The effects of substrate interaction on the chemical properties of atomic layer deposited ultrathin ceria layers

7. DPR – Thin films, coatings and depth profiling

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Nowadays, atomic layer deposition (ALD) has gained prominence in the materials and surface science communities owing to its well-controlled layer-by-layer deposition and growth 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 preferentially be used in certain applications. For example, the formation, diffusion, and recovery of oxygen vacancies in reducible metal oxides can be favored in disordered films compared to more ordered deposits, whereas interdiffusion processes can critically affect the film/substrate interface region. However, most ALD-based studies deal with relatively thick layers (>10 nm) that neglect film/substrate interaction, which might initially modify the growth reaction mechanism, create complex interfaces, and change the electronic and chemical properties.

These effects have extensively been studied for thin ALD-ceria films grown using the commercial $Ce(thd)_4$ organometallic precursor and O_3/O_2 by combining in-situ and ex-situ characterization techniques in our lab [2] and at synchrotron radiation facilities, focusing on its early stages of growth, the effects of film/substrate interaction on catalytic applications, and its reducibility at low temperatures as a function of different growth parameters. 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) ALD-ceria films 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 techniques [3]. Interestingly, these experiments combined with hard-X-ray photoemission spectroscopy (HAXPES) measurements have shown that this reducibility at moderate temperatures critically depends on the film/substrate interaction, inhibited for alumina substrates due to the formation of aluminates at the interface regions, which prevent further oxidation. Furthermore, the comparison with more ordered films grown by other methods indicates a key role of the defective structure of ALD films in Ce^{3+}/Ce^{4+} conversion.

Selected references

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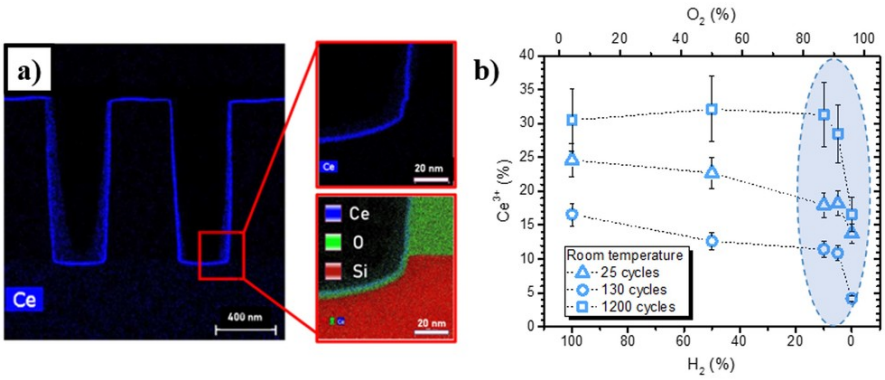

Figure 1. *a) Ce-EDX false color TEM images of CeO_x (150 cycles) deposited on Si-nanostructured substrates; b) percentage of Ce^{3+} states as a function of H_2 content in the H_2/O_2 mixture at room temperature.*