ALD Fundamentals: Growth and Characterization
Room HB Plant Ballroom - Session AF2-TuA

ALD Metrology/Characterization II

Moderators: Henrik Pedersen, Linköping University, Sweden, **Angel Yanguas-Gil**, Argonne National Lab

4:00pm **AF2-TuA-11 ALD Outstanding Presentation Award Finalist: Where Does the Reaction Happen? Concurrently Monitoring Ultrafast Surface and Gas-Phase Dynamics in Solid–Gas Interfacial Reactions***, Keith Blackman, Eric Segrest, Aakash Gupta, S. Novia Berriel, Parag Banerjee,* ***Mihai E. Vaida,*** University of Central Florida

Understanding and controlling surface-limited reactions while minimizing parasitic gas-phase chemistry remains a central challenge in atomic layer deposition (ALD). Conventional in situ ALD diagnostics typically infer surface and gas-phase processes indirectly, making it difficult to disentangle their contributions. To address this, we present an experimental technique that directly distinguishes reaction products originating from the surface and the near-surface gas phase while simultaneously resolving their ultrafast dynamics, enabling detailed mechanistic insight into the underlying chemical processes. This method allows simultaneous, real-time monitoring of ultrafast reaction dynamics at the surface and above the surface during photoinduced heterogeneous reactions.

The technique combines femtosecond pump-probe spectroscopy with mass spectrometric detection, allowing concurrent observation of reaction intermediates and products formed at the solid-gas interface and within the adjacent gas phase. As a model system, we investigate the photoinduced reaction of methyl iodide on a cerium oxide surface. Species detected simultaneously from the surface and gas phase exhibit distinct signatures in the mass spectra, characterized by a sharp peak followed by a broader shoulder. Time-resolved analysis assigns the sharp peak to species emitted directly from the surface, while the broader shoulder originates from species formed in the gas phase above the surface.

By tracking the evolution of these spectral features as a function of pump-probe delay, we resolve the ultrafast dynamics governing surface-confined reactions and gas-phase processes on femtosecond to picosecond timescales. SimION simulations further corroborate the spatial origins of the detected ions. This approach enables real-time differentiation of surface and gas-phase reaction pathways, opening new possibilities for investigating precursor activation, reaction selectivity, and parasitic chemistry relevant to ALD and related thin-film deposition processes.

4:30pm **AF2-TuA-13 Dual-Box Model for In-Situ Spectroscopic Ellipsometry Data Analysis in Plasma Enhanced ALD Growth Processes***, Ufuk Kilic, Yousra Traouli, Mathias Schubert,* ***Eva Schubert,*** University of Nebraska - Lincoln

We employ in-situ spectroscopic ellipsometry (SE) to investigate the growth dynamics of ultrathin transition metal oxide films (ZnO, WO_3, TiO_2, Ga_2O_3) during plasma-enhanced atomic layer deposition (PE-ALD). To analyze the dynamic optical response, we introduce a dual-box regression model: the first box represents surface roughness using an effective medium approximation (EMA), while the second box captures cyclic variations in the subsurface layer thickness arising from molecular rearrangements during each ALD cycle. This approach provides a time-resolved, quantitative view of both surface roughness and subsurface film growth dynamics, enabling accurate characterization of layer-by-layer deposition.

The accurate extraction of film thickness, density, and roughness at elevated substrate temperatures requires knowledge of the temperature-dependent dielectric function (TDF) of the transition metal oxides, which can significantly vary from room-temperature values. In this work, the TDF was determined via a multi-sample analysis, using optical data from films of varying thickness measured at different stages during the growth process. The incorporation of experimentally verified dielectric functions ensures that the dual-box model reliably describes the evolving optical response during high-temperature deposition, enabling detailed monitoring of sub-monolayer coverage, interface formation, and roughness evolution throughout the ALD process.

The ALD processes employ organometallic precursors with remote oxygen plasma and water co-reactants, providing controlled stoichiometry, high uniformity, and optimized interface quality. Temperature-dependent studies further elucidate the influence of surface kinetics on nucleation, growth rate, and steady-state dynamics, linking chemical reactions and surface rearrangements.

Post-deposition structural and chemical characterization, including scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS), corroborates the in-situ optical measurements and provides complementary insight into film crystallinity, morphology, and composition.

[1] U. Kilic, A. Mock, D. Sekora, S. Gilbert, S. Valloppilly, G. Melendez, N. Ianno, M. Langell, E. Schubert, M. Schubert, Precursor-surface interactions revealed during plasma-enhanced atomic layer deposition of metal oxide thin films by in-situ spectroscopic ellipsometry [https://scholar.google.com/citations?view_op=view_citation&hl=en&user=pAVudUUAAAAJ&cstart=20&pagesize=80&citation_for_view=pAVudUUAAAAJ:vV6vV6tmYwMC], Scientific reports 10 (1) 10392 (2020).

[2] Y. Traouli, U. Kilic, S. G Kilic, M. Hilfiker, D. Schmidt, S. Schoeche, E. Schubert, M. Schubert, In-cycle evolution of thickness and roughness parameters during oxygen plasma enhanced ZnO atomic layer deposition using in situ spectroscopic ellipsometry [https://pubs.aip.org/avs/jva/article/42/5/052403/3311662], J. Vac. Sci & Technol. A 42 (5) (2024).

4:45pm **AF2-TuA-14 Imaging Ellipsometry with LHAR Test Structure for Characterizing ALD Conformality***,* ***Hiroshi Nishizato,*** Kumamoto University, Japan*; Yugo Nakaya,* HORIBA STEC, Co., Ltd., Japan*; Lianhua Jin,* University of Yamanashi, Japan*; Takeshi Momose,* Kumamoto University, Japan

We developed a novel methodology to quantitatively evaluate the penetration depth (PD) of films in three-dimensional (3D) features deposited by atomic layer deposition (ALD), combining our developed imaging ellipsometry with an in-house lateral high-aspect-ratio (LHAR) test structure. The effectiveness of this methodology was confirmed using ALD Al_2O_3 from trimethylaluminum (TMA) and H_2O.

ALD is widely used in the fabrication of 3D semiconductor devices that require high conformality. The PD is a consequence of ALD kinetics, including adsorption, desorption, and surface reactions; therefore, it is a critical parameter for assessing conformality in such complex 3D architecture. PD was thus evaluated using the LHAR structure comprising a Si substrate with a shallow, wide groove at the edge, capped with a quartz plate. The LHAR structure has an aperture of 20 µm × 4 mm and a depth of 6 mm. Sample imaging was enabled by installing an Offner optical system on our custom-built ellipsometer, allowing the PD formed in a groove on the Si substrate to be determined. To enhance imaging contrast, the retarders were set to 150° on the light-source side and 30° on the camera side, while both polarizers were set to 0°. The ALD Al_2O_3 film, with a thickness of 6-60 nm, was captured under these settings. Experimental results showed that the growth per cycle (GPC) measured on planar Si substrates with a 3 nm thermal SiO_2 underlayer was independent of the TMA dosing, while the PD in the LHAR structure increased with increasing TMA dosing. In this manner, we established a methodology to evaluate PD using imaging ellipsometry with the LHAR test structures. As it is in an offline setting, we plan to install them in an ALD chamber for real-time PD monitoring. On such occasions, precise control of the concentration and supply duration of both the precursor and the reactant is essential for accurately determining time-dependent PD evolution. Therefore, a piezoelectrically controlled vapor delivery system has already been installed on our ALD equipment for both TMA and H_2O, enabling precise, rapid dose control by adjusting the valve opening ratio and duration.

References

[1] L. Jin, T. Tanaka, E. Kondoh, B. Gelloz, K. Sano, I. Fujio, Y. Kajiyama, and M. Uehara, "Rotatable Offner imaging system for ellipsometric measurement," Rev. Sci. Instrum. 88, 013704 (2017).

[2] L. Jin, E. Kondoh, Y. Iizuka, M. Otake, and B. Gelloz, "Lateral ellipsometry resolution for imaging ellipsometry measurement," Jpn. J. Appl. Phys. 60, 058003 (2021).

5:00pm **AF2-TuA-15 Surface Chemistry Investigation for ALD of SiOCH Using in-Situ Reflection Absorption Infrared Spectroscopy (RAIRS)***,* ***Sjoerd van der Werf,*** Eindhoven University of Technology, Netherlands

There is a need to replace silicon nitride inner spacers in gate-all-around field-effect transistors by low-k materials to reduce parasitic capacitance in these 3D architectures. Atomic layer deposition (ALD) is the method of choice for the fabrication of this material, due to the need for good conformality for this application. For this work the specific interest is in the surface chemistry that occurs throughout potential half-cycles to establish successful ALD cycles for carbon-containing SiO2.

The study focused on the adsorption of the silicon-carbon precursor BTDMASM (composed of two silicon atoms bridged by a CH2 group and six ligands), by identifying relevant surface groups and looking into the reaction of the surface groups with different reactants. These reactants include water, ethylene glycol, and an organic acid. In addition, more complex chemistries were considered, including ABC-type approaches, for example to activate surface groups or more efficient ligand removal.

The surface reactions were studied using in-situ RAIRS measurements, which resulted in a clear understanding of the surface reactions during an ALD cycle. For example, the organic acid was shown to react with the ligands of BTDMASM very efficiently, where all ligands are removed upon exposure to the acid. The adsorption of the organic acid on the surface leads to the removal of surface attached ligands from the precursor, which is observed in the CH stretch region as well as based on C=O and C-O bonds.

The data on the adsorption of BTDMASM on SiO2 suggests that the precursor is susceptible for adsorbing on hydroxyl groups. The organic acid does not result in the replenishment of reactive adsorption sites. Therefore, water was introduced as a second co-reactant to remove the acid and replenish hydroxyl groups, which is observed by the removal of groups related to the adsorbed acid. The removal of the organic acid is temperature dependent where for a temperature of 350 C degrees the C=O and C-O bonds are no longer present at the surface. The surface chemistry of water and the acid in combination with BTDMASM was investigated for different conditions, where temperature series have shown that the surface groups are temperature dependent, as is subsequent precursor adsorption. Overall, a better understanding is achieved regarding the surface chemistry for the thermal ALD of SiOCH with the use of RAIRS.

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