

# In Situ X-Ray Photoelectron Spectroscopy Study of Atomic Layer Deposited Cerium Oxide on SiO<sub>2</sub>: Substrate Influence on the Reaction Mechanism During the Early Stages of Growth

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Thermal atomic layer deposition (ALD) of cerium oxide using commercial Ce(thd)<sub>4</sub> precursor and O<sub>3</sub> on SiO<sub>2</sub> substrates is studied employing in-situ X-ray photoelectron spectroscopy (XPS). The system presents a complex growth behavior determined by the change in the reaction mechanism when the precursor interacts with the substrate or the cerium oxide surface. During the first growth stage, non-ALD side reactions promoted by the substrate affect the growth per cycle, the amount of carbon residue on the surface, and the oxidation degree of cerium oxide. On the contrary, the second growth stage is characterized by a constant growth per cycle in good agreement with the literature, low carbon residues, and almost fully oxidized cerium oxide films. This distinction between two growth regimes is not unique to the CeO<sub>v</sub>/SiO<sub>2</sub> system but can be generalized to other metal oxide substrates. Furthermore, the film growth deviates from the ideal layer-by-layer mode, forming micrometric inhomogeneous and defective flakes that eventually coalesce for deposit thicknesses above 10 nm. The ALD-cerium oxide films present less order and a higher density of defects than films grown by physical vapor deposition techniques, likely affecting their reactivity in oxidizing and reducing conditions.

## 1. Introduction

Rare-earth metal oxides have been extensively applied in many fields, including coatings,<sup>[1,2]</sup> optical applications,<sup>[3]</sup>

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microelectronic,<sup>[4]</sup> energy storage,<sup>[5]</sup> heterogeneous catalysis,<sup>[6-8]</sup> and sensing.<sup>[9]</sup> In particular, cerium oxide (CeO<sub>2</sub>) has attracted considerable attention thanks to a relatively high abundance on Earth's crust (66 parts per million for Ce, similar to that of Cu or Zn) and especially to the facile exchange between the Ce4+ and Ce3+ states under slightly reducing conditions, promoting a large number of oxygen vacancies that result in understoichiometric  $CeO_{2-x}$ , which can be fully re-oxidized in oxidizing conditions. This behavior makes cerium oxide a wellknown material in catalysis,<sup>[10–12]</sup> energy storage systems,<sup>[13]</sup> and gas sensing.<sup>[14,15]</sup>

In parallel to exploring its applicability, great efforts from the surface science community have been invested in unraveling the formation of such oxygen vacancies on the surface and their diffusion into the bulk under different conditions.<sup>[16]</sup> On the one hand, the cerium oxide surface presents a 30%

lower oxygen vacancy formation energy compared to the bulk, also depending on the crystallographic orientation of the surface as (111) < (110) < (100).<sup>[17,18]</sup> Other factors, such as differences in surface atomic termination, creation of defects, coordination environment, surface reconstruction, and compactness, can determine an increase in reactivity toward oxygen vacancy formation.<sup>[19]</sup> Furthermore, a correlation between oxygen vacancy concentration and cerium oxide crystal size has been pointed out, implying a larger reducibility of nanostructures compared to thick films.<sup>[20-23]</sup> On the other hand, the cerium oxide chemical properties can be modified via interaction with substrates, which is especially relevant for ultra-thin deposits. For example, ceria on Ni(111) can easily reduce upon annealing under vacuum conditions due to the formation of NiO at the interface,<sup>[24]</sup> while its reduction on Pt(111) has been related to the formation of Pt-Ce alloys.<sup>[25]</sup> In terms of combining structure, oxidation state, reactivity, and the synergistic role of cerium oxide/metallic substrate interaction, the in-situ, real-time studies performed with low-energy electron microscopy (LEEM) are

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especially relevant.<sup>[26]</sup> The use of specific growth parameters in terms of temperature and oxygen partial pressure allows fine control of coverage, size, crystallographic orientation, and chemical oxidation state of cerium oxide islands, which have been shown to decisively impact their reactivity toward reducing and oxidizing atmospheres.<sup>[27-29]</sup> For example, continuing with the last mentioned CeO<sub>v</sub>/Pt(111) system, the LEEM technique allowed the direct observation of dynamic changes in morphology, structure, and electronic properties of cerium oxide as a function of redox treatments, pointing out a strong dependence of its reversibility on cerium oxide initial morphology and thickness, and thus, on interaction with the substrate.<sup>[30]</sup> In the case of nonmetallic substrates, the early stages of growth are also significantly influenced by the cerium oxide/substrate interfacial interaction. For example, the oxidation state of ultra-thin (<1 nm) cerium oxide films grown on Si(111) strongly depends on the substrate preparation route, increasing the amount of Ce4+ states if the silicon surface has been previously passivated,<sup>[31,32]</sup> which prevents the formation of silicates.<sup>[33,34]</sup> The formation of Ce–O–Si states at the interface has also been reported for SiO<sub>2</sub> substrates.<sup>[35]</sup>

This brief overview of insights gained from surface science studies mainly comprises works using 1) physical vapor deposition (PVD) techniques, i.e., reactive thermal evaporation of metallic Ce under an oxygen atmosphere, pulsed laser deposition (PLD), and magnetron sputtering, 2) well-controlled conditions, i.e., ultra- and high-vacuum conditions, and 3) welldefined substrates.<sup>[16]</sup> Although this fundamental approach has proven very useful in understanding the reaction mechanisms of crystalline cerium oxide, many applications present a higher degree of complexity due to a less ordered cerium oxide structure, ranging from polycrystalline to amorphous films, and different amounts of defects that may directly impact CeO<sub>x</sub> reactivity. Furthermore, this lack of studying more complex, not-sowell-defined cerium oxide systems is particularly important for certain chemical vapor deposition (CVD) techniques usually considered dirty by the surface science community due to the use of relatively higher pressures (in the 1-10 mbar range), lower temperatures than PVD techniques, and metalorganic precursors, whose use has spread out in many industries for different applications. An example of increasing importance is atomic layer deposition (ALD), which has gained prominence in the materials community in the last decades owing to its high potential for integration as a scalable process in microelectronics.[36-38] ALD's largest strengths are its well-controlled layer-by-layer deposition and conformal growth on 3D structures thanks to a self-limiting reaction process achieved by subsequent pulsing of the reactants.<sup>[39,40]</sup> Yet, the ALD technique is also well known to lead to amorphous and defective, nonstoichiometric thin films, resulting in modified material properties that may even preferentially be used in certain applications. Therefore, fine-tuning ALD-based films requires a thorough understanding of the ALD process, comprising the interaction between surface and precursor to characterize the cerium oxide deposits and the crossinteractions with the substrate.

Despite the lower number of studies targeting ALD compared to PVD techniques, several attempts to characterize the ALD process under *operando*, i.e., directly during the film growth process, and in-situ conditions, i.e., after the film deposition preserving a well-controlled sample environment, have been reported 4DVANCED

in the last twenty years. For example, Devloo-Casier and coworkers have summarized in-situ synchrotron-based X-ray techniques used for the characterization of ultra-thin ALD deposits,<sup>[41]</sup> such as X-ray reflectivity (XRR), grazing incidence small-angle X-ray scattering (GISAXS), X-ray fluorescence (XRF), X-ray absorption (XAS), or X-ray photoelectron spectroscopy (XPS). In the case of XPS, operando studies have recently been performed using flow-type reaction cells in differentially pumped XPS setups.<sup>[42]</sup> However, these experiments require a high photon flux due to the combination of high pressure (up to 1 mbar) and a small amount of material during the first cycles and are thus restricted to synchrotron facilities. A more approachable setup includes an ALD reactor attached to the XPS ultra-high vacuum (UHV) system to perform in-situ characterization,<sup>[43,44]</sup> which can also be combined with other operando techniques, such as XRF and GISAXS,<sup>[45]</sup> ellipsometry,<sup>[46,47]</sup> or infrared and quadrupole mass spectroscopy.<sup>[48]</sup>

Coming back to CeO<sub>2</sub>, to our knowledge there are no reports regarding in-situ nor operando characterization of atomic layer deposited cerium oxide despite its use in thin films permittivity enhancement,<sup>[49]</sup> solid oxide fuel cells,<sup>[50-52]</sup> or novel catalysts.<sup>[53–55]</sup> Whereas under specific conditions epitaxial CeO<sub>2</sub> growth has been achieved,<sup>[56]</sup> the ALD technique mostly leads to amorphous and defective, nonstoichiometric thin films.<sup>[53,57]</sup> Therefore, to understand the particularities of ALD-based cerium oxide deposits and tune them for specific uses, it is necessary to focus on the early stages of growth, particularly on the previously mentioned interaction with the substrate and its intrinsic defects. This paper presents an in-situ characterization of the ALD-cerium oxide films grown using an ALD flow-type reactor attached to a UHV-XPS system, completed by a set of ex-situ characterization techniques. By iteratively combining ALD cycles with subsequent XPS measurements, we show a complex interaction of the cerium organometallic precursors and  $O_3/O_2$  coreactants with the SiO<sub>2</sub> substrate that leads to a variation in the growth per cycle (GPC) accompanied by a gradual transition from Ce<sup>3+</sup> to Ce<sup>4+</sup> states and a decrease of the carbon contamination on the surface. As such, these findings may help to understand the origin and role of catalytically active Ce<sup>3+</sup> states in ultrathin, highly defective ALD-CeO, deposits, which could have a significant impact on tailoring the catalytic performance of ALD-based, ultrathin cerium oxide active coatings. Furthermore, owing to the rather generic requirements for the occurrence of the observed phenomena, we consider these characteristics not a unique feature of the CeO<sub>v</sub>/SiO<sub>2</sub> system, but rather general effects that should similarly be expected to occur in other film substrate combinations involving metal cations with different oxidation states.

The manuscript is structured as follows. First, the quality of the optimized ALD process is confirmed by the high degree of homogeneity and conformability at the micrometric scale for ultrathin films and by comparing the chemical, structural, and morphological properties of thick films ( $\approx$ 20 nm) to those reported in the literature using the same deposition conditions. Once the quality of the ALD process is established, we present an in-situ XPS study of the early stages of growth, distinguishing between two stages, referred to as "homo-deposition" and "hetero-deposition" regimes in the following, depending on the cross-interactions established between the substrate, film, and precursor molecules. The in-situ XPS measurements are subsequently complemented

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Figure 1. a) TEM cross-section image of a lamella prepared from an ALD-cerium oxide ultrathin deposit (150 cycles) on a nanostructured silicon substrate; b) false color of the figure (a) where the conformal cerium oxide deposit is highlighted in blue (Ce-EDX signal from EDX mapping). c) and d) present a magnified view of the region delimited by the red rectangle on (b), showing the cerium oxide deposit through Ce-EDX signal (c) and the EDX mapping with the signals from Ce, O, and Si elements.

by ex-situ characterization to correlate the average chemical and morphological information extracted from XPS measurements with the local inhomogeneities identified in ALD-CeO<sub>x</sub> deposits.

## 2. Results and Discussion

The conformality of the ALD optimized process was proven by transmission electron microscopy (TEM) cross-section measurements taken on  $\approx$ 3 nm thick cerium oxide deposits (150 cycles) on Si nanostructured substrates, as shown in Figure 1. The estimated growth per cycle is  $\approx 0.2$  Å per cycle, in line with previous values ranging between 0.2 and 0.3 Å per cycle.[53,56,57] In particular, the energy-dispersive X-ray (EDX) Ce signal distribution (Figure 1b, mapped in blue) indicates a very high degree of deposit homogeneity and conformality on complex 3D structures over relatively large areas (>1 µm), without visible pinholes in the walls or bottom part of the trenches. This fact is especially remarkable on the bottom 90° edges, zoomed in Figure 1c,d, where their EDX mapping is shown for only Ce and in combination with Si and O, respectively. Furthermore, the ALD-CeO, growth does not seem to be strongly affected or even inhibited by the Si-based surface underneath, as there is no visible discontinuity between cerium oxide grown on the native SiO<sub>x</sub> of Si (bottom of the trench) and the SiO<sub>x</sub> covering the vertical walls and upper parts of the trenches.

Relatively thick samples of  $\approx 20$  nm (1000 cycles) deposited on unstructured (i.e., flat) SiO<sub>2</sub> wafers were thoroughly characterized following the same methods presented in the literature for equivalent ALD films using Ce(thd)<sub>4</sub> precursor and similar reactor conditions.<sup>[53,56,57]</sup> First, atomic force microscopy (AFM) measurements show a granulated surface, with clusters between 90 and 130 nm, similar to those reported by Ivanova et al.<sup>[53]</sup> for a substrate temperature of 250 °C (see Figure 2a). Besides, the insitu recorded XPS Ce 3d spectrum in Figure 2b shows almost completely oxidized cerium oxide, i.e., CeO<sub>1.95</sub>, resulting from the linear combination of CeO2 and Ce2O3 reference spectra. This value is slightly lower compared to ex-situ XPS measurements where fully oxidized films were reported<sup>[32]</sup>; however, we note that our estimation has been performed without exposing the film to the atmosphere at ambient conditions, thus avoiding potential post-oxidation processes. Finally, Figure 2c shows the  $2\theta$ 

XRD patterns acquired by irradiating the sample at three different positions as shown in the top right inset. In line with previous reports on multiple substrates,<sup>[51,53,57]</sup> our ALD-cerium oxide films exhibit a polycrystalline texture, with diffraction peaks at 28.5°, 32.9°, 47.6°, and 56.4° that are associated with the (111), (200), (220), and (311) crystallographic planes of the cubic fluorite structure, respectively. As the ratios between the various diffraction peak intensities are largely preserved, our XRD measurements corroborate a high homogeneity, i.e., the same overall texture across the sample. Together with the AFM measurements, these results confirm that our relatively thick ALD-cerium oxide films are homogeneous.

Up to this point, we have discussed the same kind of characterization previously reported in the literature regarding ALDbased cerium oxide, particularly for relatively thick films using ex-situ techniques. However, we consider this review exercise important in two ways: first, to confirm the self-limiting nature of our ALD process with an expected GPC value (cf. TEM crosssection, Figure 1), and second, to cross-check the reproducibility of structural and chemical properties of thicker films (AFM, XPS, and XRD, Figure 2). Together, these techniques establish a solid basis to focus on studying cerium oxide atomic layer deposition on SiO<sub>2</sub> in situ, i.e., not only after the complete ALD process but especially after successive ALD cycles.

Figure 3 shows the normalized XPS Ce 3d spectra after a series of ALD cycles performed on the same sample. The Ce 3d region is highly complex, encompassing a total of ten peaks representing intermediate  $CeO_x$  stoichiometries (1.5 < x < 2), six for CeO<sub>2</sub> and four for Ce<sub>2</sub>O<sub>3</sub>.<sup>[34,58,59]</sup> Although an XPS fitting routine is necessary to extract the  $Ce^{3+}/Ce^{4+}$  ratio precisely, we start by simply considering the qualitative changes in the region. At first glance, we observe a gradual transition as the total number of ALD cycles, i.e., film thickness, increases, with the appearance of two valleys at  $\approx$ 888 and  $\approx$ 908 eV (indicated by arrows) and a relative intensity increase of the peak at ≈918 eV. By directly comparing with the CeO<sub>2</sub> and Ce<sub>2</sub>O<sub>3</sub> reference spectra of Figure 2b, these changes indicate a transition from an initial mixture between Ce<sup>3+</sup> and Ce<sup>4+</sup> states to almost fully oxidized cerium oxide. Although similar results have previously been reported during the early stages of growth using PVD techniques<sup>[32,34,35,60]</sup> and in ALD using Ce(iPrCp)<sub>3</sub> with H<sub>2</sub>O,<sup>[61]</sup> we find it unexpected in our

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**Figure 2.** Cerium oxide deposit on flat SiO<sub>2</sub> substrate with 1000 ALD cycles: a)  $2.5 \times 2.5 \,\mu$ m<sup>2</sup> AFM image; b) Ce 3d XPS spectrum of cerium oxide films (black circles). The red line corresponds to the fit resulting from the linear combination of CeO<sub>2</sub> and Ce<sub>2</sub>O<sub>3</sub> reference spectra, shown below in blue and green, respectively. c) XRD diffractograms corresponding to three consecutive spots ( $\emptyset = 2 \, \text{mm}$ ), as indicated in the surface optical image of the top-right inset.

case due to the highly oxidizing conditions  $(O_3/O_2 2.5 \text{ s dose at 3} \text{ mbar and 250 °C})$  and the fact that the Ce cation in the Ce(thd)<sub>4</sub> molecule already represents a Ce<sup>4+</sup> oxidation state. The initial charge transfer toward the metallic cation promoting Ce<sup>3+</sup> states suggests a change in the reaction mechanism of the ALD process mediated by the interaction with the substrate compared to the growth on the cerium oxide surface.

Generally, the reaction mechanism of the Ce(thd) $_4$ /O $_3$  system is still barely investigated, just proposed a ligand exchange reaction mechanism for the yttria-stabilized ZrO<sub>2</sub> substrates.<sup>[56]</sup> As pointed out by S. Elliot,<sup>[62]</sup> the ALD reaction mechanism can present differences in two stages: (i) during an initial heterodeposition on the substrate, (ii) followed by the transition to a homodeposition or steady-state regime where the ALD reaction mechanism remains constant and unaltered. On the one hand, in the simplest model, both stages would share an equivalent reaction mechanism, and thus, the growth is only modified by the different coverage of reactive species on both surfaces, e.g., hydroxyl groups. On the other hand, the reaction mechanisms of both stages could be different, and non-ALD side reactions might occur on the substrate surface, leading to extra product or growth inhibition.<sup>[63]</sup> Moreover, substrate and product could mix when using aggressive oxidizing agents, such as in our case, thus forming an extended interlayer with particular growth chemistry. This last situation seems to happen in our ALD-CeO<sub>x</sub> on SiO<sub>2</sub> substrates. In parallel to the transition from Ce<sup>3+</sup> to Ce<sup>4+</sup> states that extends over at least five nm, the Si 2s spectra depicted in Figure 4 show the formation of silicate  $(CeSi_xO_y)$  species at the interface, clearly noticeable by the appearance of a second component shifted by 1.9 eV to lower binding energies with respect to the silicon dioxide line.<sup>[64,65]</sup> Similar CeO<sub>x</sub>/SiO<sub>x</sub>/SiO<sub>2</sub> interfaces have previously been reported for CeO<sub>x</sub> ultrathin films grown by nonreactive magnetron sputtering,<sup>[35]</sup> as well as for cerium oxide growth on Si substrates using molecular beam epitaxy.<sup>[31,32,34]</sup> Thus, as with physical vapor deposition methods, the film/substrate interaction also seems to play a fundamental role during the ALD-ceria process, at least using the experimental conditions and reactants described here.

To shed light on the changes in the ALD reaction mechanism in relation to the early stages of growth, we first performed an XPS quantitative analysis of the cerium oxide deposition in two different ways, i) using the intensities of the Ce 3d and Si 2s XPS peaks to estimate the average GPC and ii) analyzing the inelastic background to assess the GPC at each individual step. In the first approach, the applied model considers a homogeneous, continuous cerium oxide layer across the whole surface, including an ALD-residue carbon top layer with constant thickness. To account for this top-carbon layer, the maxima intensity values of Ce 3d and Si 2s peaks were taken from clean CeO<sub>2</sub> and SiO<sub>2</sub> reference samples measured in the same system (the details of this ALD carbon residue layer will be discussed in the following paragraphs). The results are depicted in Figure 5a, where the intensities of the Ce 3d and Si 2s peaks are represented as a function of the number of ALD cycles. Both fits show similar GPC values of 0.1 Å per cycle, slightly lower than the estimation performed through the TEM cross-sections. Nevertheless, the applied fit model assumes the simplest scenario where the hetero- and homo-deposition ALD stages share the same chemical reaction pathways. Thus, it does

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**Figure 3.** Ce 3d XPS spectra as a function of the total number of ALD cycles for the growth of CeO<sub>x</sub> on SiO<sub>2</sub> substrates.

not consider possible deviations from layer-by-layer growth for the very early stages of growth (on a larger scale than shown by TEM images in Figure 1), different GPC depending on the cerium oxide oxidation state, or a complex evolution of the ALD carbon residues on the top surface due to non-ALD side reactions taking place at different growth stages.

To overcome these issues, we also performed an inelastic peak shape analysis (IPSA) of the XPS spectra. This method has been implemented in the QUASES software,<sup>[66]</sup> and uses the elastic peak intensity and the background produced by the inelastically scattered electrons to determine the morphology and composition of layers and nanostructures on the surface.<sup>[67]</sup> Therefore, this method uses the changes in the inelastic background that can be observed (see spectra in Figure 3) as a function of the number of ALD cycles (a higher energy range is actually needed, not shown). Usually, the results obtained from this method are visualized by displaying the variation of the height of the film/nanostructures as a function of the coverage, but for the sake of simplicity, we have directly extracted the individual GPC for each growth stage and plotted them as a function of the number of ALD cycles. The results are shown in Figure 5b, where for



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**Figure 4.** Si 2s XPS spectra as a function of the total number of ALD cycles for the growth of  $CeO_x$  on  $SiO_2$  substrates. The red line corresponds to the fit resulting from the Si 2s deconvolution into two components, SiO2 (in blue) and  $CeSi_xO_y$  (green).

comparison purposes the black and red dashed lines indicate the average GPC estimated from Figure 5a for the film and substrate signals, respectively. Two different models have been applied in the inelastic peak shape analysis, schematically depicted as insets in Figure 5b. On the one hand, we have considered a buried layer model, where a continuous cerium oxide layer is buried by a carbon layer. In this case, the thickness of both layers varies as a function of the number of ALD cycles, and the GPC is estimated by taking only the cerium oxide layer thickness. On the other hand, the islands model considers a unique deposit of cerium oxide (without a carbon layer) but with a more complex morphology, being initially deposited in islands that coalesce into a single layer only after many ALD cycles. In this case, the GPC is estimated by considering the thickness of these islands, all sharing the same thickness. As can be seen, both approaches yield very similar

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**Figure 5.** a) XPS intensities of the Ce 3d and Si 2s peaks (black circles and red squares, respectively) for the  $CeO_x/SiO_2$  deposition as a function of the total number of ALD cycles. Dashed lines correspond to the fits of those intensities, supposing a cerium oxide growth model with a top carbon layer and constant growth per cycle. b) Growth per cycle values obtained from the inelastic X-ray photoemission spectroscopy peak shape analysis (IPSA) performed with the QUASES software and calculated by the buried layer (circles) and islands (squares) models, respectively. The insets depict sketches of both models. The results are compared with those obtained from (a) using black and red dashed lines to indicate the average GPC values obtained from the Ce 3d and Si 2s XPS signals.

results, with two distinguishable regimes. Below 200 ALD cycles, the GPC gradually decreases from a significantly high value of 0.3 Å per cycle to a more expected one of 0.15 Å per cycle,<sup>[53,56]</sup> particularly becoming constant from 400 cycles. Again, the GPC value for the steady (homodeposition) regime is slightly lower than those estimated here by TEM and reported in the literature. Although the multiple approximations within this approach could bring up deviations in the absolute values of the GPCs, we highlight that their trend as a function of the number of ALD cycles is real and provides an average picture of the whole sample as the XPS spot is  $\approx 10 \times 10 \text{ mm}^2$ , which approximately is the sample size of our SiO<sub>2</sub> substrates. As we will discuss later, the initial cerium oxide growth corresponds to an intermediate situation between both models, where initial micrometric flakes covered by a carbon residue layer are deposited until they coalesce, explaining how such a priori different models provide equivalent results.

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www.advmatinterfaces.de The two GPC regimes can be straightforwardly related to the hetero- and homodeposition stages previously discussed. Moreover, the thickness of the residue carbon layer can be extracted from the QUASES analysis using the buried layer model and subsequently compared to the evolution of the XPS C 1s intensity, as shown in Figure 6a. We observe a gradual decrease in the amount of carbon, i.e., thickness and intensity, with an average thickness of  $\approx$ 4 Å that recalls the values obtained from the XPS quantitative analysis of the elastic peaks depicted in Figure 5a. Furthermore, this residue layer is clearly visible in the TEM-EDX linear profile extracted from the same trench shown in Figure 1 (see Figure 6b). Accompanying the residual carbon, we can observe a tail of oxygen and cerium, confirming that this organic residue is composed of not fully oxidized precursor molecules. As observed by the EDX line profile, this carbon-based layer is about ten times thicker than what was estimated by XPS. However, it should be taken into account that the analysis in XPS has been done considering a compact layer formed by pure elemental carbon to estimate its inelastic mean-free path. As the TPP-2M formalism considers, among other parameters, the bulk density and the number of valence electrons per atom or molecule, thicker but less dense and hydrogenated layers will give the same equivalent results as thinner, more compact, pure carbon layers. In addition, the normalized EDX-line profile in Figure 6b shows that the carbon signal-to-noise ratio of the carbon signal is low, in line with a relatively low-density layer. Continuing with the trend observed in Figure 6a, a higher amount of carbon during the heterodeposition stage could be related to more frequent non-ALD side reactions between the Ce(thd)<sub>4</sub> precursor and the SiO<sub>2</sub> substrate. At this point, we would like to emphasize that the QUASES analysis has been performed using the Ce 3d signal, not the carbon. Thus, the impressive degree of correspondence between the evolution of the C-layer thickness and the C 1s intensity, together with the confirmation of the top carbon-oxygen-cerium layer via TEM-EDX measurements, indicates the robustness of our quantitative XPS analysis combining different approaches, exemplifying how the in-situ XPS characterization can be used to discuss not only the oxidation state but also the deposit morphology and the reaction mechanism details of the ALD processes. We now focus on the chemical analysis of the XPS measure-

ments. Figure 7a shows the Ce 3d spectra introduced in Figure 3 after background subtraction and fitted by linear superposition of reference Ce<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub> spectra. The results concerning cerium oxide composition, i.e., CeO<sub>x</sub>, where 1.5 < x < 2, are presented in Figure 8a (open red circles). In line with the two GPC regimes, the ALD-CeO<sub>x</sub> deposit rapidly transitions from an initial dominance of Ce3+ states, giving a high oxygen deficiency on CeO<sub>17</sub> films, to a saturation stage upon 350 cycles, with a maximum oxidation of CeO<sub>1.95</sub> for 1000 cycles. Considering the work of Coll et al.,<sup>[56]</sup> which used the same Ce(thd)<sub>4</sub>/O<sub>3</sub> reactants under virtually identical conditions, we do not expect this chemical change to be accompanied by a structural transformation as a function of the number of ALD cycles; on the contrary, cerium oxide would preserve the fluorite structure while the substrate/precursor interaction would mediate the incorporation of oxygen via the ALD-reactions taking place at the surface. In order to test the influence of other factors on the initial reduction of cerium oxide, we repeated the same experiment but now restricting the precursor dose, i.e., reducing the precursor pulse





**Figure 6.** a) Thickness of the residual carbon layer obtained from inelastic X-ray photoemission spectroscopy peak shape analysis (IPSA) performed with the QUASES software using the buried layer model. As a comparison, the right axis shows the C 1s intensity after background subtraction as a function of the total number of ALD cycles. b) Normalized Si, O, Ce, and C intensities of the EDX line profile performed on the cross-section of 150 ALD cycles  $CeO_x/SiO_x$  deposit (top-left inset).



**Figure 7.** Ce 3d XPS spectra after background subtraction as a function of the total number of ALD cycles for the a) regular growth of  $CeO_x$  on SiO<sub>2</sub> substrates, and b) by constricting the exposure to Ce-precursor (black circles). The red and blue lines correspond to the fit resulting from the linear combination of CeO<sub>2</sub> and Ce<sub>2</sub>O<sub>3</sub> reference spectra. The top scheme shows the growth model followed by cerium oxide in each situation.

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**Figure 8.** a) Stoichiometry of CeO<sub>x</sub> deposits estimated from XPS Ce 3d spectra as a function of the total number of ALD cycles for regular Ce(thd)<sub>4</sub>/O<sub>3</sub> ALD growth (open red circles) and constricted exposure to Ce-precursor (filled red triangles), respectively. The stoichiometry of CeO<sub>x</sub> deposits on amorphous ALD-Al<sub>2</sub>O<sub>3</sub> on Si and c-sapphire are plotted in open green squares and blue triangles, respectively. b) Growth per cycle (GPC) values obtained from the inelastic X-ray photoemission spectroscopy peak shape analysis (IPSA) performed with the QUASES software and calculated by the buried layer for CeOx growth on SiO2 (open red circles), ALD-Al2O3 (open green squares), and c-sapphire (open blue triangles) using the regular recipe as indicated in the experimental section.

duration, thus limiting the number of nucleation sites and preventing the complete coalescence of the cerium oxide islands (see growth scheme in Figure 7). As before, Figure 7b shows the fitted XPS Ce 3d spectra after background subtraction. The first difference with the previous series consists of a lower signal-tonoise ratio, which is related to a drastic decrease in the amount of deposited cerium oxide, covering only 20% of the surface after 2000 cycles. Although we also observe a transition from reduced to oxidized cerium oxide, it takes place from a film that initially is completely reduced, i.e., CeO<sub>1.5</sub>, and takes more cycles to achieve similar oxidized values of about CeO19, as shown in Figure 8a (filled red circles). Although not shown here, the GPC (estimated by QUASES) and amount of carbon (followed by C 1s intensity and QUASES estimation of C-layer thickness) indicate the same trends as for the optimized ALD growth, showing almost identical GPC values for the same number of cycles if only the thickness of the islands is considered (not the total coverage

of the whole surface). Therefore, limiting the Ce(thd)<sub>4</sub> dose does not affect the chemical reaction paths and the distinct nature of the hetero- and homodeposition stages, but only the deposit morphology. Hence, we can conclude that morphology also plays a role in the oxidation state of ALD-cerium oxide, as it has been previously reported for nanostructures<sup>[68]</sup> and thin films deposited by PVD methods,<sup>[31,34,35,69]</sup> probably related to a higher ratio between surface and bulk compared to a continuous film.

In addition to the growth of cerium oxide on SiO<sub>2</sub> substrates under the two conditions discussed above, Figure 8a also shows the stoichiometry evolution of ALD-CeO<sub>x</sub> ultrathin films as a function of the total number of ALD cycles for two other substrates: amorphous Al2O3 deposited by ALD at room temperature on Si wafers and c-sapphire. Although there are some variations in the Ce oxidation state, e.g., higher reduction at the early stages of growth related to the formation of aluminates, the trend is similar in all cases. Besides, Figure 8b shows the GPC evolution for each substrate derived from the inelastic peak shape analysis using the buried layer model, as described in detail for the SiO<sub>2</sub> substrate case. Again, although the GPC value at the steady stage for both aluminum oxide substrates is slightly lower than for SiO<sub>2</sub> (which seems to be an artifact related to a slower coalescence than on SiO<sub>2</sub> substrate and the used model), the same trend is observed in all substrates. Thus, the shared evolution of both Ce oxidation state and GPCs confirms that the previously discussed classification into hetero- and homo-deposition stages is not uniquely related to the choice of SiO<sub>2</sub> but can be generalized to other metal oxide substrates. Within this scenario, the specific nature of the film substrate and reactant/substrate interactions will, in each case, determine the detailed characteristics of the hetero-deposition stage and the transition to the homodeposition limit.

Finally, we studied by ex-situ µ-Raman spectroscopy and laser interferometry measurements (see Figures 9 and 10) the ALDcerium oxide deposit on SiO<sub>2</sub> during the early stages of growth, and the relationship between cerium oxide composition, interaction with the substrate, structure, and morphology. In the case of 1 nm ultrathin deposits (100 cycles, Figure 9a,b), cerium oxide micrometric flakes of  $\approx 10 \times 10 \ \mu m^2$  are visible employing optical microscopy, which confirms the initial growth of islands (we call them flakes to differentiate these deposits from PVD nanoislands) that eventually ripen into a continuous film. This growth process can be tracked by laser interferometry (Figure 10), which allows acquiring images of extended areas (close to  $1400 \times 1000 \,\mu\text{m}^2$ ), showing, for 400 cycles, large regions (>200 µm<sup>2</sup>) completely covered by cerium oxide, whereas the bare substrate is still visible in certain places. It is worth noting that although the average thickness is  $\approx 8$  nm, in line with our previous GPC values estimated from TEM and XPS measurements, we find that the flakes' borders present lower thickness while the centers are thicker, suggesting a diffusion process toward the substrate surface. Furthermore, these different thicknesses correspond to local variations in the GPC between 0.15 and 0.3 Å per cycle (if the average of the 400 cycles is considered in all spots). This local dispersion in the GPC values within the same sample, particularly until the homodeposition stage is reached, is relevant considering the range of GPC values (0.2-0.35 Å per cycle) reported in the literature. The GPC strongly depends on the local state of the surface with which the precursor molecules interact www.advancedsciencenews.com

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**Figure 9.** a) From bottom to top selected individual Raman spectra for 100 ALD cycles taken at the border and center of the micrometric flakes, and 1000 ALD cycles. b) As delimited by the white square overlapping the optical image of 100 ALD cycles CeOx/SiO<sub>2</sub>,  $15 \times 15 \mu m^2$  Raman mappings showing the shift (top right, red), FWHM (bottom left, green), and intensity (bottom right, blue) of cerium oxide Fe<sub>2g</sub> peak. In c) and d), as delimited by the white squares overlapping the optical images of 100 ALD cycles CeO<sub>x</sub>/SiO<sub>2</sub>,  $71.5 \times 15 \mu m^2$  Raman mappings, respectively, showing the shift (top right, red), FWHM (bottom left, green), and intensity (bottom right, blue) of cerium oxide F<sub>2g</sub> peak.

and, therefore, will present a strong dependence on the nature and preparation history of the substrate, resulting in possible strong inhomogeneities during the early stages of growth until the coalescence is reached. Therefore, the experimental method used to estimate the thickness (X-ray reflectivity, ellipsometry, interferometry, etc.) or deposit amount (quartz crystal microbal-



Figure 10. 1390  $\times$  1070  $\mu m^2$  laser interferometry mapping of 400 ALD cycles CeOx/SiO\_2.

ance), together with the growth mode and total coverage of the particular ALD growth, can strongly influence or even bias the reported GPC for very thin deposits (< 20nm), albeit within a tolerable range. Finally, the flakes coalesce to form a continuous layer for even more cycles, as shown in Figure 9c,d for a deposit of 1000 cycles. We note that the length scales used in these three cases (Figure 9) are significantly larger than those typically reported for AFM or TEM measurements (also used in this work in Figures 1 and 2a), and thus growth inhomogeneities as those shown here could go unnoticed by local probes that are conventionally employed.

Spatially resolved Raman spectroscopy data were recorded on cerium oxide films with 100 and 1000 ALD cycles in the same areas as the optical images, which after processing yielded detailed 2D information ("Raman maps") on local sample structure, morphology, and chemistry. Figure 9a shows three selected individual Raman spectra: cerium oxide film after 1000 ALD cycles (top), and 100 ALD-cycle deposits at the border and center regions of the micrometric flakes (as indicated). The intense Raman signal from the Si substrate at 302 cm<sup>-1</sup> overlaps with cerium oxide bands related to surface phonon modes appearing at 270 and 315 cm<sup>-1</sup> for crystal sizes below 10 nm, preventing a straightforward intensity comparison to the  $F_{2g}$  band at  $\approx$ 460 cm<sup>-1</sup> that is characteristic for CeO<sub>2</sub> to evaluate the



crystallite size distribution.<sup>[70]</sup> Unfortunately, we find a similar situation when trying to analyze the broad D-band at 550-600 cm<sup>-1</sup> pinpointing cerium oxide defects as it overlaps with the main Si band at 520 cm<sup>-1</sup>. Therefore, we limit our study to the most intense cerium oxide  $F_{2g}$  band.<sup>[71]</sup> In the case of 1 nm thin flakes (Figure 9b), no cerium oxide-related Raman signal could be detected outside them, likely indicating the absence of cerium oxide deposition on the bare substrate that could not be seen in the optical image. Moreover, the  $F_{2g}$  intensity (blue) increases in the center of the flake, in line with the interferometry thickness mapping in Figure 10. Besides, the analysis of the local distributions of wavenumber (peak position, Raman shift indicated as  $F_{2\alpha}$ shift) and full width at half maximum (FWHM) show a significant redshift and broadening toward the center of the flake. Such kind of variations have been related to a decrease in the crystallite size below 50 nm.<sup>[72,73]</sup> However, it seems counterintuitive that the center of the flake, which is thicker than the border, presents more remarkable size effects than the latter. Alternatively, we consider that the broadening and redshift of the  $F_{2g}$  band are related to the presence of defects<sup>[72-74]</sup> and variations in surface strain.<sup>[72,73,75]</sup> Although this interpretation should be confirmed by growing ALD-cerium oxide on alternative substrates that allow analyzing the cerium oxide D-band, it is worth highlighting the spatial inhomogeneities of ultrathin ALD-cerium oxide deposits, which could be related to the spatial distribution of Ce<sup>3+</sup> and Ce4+ states and thus have important implications in terms of surface reactivity. Moreover, Figure 9c,d depicts the same kind of Raman maps of the F<sub>20</sub> band intensity at two different length scales for 20 nm thick samples, showing remarkable homogeneity among the entire surface. Furthermore, the central Raman shift and FWHM of the  $F_{2g}$  band show almost constant values, indicating a lower presence of defects and strain compared to the center of ultrathin flakes. This fact points to a defect-healing process combined with a relaxation of the cerium oxide structure as the thickness increases, possibly enhanced by the direct interaction between the precursor and cerium oxide surface, allowing a higher concentration of oxygen in the cerium oxide matrix. Nevertheless, we cannot rule out the influence of the time that the sample is kept at 250 °C during the ALD growth, which could also induce a gradual crystallization of the layer, similar to post-annealing processes.<sup>[56]</sup> Therefore, the hetero- and homodeposition ALD regimes, in combination with the deposition conditions, might also have a distinct impact on the presence of defects and strain in cerium oxide structure, giving rise to a more defective and inhomogeneous cerium oxide on a macroscopic scale during the early stages of growth, which can also be related to the presence of Ce<sup>3+</sup> states in addition to the previously discussed initial strong film substrate interaction that alters the ALD reaction mechanism during the very early stages of growth, which results in the formation of Ce-O-Si species at the interface. The ALD-cerium oxide deposits present certain particularities

The ALD-cerium oxide deposits present certain particularities that distinguish them from physical vapor-deposited cerium oxide films, and which can only be followed by a surface science approach that allows correlating growth morphology, structure, oxidation state, and interaction with the substrate. We have seen how the ALD reaction mechanism deviates from the ideal layerby-layer growth expected for a self-limiting reaction process, a behavior that has also been confirmed when using other substrates such as amorphous Al<sub>2</sub>O<sub>3</sub> and c-sapphire. The differences www.advmatinterfaces.de

in the chemical reaction paths for the hetero- and homodeposition regimes strongly impact the GPC, the carbon residues on the top surface, and the oxidation state of cerium oxide, i.e., the number of oxygen vacancies.

The mechanism of a particular ALD chemisorption process can be estimated using Puurunen's theoretical model,<sup>[76]</sup> which, based on the mass balance of the reaction, relates the total amount of metal atoms attached per cycle with the size of the ligands (i.e., steric hindrance effect) and reactivity toward a specific surface (i.e., active sites available). On the one hand, a ligand exchange reaction is likely to prevail during the homodeposition stage, as stated previously by Coll and coworkers.<sup>[56]</sup> In this case, the density of Ce cations attached to the surface after a growth of 0.2 Å per cycle ranges from 0.45 to 0.50 nm<sup>-2</sup> for CeO<sub>1.5</sub> and CeO<sub>2</sub>, respectively, which are higher than the theoretical value assuming that no ligand release occurs (0.25 nm<sup>-2</sup>). This situation is similar to that reported by Puurunen for the ALD growth of Y<sub>2</sub>O<sub>3</sub> using Y(thd)<sub>3</sub> and O<sub>3</sub>.<sup>[77]</sup> In our case, it is probable that two ligands are exchanged, giving a maximum cerium surface density of 0.51 nm<sup>-2</sup>, reasonably close to the experimental value. On the other hand, the maximum GPC reported for the CeO<sub>v</sub>/SiO<sub>2</sub> hetero-deposition stage increases by 50%, giving Ce cation surface densities of  $0.68 \text{ nm}^{-2}$  for CeO<sub>15</sub>. Here, we assume that the ligand exchange reaction mechanism does not change, which seems reasonable considering the abovementioned limit for no ligand release. In that case, an increase in GPC cannot be explained if the steric hindrance effect controls the surface saturation during the homodeposition stage. On the contrary, the increase in GPC should be related to a higher initial density of active sites on the SiO<sub>2</sub> surface than on the cerium oxide, e.g., OH<sup>-</sup> groups. However, the surface concentration of hydroxyls chemisorbed on SiO<sub>2</sub> cannot unambiguously be determined from our in-situ O1s XPS data due to the substantial overlapping of several peaks representing the contributions from CeO<sub>x</sub>, SiO<sub>2</sub>, and precursor residues during the early stages of growth. Similarly, Puurunen could simulate the changes in the GPC during the first cycles as a function of the available active sites using the same model.<sup>[76]</sup>

The higher amount of carbon during the initial stages of growth could be related to ALD side reactions promoted by the more active substrate surface.<sup>[62]</sup> If the oxidation with O<sub>3</sub> remains incomplete, in addition to H<sub>2</sub>O and CO<sub>2</sub>, some CO and hydrocarbons could form. These may partially adsorb at the surface and serve as additional active sites in the next cycle, which would imply their subsequent removal. However, as these species may form in sequential ALD cycles, this process results in an effective stabilization of C-containing species in the near-surface region. Furthermore, the initial Ce<sup>3+</sup> states have been shown to be related to a highly defective cerium oxide matrix, the morphology (i.e., high surface/bulk ratio), and particularly to the formation of bridge-like Ce-O-Si bonds at the interface, reducing the initial  $Ce^{4+}$  cation from the  $Ce(thd)_4$  precursor by a charge transfer from the silicon. The formation of these silicate species has been extensively reported for a variety of growth techniques on Si and SiO<sub>2</sub> substrates. Recent density functional theory (DFT) calculations performed for the novel Ce(dpdmg)<sub>3</sub> precursor have shown how, depending on the chosen surface and co-reactant, films with different Ce<sup>3+</sup>/Ce<sup>4+</sup> ratios can be deposited by a change in the specific reaction mechanism.<sup>[78,79]</sup> The complexity of

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nonperfect surfaces, i.e., defects and chemical inhomogeneities, as well as experimental conditions that are far away from the reality of classical surface science, make it challenging to isolate and identify all occurring processes. However, we believe that our approach provides valuable insights into the synergistic interaction between substrate, film, and reactants, whose understanding and exploitation will likely play a key role in the realization of ultrathin devices.

It is well known that other intrinsic factors of cerium oxide, such as facile surface reduction compared to the bulk, also determine the final Ce<sup>3+</sup>/Ce<sup>4+</sup> ratio depending on the deposit morphology. However, ALD has been shown to provide more defective cerium oxide films than other PVD techniques on SiO<sub>2</sub> substrates, which is especially remarkable for ultrathin deposits where the cerium oxide flakes present a spatial inhomogeneity in the degree of defects and strain. Although the role and effect of such defects in cerium oxide remain an open discussion,<sup>[80,81]</sup> they could potentially impact cerium oxide's reactivity toward oxidizing or reducing conditions. In this line, special emphasis must be put on substrate surface preparation, which could lead to variations in the hetero-deposition regime, thus potentially impacting the total coverage, growth morphology, or the interaction between substrate and ALD deposit. Furthermore, annealing of ALD-CeO<sub>2</sub> has been proven to enhance the order and crystallinity of ultrathin films (<5 nm),<sup>[56]</sup> which has been indirectly shown in our case by comparing 1 and 20 nm thick films by µ-Raman spectroscopy maps. Further studies combining different substrates, thicknesses, and post-annealing processes are required to unravel the three-party cross-interactions between substrate, precursor, and CeO<sub>v</sub> deposit on film growth, as well as the relation between ALD-cerium oxide intrinsic defects and chemical reactivity compared to PVD-cerium oxide films, which generally exhibit a higher degree of crystallinity and order.

### 3. Conclusion

Atomic layer deposited cerium oxide using commercial Ce(thd)<sub>4</sub> and O<sub>3</sub> on SiO<sub>2</sub> substrates presents a complex growth model determined by the change in the reaction mechanism when the precursor interacts with the substrate or the cerium oxide surface, i.e., the hetero- and homodeposition regimes, respectively. During the first regime, non-ALD side reactions might affect the GPC, the amount of carbon residue on the surface, and the oxidation degree of cerium oxide, as in-situ XPS measurements have been directly demonstrated. Besides, Raman and laser interferometry measurements have shown an inhomogeneous deposition during the first cycles, initially growing micrometric flakes that eventually coalesce for deposits  $\approx 10$  nm thick. Those flakes show spatial inhomogeneities in terms of strain and amount of defects, which could also be related to the observed difference in the Ce<sup>3+</sup>/Ce<sup>4+</sup> ratio comparing ALD-cerium oxide deposits of the same thickness and different morphology. Therefore, the intrinsic defects expected for ALD deposits compared to more ordered PVD deposits are strongly correlated with the nature of the substrate (predefining the initial precursor/substrate chemical interaction) and the cerium oxide morphology (determining the ratio between surface and bulk species), which is also strongly influenced by the initial precursor/substrate interaction. On the contrary, the steady homo-deposition regime presents stable GPC values, with lower carbon residue and almost complete film oxidation, in line with previous reports focused on relatively thick ALD-cerium oxide layers using the same  $Ce(thd)_4/O_3$  reactants. The clear distinction between the hetero- and homo-deposition regimes, in terms of the evolution of Ce oxidation state and GPCs values, is not unique to SiO2 substrates: it has also been reproduced when using as substrates amorphous Al<sub>2</sub>O<sub>3</sub> deposited by ALD at room temperature and c-sapphire, thus confirming that the film substrate and reactant/substrate interactions affect the ALD process. In particular, we have provided a qualitative model that relates the initial acceleration of the ligand exchange chemisorption mechanism during the hetero-deposition stage to the presence of more active sites on the surface of the substrate and the formation of Ce-O-Si bonds at the interface. Although we do not provide a detailed model of all the chemical reactions, this in-situ surface science approach provides insights to develop theoretical models, which can be adapted to different precursors/co-reactants and substrates to predict both growth behavior and film properties of systems of interest.

Even though other intrinsic factors of cerium oxide, such as morphology, also determine the final  $Ce^{3+}/Ce^{4+}$  ratio, ALD has been shown to provide more defective cerium oxide films than other PVD techniques, being especially remarkable for ultrathin deposits. Further studies combining different substrates, thicknesses, and post-annealing processes are required to unravel the cross-interactions between precursor,  $CeO_x$  deposit, and substrate on film growth, as well as the role of ALD-cerium oxide intrinsic defects on the reactivity compared to PVD-cerium oxide films with a higher degree of crystallinity and order. In addition, understanding the role of the catalytically active Ce3+ states in ultrathin, highly defective ALD-CeOx deposits will potentially enable a rational design of ALD-based, ultrathin, chemically active coatings for numerous future applications in heterogeneous catalysis and sensing.

## 4. Experimental Section

The cerium oxide atomic layer deposition on SiO<sub>2</sub> substrates was performed in a stainless steel, home-made reactor attached to the preparation chamber of a UHV-XPS system.<sup>[82]</sup> The cerium oxide was deposited by thermal ALD using the commercial ALD-precursor tetrakis(2,2,6,6tetramethyl-3,5-heptanedionato)cerium(IV), Ce(thd)<sub>4</sub>, 99.99% pure from EpiValance, in combination with ozone, ( $\approx$ 7%, O<sub>3</sub>/O<sub>2</sub> mixture) generated with an OXP-30 Ozone Generator from Oxidation Technologies fed with O2 (99.9995%, Air Liquid). The ALD reactor was operated in flow-type mode using N2 (99.9999%, Air Liquid) as carrier gas controlled by independent mass flows (F-111B 200, Bronkhorst), consisting of two lines for the precursor and the oxidant, respectively. The gas input was regulated by ALD pneumatic valves (Swagelok) controlled by LabVIEW-based (2020 SP1) homemade software. During the deposition, the turbopump of the ALD reactor is bypassed, which in this case is directly pumped by a scroll pump (base pressure of  $8 \times 10^{-3}$  mbar in these conditions). The electropolished stainless steel bubbler (STREM) containing the Ce(thd)4 precursor was heated to 140 °C, while the  $N_2$  and  $O_3$  lines were set to 90 °C and the walls of the ALD reactor to 120 °C. A substrate temperature of 250 °C, within the previously reported ALD temperature window,[53,57] was accomplished by radiative heating. The ALD recipe consisted of 1 s  $\mbox{Ce(thd)}_4$  pulse followed by 1.5 s of  $N_2$  purging flow, continued by an  $O_3$ dose of 2.5 s and subsequent 3 s of N<sub>2</sub> for purging. Additionally, the reactor was purged for 40 s between the cycles by pumping with the scroll pump ( $<10^{-2}$  mbar). The N<sub>2</sub> flux was set to 60 sccm, giving a pressure



range of 1–3 mbar during the precursor, oxidant, and purging gas doses. As discussed later, the estimated average GPC is  $0.2 \pm 0.05$  Å per cycle in line with reported values from the literature.<sup>[53,56,57]</sup> The ALD recipe was optimized by fixing the substrate temperature and N<sub>2</sub> flux and individually varying the precursor and oxidant doses from lower to higher values in respective intervals of 50 cycles until a stable GPC could be derived from in-situ XPS measurements. Before the deposition, the substrates, 300 nm thick thermal oxidized SiO<sub>2</sub> on Si (100) wafers from Crys-Tec, were annealed at 250 °C under UHV to remove the adventitious carbon as confirmed by XPS. For comparison, the same ALD-CeO<sub>x</sub> procedure was repeated on two more substrates: amorphous Al<sub>2</sub>O<sub>3</sub> films (12 nm) grown on Si wafers by atomic layer deposition at room temperature<sup>[82]</sup> and c-sapphire single crystal substrates from MSE Supplies.

In-situ XPS measurements were performed with an Omicron EA 125 hemispherical electron analyzer using nonmonochromatized Mg K<sub>a</sub> radiation to avoid the overlap of the Ce 3d main photoemission region and the Auger MNN signals from Ce. The pass energy was set to 20 eV, yielding an overall spectral resolution of  $\approx$  1.0 eV. The initial calibration of the energy scale and resolution of the XPS system was carried out using a silver (Ag 3d<sub>5/2</sub> at 368.2 eV)<sup>[83]</sup> polycrystalline film deposited in-situ by thermal evaporation. The sample charging was corrected considering the Si 2s peak from the SiO<sub>2</sub> substrate as an internal reference.<sup>[64,65]</sup> Peak fitting of the Si 2s core-level spectra was performed by considering a symmetrical Gaussian-Lorentzian (G-L) sum, fixing the same full with at half maximum (FWHM) and G-L ratio for each component and subtracting a Shirley-type background. After removing the X-ray satellites, the XPS Ce 3d spectra were fitted as a linear combination of Ce 3d reference spectra from pure  $Ce_2O_3$  and  $CeO_2$ , following the same procedure as Allahgholi and coworkers.<sup>[34]</sup> The spectra have been fitted using the XPS Peak software, version 4.1. Inelastic peak shape analysis (IPSA) was carried out using the QUASES-Generate software,[66] taking the Ce3d extended region and a bulk CeO<sub>2</sub> reference sample. The inelastic electron mean free path (IMFP) through the cerium oxide matrix was calculated using the Tanuma, Powell, and Penn formula IMFP-TPP2M.<sup>[84]</sup>

The CeO<sub>x</sub>/SiO<sub>2</sub> characterization was completed ex-situ through morphological, structural, and crystallographic techniques. Transmission electron microscopy (TEM) and energy-dispersive X-ray (EDX) spectroscopy measurements were performed with a FEI Tecnai Osiris instrument operated at 200 kV, using nanostructured Si substrates fabricated at the Leibniz-Institut für innovative Mikroelektronik (IHP) facilities. The surface morphology was characterized by atomic force microscopy (AFM) measurements conducted in noncontact mode using a neaSNOM system from NEASPEC and metal-coated Si tips with a nominal resonance frequency of 75 kHz (Multi75E-G). The crystallographic and structural properties were investigated by grazing-incidence X-ray diffraction (GIXRD, Rigaku Model SmartLab, Rigaku Corporation) using monochromatized Cu  $K_{\alpha}$  radiation provided by a rotating anode (9 kW, line-focus). A parallel beam setup and a 5° Soller slit in the receiving optics were chosen to obtain sufficient signal intensity in the scintillation counter. The incidence angle  $\alpha$  was fixed to 0.5°, with a 2 $\theta$  scan range from 20° to 80°. Film coverage and structural homogeneity were characterized by µ-Raman spectrometry, using a Renishaw InVia µ-Raman spectrometer equipped with a 532 nm wavelength laser. Finally, thickness and deposit homogeneity were assessed by employing 3D laser interferometry (LSM VK-X3000, Keyence).

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# **Conflict of Interest**

The authors declare no conflict of interest.

# **Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

# Keywords

ALD, cerium oxide, growth model, in-situ, XPS

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