ_{Ru-eff}, MOS devices were also measured. Some devices were annealed at 500 °C for 60 min in H_2/N_2.

Representative (IPE yield)$^{1/2}$ vs. photon energy (2-5 eV) plots (Fig. 1) under negative and positive polarity allow extraction of voltage dependent spectral thresholds for the (a) Ru/Al_2O_3 interface and (b) TaN/Al_2O_3 interface, respectively. Schottky plots of spectral thresholds vs. field$^{1/2}$ reveal ϕ_{Bn} of 3.7 eV and 2.9 eV for as-deposited Ru and TaN, respectively (Fig. 2). Using an electron affinity of 1.4 eV for Al_2O_3, we estimate $\Phi_{M,eff}$ at 5.1 eV and 4.3 eV for Ru and TaN, respectively, both consistent with reports for sputtered films.[5]

ALD Ru and RuO_2 ϕ_{Bn} with Al_2O_3 and HfO_2 in MIM and MOS devices before and after annealing in H_2/N_2 will be reported and compared to Φ_{Ru-eff} extracted using C-V techniques as well as IPE results on amorphous metals[3,4] and reported values for sputtered Ru.

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AF5-MoP-7 Growth and Characterization: Low Temperature ALD*, **Birol Kuyel**, A Alphonse, K Hong, J Marshall,* Nano-Master, Inc.

Growth and film deposition characteristic in a downstream ICP PEALD reactor are studied using a unique new process called Continuous Flow Process* that cuts the cycle time in half. This process is implemented in a PEALD reactor where uniform variable density O_2 and N_2 or H_2 plasmas are produced but any contact of the plasma with the substrate is prevented. Precursors are not allowed to enter the plasma production region making it possible to obtain repeatable operation free of deposits or plasma instabilities. This Continuous Flow Process is used for depositing PEALD GaN, Al_2O_3, and AlN films on Si substrates. It is shown that with this process ultra-smooth and uniform films with thickness linearly proportional to the number of cycles are deposited. Then it is applied to low temperature deposition of Si_3N_4 and SiO_2 films on Si wafers. The film surface roughness, thickness, uniformity, index of refraction, composition, and stress are studied down to room temperature depositions. Results are compared to thermal deposition in the same reactor and others' reported findings.

*US Patent # 9,972,501 B1 May 15, 2018

AF5-MoP-8 Etch Rate Characterization of Oxide ALD Films*, **Martin M. Winterkorn**, H Kim, J Provine, F Prinz, T Kenny,* Stanford University

For designing any kind of nanofabrication process, knowing the etch rates of available thin films, as well as their compatibility with commonly used processing chemicals is crucially important. Previous work by Williams et al. [1][2] tabulating rates for large numbers of film-etchant combinations has gained great popularity in the nanofabrication community, but does not include any ALD films. While there have been examinations [3] for select ALD processes and etchants since, the etch rates of ALD films have not yet been studied in comprehensive fashion.

We report on the characterization of the etch rates of 9 oxide ALD films in 20 different wet and vapor etchants, which include many commonly used silicon etchants, oxide etchants and metal etchants, as well as solvents, cleaning solutions and photoresist strippers. Each of the 180 etch rates is based on data from a minimum of 4 separate etches, with a total of over 1500 thickness measurements performed by ellipsometry. To allow efficient coverage of such a large scope, a high-throughput sample fabrication and measurement workflow was developed and successfully employed. Extension of the work to nitride ALD films is currently underway.

All oxide films were deposited at 200°C in Veeco / Cambridge Nanotech Fiji F202 ALD reactors, employing both thermal and plasma-enhanced ALD (PEALD), when available. To achieve representative results, standard deposition recipes were used, which are not optimized for low etch rates or any other specific metric, but have been developed for general purpose use. Chemicals were freshly poured for all wet etching. Film compositions as deposited were characterized using X-ray photoelectron spectroscopy (XPS).

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AF5-MoP-9 Structure and Properties of Amorphous Thin Films Vary with Nanometric Thickness*, **Yael Etinger-Geller**,* Technion-Israel Institute of Technology, Israel

Amorphous materials, in contrast to crystalline ones, lack long-range order. Its order decays rapidly with the distance and while the local environment for a particular type of atom is quite similar, it is not identical; these fine changes in the atomistic structure of the materials lead to new and very interesting phenomena which are unique for amorphous materials. Although many aspects of science and technology rely on amorphous materials, much less research is conducted about their structure than on their crystalline counterparts.

In nature there are many organisms that use crystallization via an amorphous phase in order to achieve controlled mineralization. One of the main advantages of this method is that it enables the organism to exert control over the resulting polymorph, which is not necessarily the thermodynamically-stable one, by first controlling the short-range order in the amorphous phase.

In this research we draw inspiration from nature and study the ability to control various structural aspects of amorphous materials via nanometer size effects. We chose atomic layer deposition (ALD) as our material deposition method, since it is a technique that can provide extremely precise, sub-nanometric, thickness control and can deposit conformal and pinhole-free amorphous films of various materials.

Amorphous thin films of aluminum oxide deposited by atomic layer deposition method were found to vary structurally as a function of size; thinner films, as predicted previously, exhibited more 4-coordinated Al sites. These atomistic alterations were expected to change the amorphous thin film's average density, and indeed it was found to vary with the alumina layer thickness. This effect is explained in terms of the deposition process, where each newly deposited layer is a new surface layer that 'remembers' its structure, resulting in thin films of substantially lower density. This further encouraged us to study the effect of size on different density-dependent properties and it was indeed found that the refractive index and dielectric constant of these layers also change with the thin films' thickness. We believe that the ability to tune one property or another solely by size, according to a specific requirement, can open new possibilities for materials selections and applications, in science and technology.

AF5-MoP-10 Structural Aspects of Nanometer Size Amorphous Materials*,*
Yael Etinger-Geller*, A Katsman, B Pokroy,* Technion - Israel Institute of Technology, Israel

Crystallization in the course of biomineralization, often occurs via an amorphous precursor phase, allowing additional control over the mineralization process. One of the main advantages of this method is that it enables organisms to exert control over the resulting polymorph, which is not necessarily the thermodynamically-stable one, by manipulating the short-range order of the amorphous phase.

Although many aspects of science and technology rely on amorphous materials, considerably less research focuses on the structure of amorphous materials as compared to their crystalline counterparts. In this research, we draw inspiration from nature and study the ability to control the short-range ordering in amorphous materials via nanometer size effects. We chose atomic layer deposition (ALD) to deposit thin amorphous oxides since this a technique that can provide extremely precise, sub-nanometric, thickness control and can deposit conformal and pinhole-free amorphous films of various materials.

Amorphous thin films of Al_2O_3, deposited by ALD, were characterized by EELS, AR-XPS, SS-NMR and GI-XANES at SOLEIL synchrotron and found to vary structurally as a function of size. Moreover, it was shown that these films exhibit surface layer of a different short-range ordering, in comparison to its "bulk". We explain this effect from a thermodynamic point-of-view and relate it to surface reconstruction that occurs, in order to reduce the energy of the system. The structural variations were expected to cause a change within the density of the thin film and indeed, it was experimentally found the amorphous thin film's average density changes with size, as well as other density-related properties. Similar finding were obtained for other systems as well, meaning that this effect is not restricted to the Al_2O_3 case but may exist in different amorphous materials. We believe that the ability to tune one property or another solely by size, can open new possibilities for materials selections and applications, in science and technology.

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2. Y. Etinger-Geller et al., *J Appl Phys*, 2019, 125

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