

Detailed insight into HfO₂ ALD from *in situ* studies

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Atomic layer deposition (ALD) is a powerful technique for the deposition of thin film materials with atomic scale precision. Ideal ALD schemes, which always rely on the assumption of a self-limiting nature of the growth, provide guidelines to understand how the ALD growth proceeds and which structures are produced. However, in most cases the detailed surface chemistry of the ALD process is not fully understood, as a result of side reactions, possible non-self-limiting nature of the growth, influence of surface defects and gas phase reactions [1]. In our work we explore possibilities to gain exact knowledge of the surface chemistry of the ALD process from the application of *in situ* and *operando* methods, which allow the investigation of surfaces *during* reaction.

Here we report on the use of *operando* ambient pressure x-ray photoelectron spectroscopy (APXPS) and *in situ* infrared spectroscopy (IR) to monitor the evolution of the chemical composition of surfaces during ALD growth and to study the validity of the assumptions made in the ideal ALD scheme. The two techniques have been applied to the investigation of the ALD of HfO₂ on the clean and oxidised Si(111) surfaces from tetrakis(dimethylamido)hafnium (TDMAHf) and H₂O as precursors.

The ALD was carried out at 280°C. The IR data show that the adsorption of TDMAHf on the native oxide-covered Si(111) surface indeed is self-limiting at this temperature. At room temperature this is not the case. Moreover, the gas phase IR data (Fig. 1(a)) show that the molecule starts to dissociate at the process temperature, which can have a significant influence on the surface chemistry.

Operando APXPS at high temporal resolution allows us to further investigate the surface species that occur in the ALD half-cycles. As an example the evolution of the Hf 4f core level line during TDMAHf exposure is shown in Fig. 1(b). Also the N 1s and C 1s core level lines were recorded, and from a consideration of the binding energies of all three lines we can identify Hf-amido adsorbates as well as methyl methyleneimine surface species [2].

Our study illuminates the potential of surface sensitive *in situ* and *operando* methods to gain a detailed understanding of the ALD surface processes during growth. Such enhanced understanding is a crucial tool towards further improvement of ALD materials and processes.

References:

[1] F. Zaera, *Coord. Chem. Rev.* **257**, 3177 (2013).

[2] A. R. Head, S. Chaudhary, G. Olivieri, F. Bournel, J. N. Andersen, F. Rochet, J.-J. Gallet, J. Schnadt, J. *Phys. Chem. C* **120**, 243 (2016).

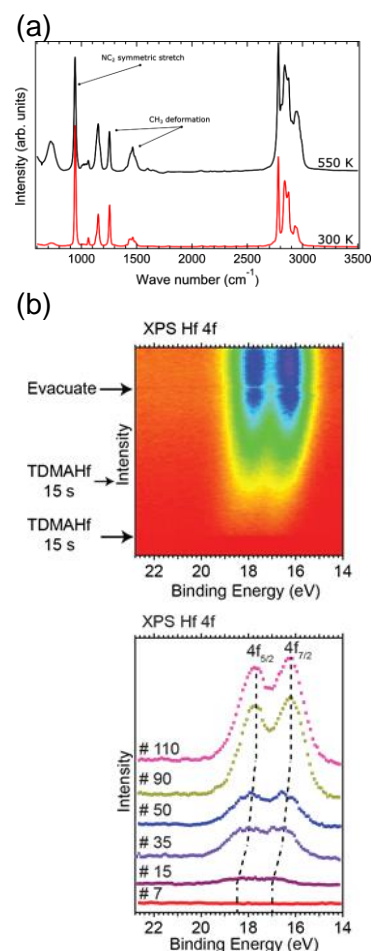


Fig. 1. (a) *In situ* IR and (b) APXPS data measured during the HfO₂ ALD from TDMAHf and water.