Atomic layer deposition of ceria on oxide substrates: the influence of interface on the Ce^{3+}/Ce^{4+} ratio

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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 most significant 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 be highly beneficial for certain applications. Besides, the relatively high temperatures required to activate certain precursor-oxidant reactions may lead to a strong interaction with the substrate, thus affecting the expected behavior of ultra-thin layers. For instance, at high temperatures, ceria (CeO_x) functional layers may interact with Al_2O_3 substrates, forming $CeAlO_3$ and thus fixing Ce^{+3} states that play a significant role on sensing and catalytic processes. To clarify these issues, we have developed an in-situ ALD reactor attached to an X-ray photoelectron spectroscopy (XPS) system, capable of switching between both pump and flow-type operation. We present a comparative study of the very early stages of growth of ceria on two different oxide substrates, SiO_2 and Al_2O_3, and using two different cerium precursors: commercial $Ce(thd)_4$ and novel $Ce(dpdmg)_3$ [1]. Different precursors allow shifting of the ALD temperature window and changing the oxidant species, modifying the experimental conditions of the deposit/substrate interaction. Although thick layers show mostly the Ce^{4+} oxidation state, during the first cycles important differences are reported on the growth mode and the Ce^{3+}/Ce^{4+} ratio. In general, ceria is found to be partially reduced at the interface region, establishing a correlation between the reduced Ce^{3+} species and the growth mode during the nucleation stage, similar to its behavior in our previous studies using molecular beam epitaxy [2].

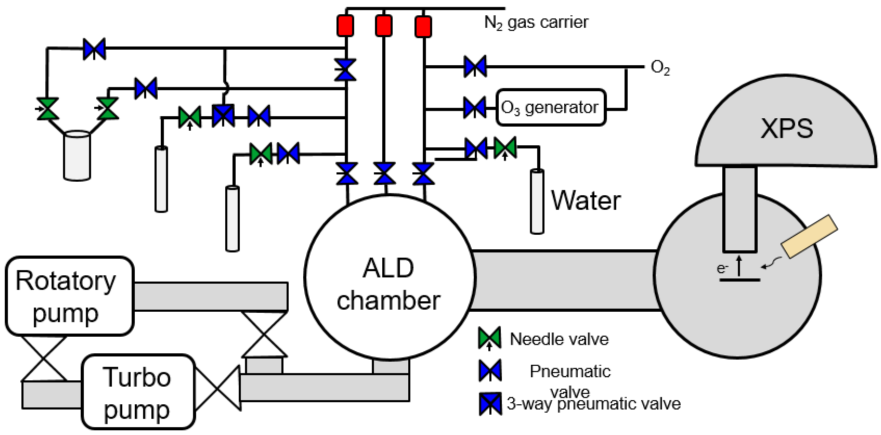

Figure 1 – ALD-XPS diagram.

References

[1] Parmish Kaur et al. Rational Development of Guanidinate and Amidinate Based Cerium and Ytterbium Complexes as Atomic Layer Deposition Precursors: Synthesis, Modeling, and Application, Chemistry A European Journal, 27, 14 (2021) 4913.

[2] J. I. Flege et al., Ultrathin, epitaxial cerium dioxide on silicon, Applied Physics Letters 104 (2014) 131604.