In vacuo LEIS and XPS studies on reaction mechanisms in ALD and ALE processes

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Atomic layer deposition (ALD) and atomic layer etching (ALE) are becoming increasingly important methods in advanced semiconductor manufacturing. With their rising utilization, there is a growing need for better understanding of chemical reactions and film growth mechanisms in these processes.

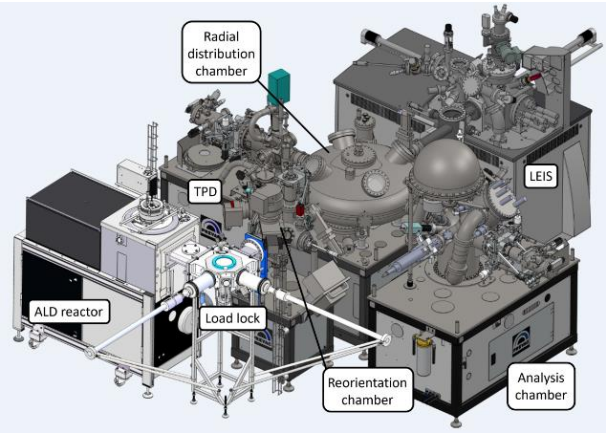

Figure 1 HelsinkiALD cluster tool.

To study the films growth in detail under *in vacuo* conditions we utilize the cluster tool setup at the HelsinkiALD laboratory (Fig. 1). The system integrates a flow-type ALD reactor with low-energy ion scattering (LEIS), X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD) spectroscopy [1]. This unique configuration allows us to analyze surface reaction intermediates formed during the cycle-by-cycle growth/etching of the films, without exposing the samples to the air. In addition, the ALD reactor is equipped with a quartz crystal microbalance (QCM) providing in situ monitoring mass changes and the film growth rates. LEIS and XPS allow us to also examine film closure, substrate-film interactions and area-selective growth.

Here we present the results focused on the growth of high-K oxides. The main emphasis will be on ALD of HfO_2 and ZrO_2 thin films (HZO) using $CpHf(NMe_2)_3$ and $CpZr(NMe_2)_3$ in combination with ozone on TiN substrates. The results of HZO growth, as measured by LEIS after varying number of ALD cycles (Fig. 2) will be demonstrated.

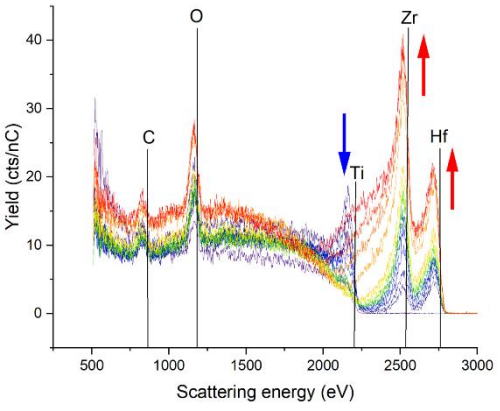

Figure 2 LEIS spectra of HZO films on TiN substrate.

We also study the ALD processes of platinum and ruthenium thin films using trimethyl(methylcyclopentadienyl) platinum(IV) ($MeCpPtMe_3$) and bis(cyclopentadienyl) ruthenium(II) ($RuCp_2$) as precursors together with O_2 as the co-reactant. We explore the underlying mechanisms of noble metal ALD processes, revealing the role of adventitious airborne hydrocarbons in directing the selectivity of these processes.

[1] H. E. Nieminen, M, Chundak, JVST A. Rev. **41**, 022401 (2023).

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