Significant reducibility of ultrathin atomic layer deposited ceria towards H_2 exposure 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 high potential for integration as a scalable process in microelectronics. ALD's largest strengths are its well-controlled layer-by-layer deposition and growth conformity on 3D structures. Yet, the ALD technique is also well known to lead to amorphous and defective, non-stoichiometric thin films, resulting in modified materials properties that may even preferentially be used in certain applications. Interestingly, initial in situ X-ray photoemission spectroscopy (XPS) measurements of ceria ALD-deposits 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 grown by ALD by exposing them to different O_2/H_2 partial pressures at moderate temperatures (< 525K). Notably, the total amount of reduction to Ce^{3+} is found to depend on the deposit thickness and initial ceria/substrate interaction. Furthermore, the intrinsic defects related to the ALD method seem to play a critical role in the reversible reduction at room temperature.

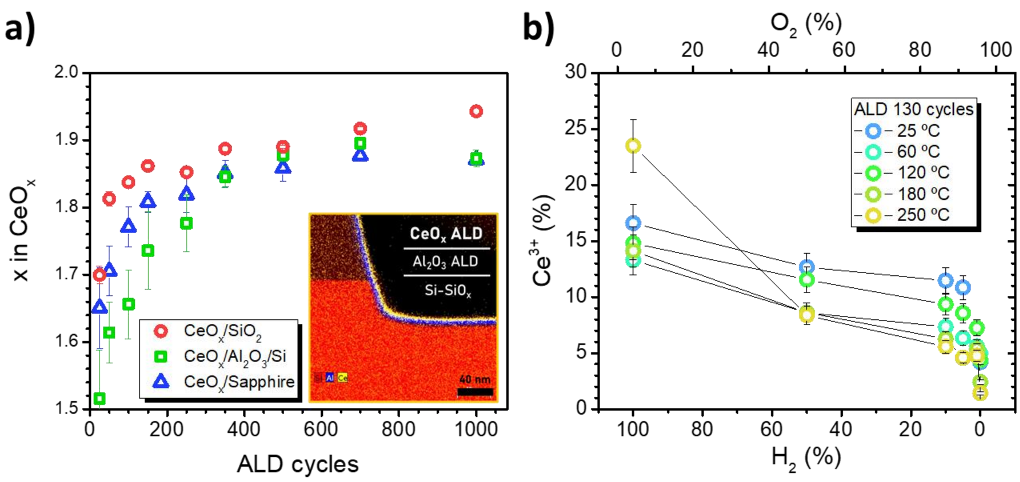

Figure a) Ce^{3+}/Ce^{4+} ratio as a function of the total number of ALD cycles and substrate; insert, transmission electron microscopy (TEM) cross-section image of the ALD-ceria ultrathin deposit. Figure b) percentage of Ce^{3+} states as a function of H_2/O_2 mixture for different sample temperatures.

Keywords: ceria, ALD, XPS, sensor, hydrogen