Significant reducibility of atomic layer deposited ultrathin ceria towards H_2 at room temperature

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In the last decades, atomic layer deposition (ALD) has gained prominence in the materials and surface science communities owing to its well-controlled layer-by-layer deposition and film conformity on 3D structures [1], finding multiple uses in various fields. Besides, the ALD technique is also well known to lead to amorphous and defective, non-stoichiometric thin films, resulting in modified material properties that may even be superior for certain applications. Yet, most ALD-based studies deal with relatively thick layers (>10 nm) that do not address the film/substrate interaction, which might initially modify the reaction mechanism, create complex interfaces, and change the electronic and chemical properties.

Here, we present a comprehensive overview of ceria-ALD ultrathin films (fig. 1a) grown using commercial $Ce(thd)_4$ precursor and reactive oxygen (O_3/O_2), focusing on the *in-situ* characterization [2] of its early stages of growth and the effects of substrate/film interaction as well as growth parameters on the film reducibility at slightly elevated temperatures. Interestingly, initial *in-situ* X-ray photoemission spectroscopy (XPS) measurements of ceria-ALD films on Al_2O_3/Si, sapphire, and SiO_2 substrates confirm a Ce^{3+}/Ce^{4+} mixture dependent on the substrate interaction, deposit thickness, and morphology. Using near-ambient pressure XPS, we have significantly reduced ultrathin (< 10 nm) ceria films deposited by ALD by exposing them to different H_2/O_2 partial pressures at lower temperatures (300 – 525 K) than thicker films grown by physical vapor deposition [3]. Notably, the Ce^{3+} concentration is found to be significantly higher for lower H_2 concentrations and dependent on the deposit thickness (fig. 1b) as well as the type of substrate. Intriguingly, the intrinsic defects related to the ALD method seem to play a critical role in the reversible reduction at room temperature compared to ceria deposited by other techniques.

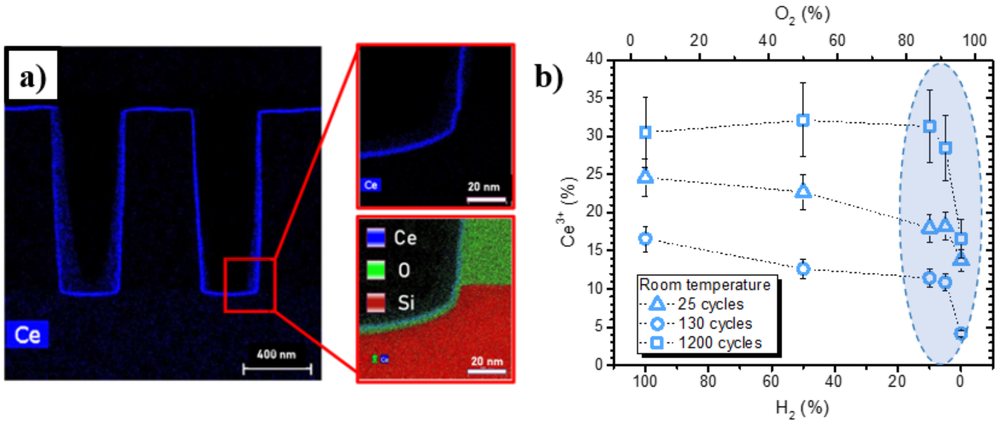

Figure 1. *a) Ce-EDX false color TEM images of CeO_x (150 cycles) deposited on nanostructured Si substrates; b) fraction of Ce^{3+} states as a function of H_2 content in the H_2/O_2 mixture at room temperature.*

References

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