ALD Fundamentals
Room On Demand - Session AF8

Growth and Characterization: *In-situ* Monitoring and Analysis

AF8-1 Optimization of Quadrupole Mass Spectrometers for In-situ Monitoring of Atomic Layer Deposition Processing, ***Chenglong Yang***, *J. Blessing,* MKS Instruments, Inc.*; U. Meissner,* MKS Instruments, Inc., Germany*; A. Wallace ,* MKS Instruments, Inc., UK

Quadrupole Mass Spectrometers (QMS) have been used widely in atomic layer deposition (ALD) for process optimization and troubleshooting. Unfortunately, QMS has had little application for in-situ process monitoring owing to its short lifetime and less persuasive value of process monitoring. This study is to improve the QMS sampling system design for ALD processes, which includes the ALD gas sampling and delivery, inlet valve design, and the range and control of the sampling system temperature. In addition, the QMS hardware and operating methods are also upgraded to improve the sensitivity and its lifetime for ALD processes. This QMS system has been applied to ALD processes for in-situ monitoring of chamber base vacuum, ALD precursors, process reaction by-products, and chamber contamination.

AF8-2 Quantitative Calorimetry of ALD: Design, Model, and Calibrate, ***Ashley Bielinski***, *A. Martinson,* Argonne National Laboratory

Pyroelectric calorimetry presents a new approach for the *in situ* study of the thermodynamics and kinetics of ALD reactions with unmatched thermal sensitivity and temporal resolution. Complementary techniques such as quartz crystal microgravimetry, spectroscopic ellipsometry, and mass spectrometry are limited by sampling times that are typically on the order of 50ms – 1s. We demonstrate response times down to 50ns and sensitivities of < 1µJ/cm^2, which corresponds to less than 1% of the heat generated by some ALD half reactions.

Large temperature changes, >10°C, as a result of ALD surface reactions have been observed on high surface area substrates. However, attempts to quantitatively measure reaction heats on planar substrates, ≪1°C, using thermocouples or pyroelectric detectors have previously been limited by hardware with insufficient thermal and temporal resolution, difficulties accounting for heat lost to cooling, and challenges with external calibration. To overcome these issues we designed and built pyroelectric calorimeters compatible with ALD systems, modeled the transient thermal and electric response, and quantitatively calibrated the system using a laser to provide precise heat generation.

This work was inspired by the techniques used in pyroelectric adsorption calorimetry, but the approaches used in this field resulted in unacceptable tradeoffs in responsivity in order to achieve the temporal resolution needed for ALD. A new calorimeter design was implemented to suspend the pyroelectric crystal with minimal physical contact. This reduced conductive cooling, enabling improved temperature sensitivity and faster responsivity.

Previously, ALD reaction energies have been computationally predicted, but not experimentally measured. ALD calorimetry contributes a new experimental technique with a wide range of applications including the study of fundamental reaction thermodynamics, the impact of non-ideal surfaces on nucleation, selective defect passivation, and growth inhibition.

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AF8-3 Atomic Layer Deposition of Hafnium Oxide on InAs: Insight from Time-Resolved *in Situ* Studies, ***Giulio D'Acunto,*** Lund University, Synchrotron Radiation Research, Department of Physics, and NanoLund, Sweden*; A. Troian,* Lund University, Dept. of Electrical and Information Technology, and MAX IV laboratory, Sweden*; E. Kokkonen,* MAX IV Laboratory, Lund University, Sweden*; F. Rehman,* Lund University, Synchrotron Radiation Research, Department of Physics, and NanoLund, Sweden*; J. Schnadt,* Lund University, Synchrotron Radiation Research, Department of Physics, and NanoLund and MAX IV laboratory, Sweden*; R. Timm,* Lund University, Synchrotron Radiation Research, Department of Physics, and NanoLund, Sweden

Despite the numerous applications of atomic layer deposition (ALD), used e.g. in the semiconductors industry to produce thin films with thickness control at the Ångström level and tunable composition, only limited knowledge exists about the kinetics of the surface chemical reaction, the reaction mechanism, and the role of the substrate. ALD-grown thin high-k oxide films, such as HfO_2 or Al_2O_3, help to significantly improve device performance of III-V semiconductor-based MOSFETs. Those materials, such as InAs, come along with an electron mobility 20 times larger than that of silicon, but unfortunately with a high defect density at the interface with its oxide. It has been demonstrated that so-called "self-cleaning" occurs during the early stage of the high-k ALD, in which the growing high-κ oxide substitutes the unwanted native oxide. However, in spite of all progress, the III-V/oxide interface still suffers from incomplete self-cleaning and too high defect levels.

In this work, we present a time-resolved study of the self-cleaning effect during the first ALD half cycle. We performed ALD of HfO_2 on InAs in the reaction cell of a synchrotron-based ambient pressure X-ray photoemission spectroscopy (APXPS) setup. Tetrakis(dimethylamido)-hafnium (TDMA-Hf) is used as the metallorganic precursor, and we followed in real time all relevant core levels to monitor the surface species during the deposition. Our findings challenge the established view of the ALD process based on the ligand exchange model and the surface's passive role. In fact, we establish a two-step reaction based on molecular adsorption followed by ligand exchange and the immediate formation of HfO_x, in which the native oxide acts as the oxygen source. In more detail, we find evidence for an As-In-O-Hf bonding configuration at the semiconductor/high-k interface.

Hence, time-resolved APXPS enables us to further understand the surface chemical process in ALD and how the III-V semiconductor/high-k interface can further be improved by optimizing ALD, promising superior device performance.

Author Index

Bold page numbers indicate presenter

— B —
Bielinski, A.: AF8-2, **1**
Blessing, J.: AF8-1, 1
— D —
D'Acunto, G.: AF8-3, **1**
— K —
Kokkonen, E.: AF8-3, 1
— M —
Martinson, A.: AF8-2, 1
Meissner, U.: AF8-1, 1
— R —
Rehman, F.: AF8-3, 1
— S —
Schnadt, J.: AF8-3, 1
— T —
Timm, R.: AF8-3, 1
Troian, A.: AF8-3, 1
— W —
Wallace , A.: AF8-1, 1
— Y —
Yang, C.: AF8-1, **1**