Time evolution of surface chemical reactions during aluminum oxide atomic layer deposition on InAs

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III-V semiconductors have highly promising properties for electronic applications. Specifically, InAs has a narrow, direct band gap and high electron mobility, making it a good candidate to outperform Si-based Metal Oxide Semiconductor Field-Effect Transistors (MOSFETs) in terms of speed and power consumption. The detrimental native oxide should thereby be replaced by a so-called high-k oxide, such as Al_2O_3, improving the gate properties. However, the performance of this system is limited by a high defect density at the InAs/Al_2O_3 interface,[1] which is attributed to the incomplete removal of the native oxide layer.

The precise deposition of Al_2O_3 on InAs is achieved via atomic layer deposition (ALD), enabling the production of thin films with atomic-scale precision. It is characterised by a layer-by-layer mechanism and the self-limiting interaction between two gaseous precursors and the substrate. In our case, two half-cycle depositions were performed using trimethylaluminum (TMA) and water as precursors. A common method for studying the chemical composition and interface quality of ALD films is to perform X-ray photoelectron spectroscopy (XPS) measurements before and after each half-cycle. Here, we instead use ambient-pressure XPS (AP-XPS) to monitor time-resolved surface chemical reactions during ALD half-cycles in the implemented ALD cell at the SPECIES synchrotron beamline of the MAX IV Laboratory.[2]

Upon ALD, the As-oxide was found to get entirely removed during the initial TMA half-cycle (TMA), as shown in **Figure 1**. This self-cleaning is far less efficient for the In-oxide, which only decreases slightly in intensity. More interestingly, the type of In-suboxide changes upon ALD, resulting in a decreased In oxidation state after TMA deposition and an increased oxidation state after water pulsing. Such a re-oxidation of the substrate material upon ALD, in parallel with the wanted formation of Al_2O_3, is unexpected, and it is in contrast with previous results from AP-XPS measurements of HfO_2 ALD on InAs.[3,4] Here, we will compare the two high-k ALD processes based on reaction dynamics observed from time-resolved In, As, Al, Hf, and C core-level spectra, including different organic ligands and reaction byproducts.

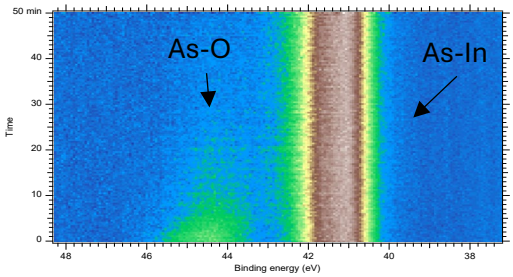

Figure 1: Time-resolved XPS data of the As3d core level at 675 eV photon energy during the 1st TMA half-cycle.

References:

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3. D'Acunto, G. *et al., ACS Applied Electronic Materials* **2**, 3915–3922 (2020).
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Supplementary Page

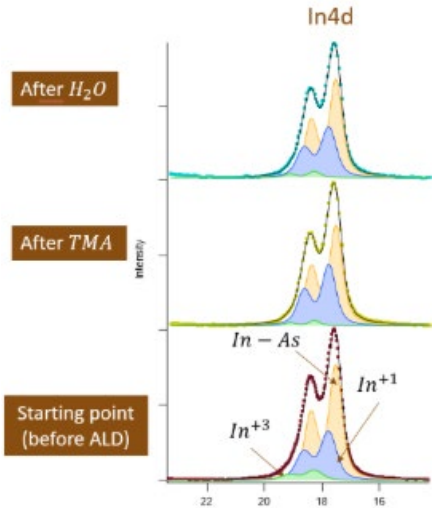
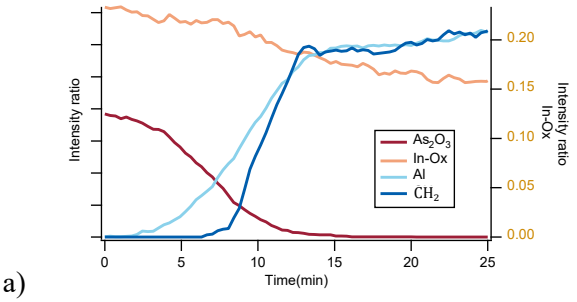


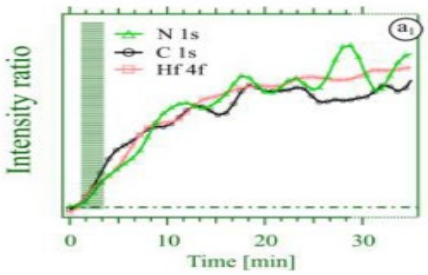
Figure 1: In4d core level spectra at 350 eV photon energy, before and after initial ALD half-cycles.

Figure 1 shows three different In components, corresponding to bulk InAs and two suboxides with In in a +1 and +3 oxidation state, respectively, before and after subsequent ALD steps.

In **Figure 2**, we plot reaction dynamics from time-resolved XPS measurements. **Figure 2a** presents the intensity of As-O, In-O, and Al as a function of time during the first TMA half-cycle of Al_2O_3 ALD. Here, we notice that the increase in Al intensity happens simultaneously with the decrease in As-O. Also, during this first half-cycle, we observe a CH_2 component in the C1S spectra as a reaction product of the TMA ligands, with the CH_2 arriving on the surface 5 min later than Al. Previously, we had conducted similar studies of HfO2 ALD on InAs, in which perfect self-cleaning of the As-oxide was observed.[3,4] **Figure 2b** presents results from that work, using TDMAHf as a metal precursor during the first half-cycle. Here, the metal and the organic ligand components of TDMAHf arrived simultaneously on the surface. In contrast, in Al2O3 ALD using TMA, a delay between the intensity increase of aluminum and of the CH_2 components was observed. Generally, TMA was found to react faster with the InAs surface than TDMAHf.



a)



b)

Figure 2: Plot of the intensity ratio as a function of time of different components during the first half-cycle of ALD using a) TMA and b) TDMAHf precursors.

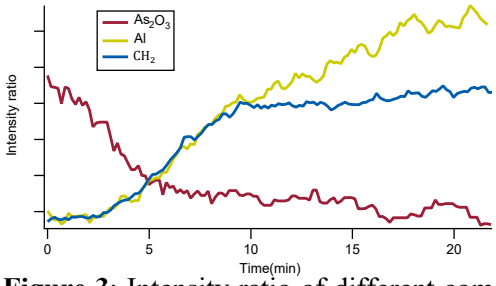


Figure 3: Intensity ratio of different components as a function of time during the first TMA ALD half-cycle for a thin oxide layer

Finally, following the above observation, we wanted to test our assumption about the different arrival times of ligands from TMA on the surface by varying the starting conditions. Previously, we used a standard oxide thickness and observed that CH_2 formed on the surface after aluminum bonding. Now, we measured a sample with a very thin oxide layer, plotted the intensity ratio of this sample as a function of time (**Fig. 3**) and observe that the organic component of TMA arrives at the same time as the aluminum component. Accordingly, this difference in reaction dynamics depends on the initial amount of oxide on the surface.