ALD Fundamentals
Room Halla Hall - Session AF1-TuA
Analysis

Moderators: Christophe Detavernier, Ghent University, Belgium, **Adrie Mackus**, Eindhoven University, Netherlands

1:45pm AF1-TuA-2 Interface Evolution in ALD of HfO₂ on TiN: LEIS and XPS in Vacuo Studies, *Mykhailo Chundak, Heta-Elisa Nieminen, Marko Vehkamäki, Laura Keränen, Matti Putkonen, Mikko Ritala,* University of Helsinki, Finland

Hafnium dioxide (HfO₂) is a high-k dielectric material that was initially introduced as a replacement for SiO₂ to overcome the scaling limitations of silicon-based field-effect transistors. HfO₂ has therefore been qualified as a material compatible with complementary metal oxide semiconductor (CMOS) technology. It has recently regained attention following the discovery of ferroelectricity in doped hafnium oxide fluorite-structure oxides. This discovery has enabled the development of ferroelectric field-effect transistors (FEFETs) and ferroelectric memories, which offer the potential for further downscaling of CMOS-compatible ferroelectric based devices. However, as the thickness of ferroelectric layers is decreased from the current 5–10 nm to approximately 3 nm or even less, their properties become increasingly influenced by the surrounding environment, making precise interface engineering crucial for device reliability. The choice of the capacitor electrode plays a key role in stabilizing the ferroelectric phase, mitigating interfacial effects, and ensuring long-term performance. Titanium nitride (TiN) is widely employed due to its moderate work function, chemical stability, and compatibility with CMOS technology, yet its interaction with ultrathin HfO₂ films, along with potential contamination and deposition conditions, can significantly impact device behavior. A detailed understanding of these effects is therefore essential to optimize material integration and enhance the performance of next-generation semiconductor devices.

To investigate the growth of these films using surface science techniques, we utilized the cluster tool setup in the HelsinkiALD laboratory[1] (Fig. 1a)). This system enables *in vacuo* growth studies, providing direct insights into surface reactions during deposition. We employed a commercial flow-type ALD reactor combined with low-energy ion scattering (LEIS) (Fig. 1b)) and X-ray photoelectron spectroscopy (XPS) (Fig. 1c)) to observe the cycle-by-cycle growth of HfO₂ thin films. The films were deposited with CpHf(NMe₂)₄ (HyALD™) precursor in combination with ozone (O₃) on TiN substrate. This approach provided critical information of the interface formation and film growth mechanisms. We determined that ~30 ALD cycles are required to achieve full coverage of HfO₂ on TiN without pinhole defects. This research is offering a valuable information for optimizing thin-film deposition for next-generation semiconductor technologies.

1. Nieminen, H.-E., et al., *In vacuo cluster tool for studying reaction mechanisms in atomic layer deposition and atomic layer etching processes.* Journal of Vacuum Science & Technology A, 2023. **41**(2).

2:00pm AF1-TuA-3 Development of a Home-Built Atomic Layer Deposition Reactor for *in-Situ* Synchrotron GISAXS and XAS Characterization, *Marina Armengol-Profitós, Jordi Prat, Montserrat Prieto, Zbigniew Reszela, Cristián Huck-Iriart, Massimo Tallarida, Eduardo Solano, Carlos Escudero,* ALBA synchrotron light source, Spain

The high photon flux and energy tunability of synchrotron facilities provide a clear advantage for the characterization of Atomic Layer Deposition (ALD) processes. At the ALBA synchrotron, a mobile custom-built reactor has been developed to enable in-situ monitoring of film growth and characterization using up to now two X-ray-based techniques: Grazing-Incidence Small-Angle X-ray Scattering (GISAXS) and X-ray Absorption Spectroscopy (XAS). The ALD reactor has been designed to be compatible with both techniques, and it can currently operate at two different ALBA beamlines (NCD-SWEET for GISAXS measurements and NOTOS for XAS) to provide complementary insights into film morphology and chemical composition.

The setup consists of a high-vacuum, pump-type reactor compatible with multiple deposition processes. It achieves a base pressure of at least 10^{-6} mbar and is equipped with a sample heater capable of reaching 1000°C, allowing in-situ annealing under different atmospheres without exposing the sample. To accommodate the specific geometries required for each X-ray technique, the mobile reactor features two different configurations: for GISAXS, two CF40 flanges with mica windows allow the passage of incident and reflected X-rays, while for XAS, two perpendicularly oriented flanges with 50 µm-thick Kapton windows enable measurements covering all the beamline energy range (4.7 - 30 keV), with the fluorescence detector used (SDD with 13 channels) at 90° relative to the X-ray beam and the sample at around 30° with respect to the incident beam. Fig. 1 A shows the reactor in the GISAXS configuration at the NCD-SWEET beamline.

To validate the reactor's performance, TiO₂ thin films were deposited using titanium isopropoxide (TTIP) as a precursor in combination with water on SiO₂/Si substrates. The process exhibited a growth rate of 0.15 Å/cycle, allowing the study by GISAXS and XAS in the sub-nanometer range during the initial growth cycles. Fig. 1 B presents XANES measurements at the Ti K-edge over 1000 ALD cycles at 200°C, revealing an increase in the XANES-edge jump intensity within the first five cycles. Since the edge jump magnitude is proportional to the TiO₂ thickness, these results indicate different growth regimes: a first stage significantly slower for 325 cycles, followed by a stage where the growth rate becomes linear. After 325 cycles, XAS measurements confirmed the formation of TiO₂ with features consistent with anatase-like coordination. The XANES features during the first 325 cycles are consistent with previously studied electronic effects in ultra-thin TiO₂ films[1]. Additionally, XAS mapping over a 20 mm x 20 mm area validated the film's uniformity.

2:15pm AF1-TuA-4 Evaluation of Initial Nucleation of Co-ALD by CCTBA Using in-Situ Reflectance Monitoring and Atomistic Simulator Based on Neural Network Potential, *Naoki Tamaoki,* The University of Tokyo, Japan*; Yubin Deng,* The University of Tokyo, China*; Jun Yamaguchi, Noboru Sato, Atsuhiro Tsukune, Yukihiro Shimogaki,* The University of Tokyo, Japan

Area-selective atomic layer deposition (AS-ALD) technology, which enables atomic-level control of the film thickness and inherently prevents misalignment in self-aligned patterning, is gaining attention in ULSI device manufacturing. AS-ALD utilizes the difference in the adsorption energies of the precursor molecules to deposit a film only on the growth surface. It is crucial to explore the surface pretreatment and process conditions that maximize the incubation time to improve selectivity. In-situ differential reflectance spectroscopy (DRS) is a simple and effective method that assists in this exploration by monitoring the nucleation density and film growth evolution during the initial deposition stages. To better understand the mechanism of AS-ALD, in-situ DRS and an atomistic-level simulator (Matlantis™) based on neural network potentials were used to study Cobalt ALD.

In this study, the initial growth process of Co thin films on SiO₂ insulating films using CCTBA (Cobalt Carbonyl Tertiary-Butyl Acetylene) precursors via ALD was evaluated. Co AS-ALD is expected to be a promising method for forming cap layers that suppress Cu diffusion and electromigration (EM) in ULSI-Cu interconnects. After APM cleaning, Co-ALD was performed for 500 cycles at different substrate temperatures (140, 150, and 160°C), and the reflectance changes at a wavelength of 740 nm were measured (Figure 1). The reflectivity gradually decreased as the island-like growth of Co began, reaching a minimum value before increasing again. By analyzing the timing of the minimum reflectivity, it is possible to determine when the initial nuclei form and evolve into a continuous film [1]. Figure 2 shows the growth per cycle (GPC) measured after film formation as an Arrhenius plot. Figure 3 shows the Arrhenius plot of the initial nucleation density calculated from the minimum reflectance point and GPC data. While GPC exhibited a mild temperature dependence with an activation energy of 14.6 kJ/mol, the initial nucleation density showed a relatively high activation energy of 100.5 kJ/mol. Although lowering the film-formation temperature may increase the concentration of carbon impurities in the film, it is expected to suppress the initial nucleation density and improve the selectivity. We will also report the results of the reaction analysis using an atomistic-level simulator (Matlantis™).

[1] N. Tamaoki et al., DPS 2024

2:30pm AF1-TuA-5 Low Energy Ion Scattering Analysis of GC/IrOX /SiO₂ Layer Structure, *Philipp Brüner, Thomas Grehl,* IONTOF GmbH, Germany*; Rens Kamphorst, Katherine S. Encalada Flores, Ruud Kortlever, Ruud van Ommen,* TU Delft, Netherlands

While ALD with its self-limiting properties and sub-nm precision provides an ideal method for growing ultra-thin coatings, the physical and chemical characterization of the obtained films is challenging for surface analytical methods. Especially for ultra-thin films consisting of only few atomic layers or even a sub-monolayer only, most analytical techniques suffer from their limited surface sensitivity, often including, and thus averaging over, both the deposited film and the growth substrate.

In this study, we present analytical results of low energy ion scattering (LEIS) applied to SiO_2 films grown by ALD on an electrodeposited IrO_x catalyst layer on glassy carbon (GC). In LEIS, the energy spectrum of noble gas ions (He, Ne, Ar) scattered from the sample surface is recorded. The elemental peaks in the resulting spectra represent the elemental composition of the first atomic layer, which can be analyzed quantitatively [1]. This extreme surface sensitivity of just a single atomic layer, combined with composition analysis, is unique to LEIS and makes it especially useful in the study of ultra-thin films. In addition, sub-surface scattering signal from deeper layers gives information about sample composition and layer thickness up to depths of 10 nm, depending on the sample composition.

We show how combining the top atomic layer sensitivity with layer thickness information allows us to quantify the surface coverage of the deposited SiO_2 films, identify surface impurities with high sensitivity, and make a statement about the growth mode of the films. While ALD should in theory grow films in a perfectly controlled layer-by-layer manner [2], the deposited films often show various degrees of island growth, where parts of the substrate are quickly covered by a multilayer film, while other parts of the substrate have not yet begun to initiate film growth.

[1] "Low-Energy Ion Scattering" in Characterization of Materials - Second Edition ISBN 978-1-118-11074-4 - John Wiley & Sons.

[2] J. R. Van Ommen, A. Goulas, and R. L. Puurunen, "Atomic Layer Deposition," in Kirk-Othmer Encyclopedia of Chemical Technology, 1st ed., Kirk-Othmer, Ed., Wiley, 2021, pp. 1–42. https://doi.org/10.1002/0471238961.koe00059

2:45pm AF1-TuA-6 Tailoring Interface and Bulk Properties: An Oxidant Co-Dosing Approach to ALD Growth of Hafnia Thin Films, *Dushyant Narayan, Dan Le, Soham Shirodkar, Soubhik De, Geon Park, Minjong Lee, Thi Thu Huong Chu, Jin-Hyun Kim,* The University of Texas at Dallas*; Walter Hernandez, Adrian Alvarez, Josh Garretson, Jeffrey Spiegelman,* RASIRC*; Jiyoung Kim,* The University of Texas at Dallas

As semiconductor devices continue to scale down and integrate into complex 3D architectures, precise control over interfacial properties becomes increasingly critical to device performance and reliability. Hafnia-based thin films have been widely adopted in industry, as they exhibit superior equivalent oxide thickness (EOT), high dielectric constant and superior leakage current properties as compared to traditional dielectrics like SiO_2. These attributes make HfO_2-based materials essential for applications such as high-k gate dielectrics, DRAM capacitors, and ferroelectric memory devices.

In our prior studies investigating the impacts of various oxidant sources on HfO_2-based films, we found that the conventional ozone (O_3)-based ALD process led to extensive oxidation of the titanium nitride (TiN) bottom electrode (BE) during metal-insulator-metal (MIM) capacitor fabrication. In contrast, the use of hydrogen peroxide (H_2O_2) in HfO_2-based ALD was not only shown to produce films with superior growth characteristics and material properties, but also effectively suppressed unwanted interface formation.[1] Building upon these findings, we have developed a unique ALD approach, where oxidants (H_2O_2, O_3, and H_2O) are strategically co-dosed/sequentially-dosed to achieve a greater control of film properties.Through this process, customizable ALD growth conditions can provide tailored properties at the interface and in the bulk. Furthermore, results of an *in-situ* Reflection Absorption Infra-Red Spectroscopy (RAIRS) experiment will be presented, investigating the underlying mechanisms at the surface and in the bulk when mixing oxidants during the deposition of hafnia. For instance, While H_2O_2 on its own produces film with superior properties, it is not known if mixing O_3 and H_2O_2 would further enhance material properties. Additional combinations including H_2O, O_3 and H_2O_2 will also be shown. Beyond IR analysis, we will also present the effect of this approach on electrical properties of hafnia thin films, with particular attention paid to dielectric constant, leakage current, and time dependent dielectric breakdown (TDDB). This study thus represents an additional process variable that can be utilized to further optimize the use of HfO_2-based materials in next-generation device applications. Detailed experimental procedure and results will be discussed.

This work is supported by RASIRC. The BRUTE® Peroxide and RASIRC Peroxidizer® are provided by RASIRC Inc. The O_3 used in this work was provided by a TMEIC Ozone Generator (OP-250H).

[1] J. Kim et. al., Applied Surface Science, **686**, 162197 (2025)

3:00pm AF1-TuA-7 Mechanical Properties and Wear Resistance of Atomic Layer Deposited Ternary Cr-Hf-O Films: A Comparative Study with Binary Chromium Oxide and Hafnium Oxide Films, *Mahtab Salari Mehr, Lauri Aarik, Taivo Jõgiaas, Hugo Mändar,* University of Tartu, Estonia

The complex materials including doped and ternary compounds have received considerable attention in the last decades due to the exhibition of superior mechanical, optical, and electrical properties compared to their binary counterparts. [1,2]. Chromium oxide is technologically an important engineering material due to its corrosion, wear resistance, and high mechanical hardness [3,4].This study presents the characterization results of ternary chromium-hafnium oxide films (($Cr_{1-x}Hf_x)_2O_3$) in thickness range from 40 to 80 nm that were deposited at 275 °C on Si substrate by atomic layer deposition (ALD) using the cycle formula of [m ($Cr(thd)_3$-O_3) + ($HfCl_4$-O_3), m=0 to 500]. The X-ray fluorescence showed the change in atomic ratio of Hf/(Hf+Cr) (x) in the films from 0.05 to 1 by changing m in the ALD cycle. Grazing incidence X-ray diffraction analysis of pure hafnium oxide film showed reflections of the monoclinic phase, whereas for pure chromium oxide film the observed reflections confirmed the presence of the eskolaite phase. For the $(Cr_{1-x}Hf_x)_2O_3$ films when $0.05{\leq}x{\leq}0.40$, the eskolaite phase was present, however, the films containing $x{\geq}0.68$ showed semi-amorphous structure. The density of the films (from X-ray reflectivity analysis) showed a linear increase from 5.57 g/cm^3 to 10 g/cm^3 when the amount of x changed from 0.05 to 1. The hardness, elastic modulus, and wear resistance of the films were measured using nanoindentation on Hysitron Triboindenter by Berkovich-type diamond tip. The results at indent displacement of 8 nm showed an increase in hardness mean values of ternary films compared with binary chromium oxide (14±1.5 GPa) and hafnium oxide (12±1.2 GPa). The highest hardness of 19±0.9 GPa was achieved when x=0.40. The study of wear resistance of the films under different loads in the range of 90 to 180 µN, using different wear cycles of 2 to 10 cycles showed an improvement of about ~70% of wear resistance of the ternary compound films compared to binary oxides (Fig. 2). Our findings showed that the deposition of multicomponent films paves the way for tailored thin film materials with enhanced mechanical properties and wear durability for various industrial applications.

References

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[3] T. Jõgiaas, A. Tarre, H. Mändar, J. Kozlova, A. Tamm, *Nanomaterials,* 2022, 12, 82.

[4] A. Michau, F. Maury, F. Schuster, F. Lomello, J-C. Brachet, E. Rouesne, M. Le Saux, R. Boichot, M. Pons, *Surf. Coat. Tech.*, 2018, 349, 1048-1057.

3:15pm AF1-TuA-8 In-situ X-ray photoelectron spectroscopy for determining oxidation state, composition, and morphology of ALD-based CeO_x, SnO_x, and $Ce_xSn_{1-x}O_y$ deposits, *Rudi Tschammer, Dominic Guttmann,* BTU Cottbus, Germany*; Marcel Schmickler, Anjana Devi,* Leibniz Institute for Solid State and Materials Research, Germany*; Karsten Henkel, Carlos Morales, Jan Ingo Flege,* BTU Cottbus, Germany

The controllability of the physical and chemical properties of ultrathin (< 20 nm) films grown by atomic layer deposition (ALD) requires a thorough understanding of the surface cross-interactions established between substrates, grown thin films of variable thickness, and the exposed reactants. In most ALD works focused on applications, samples are grown in dedicated ALD reactors on wafer-scale substrates and characterized through various *ex-situ* techniques to obtain information on film thickness, sample composition, and cation valency. However, *ex-situ* characterization bears the risk of unintentional changes due to layer contact with the atmosphere, ranging from surface contamination to changes in the surface cation oxidation state. The latter issue is especially pronounced for reducible oxides intended to switch between different oxidation states depending on factors such as gas environment or film-substrate interaction (e.g., CeO_x, widely used in catalysis and sensing). Thus, a surface science methodology supported by *in-situ* characterization becomes highly desirable to minimize changes imparted during sample transfer in the atmosphere and unravel the true structure and chemical state of the pristine active layer.

In this contribution, we examine the material composition, cation valency, and film morphology through *in-situ* X-ray photoelectron spectroscopy (XPS) and inelastic peak shape analysis (IPSA) combined with operando spectroscopic ellipsometry. By investigating the ALD deposition of CeO_x

using Ce(dpdmg)$_3$ and different oxidants (H$_2$O, O$_2$, O$_3$), we observe a distinct dependence of the cerium valency on the film thickness and the used oxidant, in all cases accompanied by changes in film morphologies and precursor residues. Similarly, a detailed XPS analysis of the early stages of SnO$_2$ deposition via TDMASn/O$_3$ reveals hitherto unreported changes that could be correlated with residual nitrogen impurities, significantly influencing the electrical resistivity of these films. Following a bottom-up approach, the results from both investigations are combined to tailor the growth of ultrathin SnO$_x$/CeO$_x$ heterostructures and mixed Ce$_x$Sn$_{1-x}$O$_2$ oxides for gas sensing applications.

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