Adsorbate-Mediated Growth of Rare-Earth Oxides on Silicon

Björn Kaemena, Jan Ingo Flege, and Jens Falta
Institute of Solid State Physics, University of Bremen, Otto-Hahn-Allee 1, 28359 Bremen, Germany
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Ultrathin cerium oxide films have been deposited on chlorine, gallium, and silver passivated Si(111) by reactive molecular beam epitaxy in a comparative study. The crystallinity of these films has been characterized by x-ray standing waves while the oxidation state of the rare-earth oxide (REOx) films and the chemical interface composition have been revealed by hard x-ray photoelectron spectroscopy. The use of Cl as passivating agent results in the epitaxial growth of highly crystalline REOx films with the RE metal in the 3+ oxidation state while effectively suppressing silicate and silicon oxide formation at the interface. In contrast, Ga and Ag preadsorption yield films of inferior quality, in the case of Ag of even lower crystallinity than without passivation. Further investigations show that Cl-passivation also results in ultrathin lanthana films of superior quality, which facilitate the growth of well-ordered ceria on lanthana REOx multilayers.

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I. INTRODUCTION

Due to their intriguing physical and chemical properties, which mainly arise from the unfilled 4\( f \) electron shell, rare-earth oxides (REOx) have been studied intensely in order to understand the nature of these extraordinary properties, with the aim of exploiting them in various kinds of technological applications. Besides their traditional utilization in fields like catalysis, some of the REOx have attracted a lot of interest in microelectronics due to their high static dielectric constants \( k \), which in the case of, e.g., CeO\(_2\) amounts to \( k > 26 \) (Refs. 2,3), and their predicted thermodynamic stability in contact with silicon, making them promising candidates for novel "high-\( k \)" dielectrics.

To maintain the progression of integration densities in microelectronics, there is a growing desire for ultrathin, well-ordered, epitaxial REOx layers with a sharp interface to the underlying silicon substrate as a replacement for the SiO\(_2\) gate oxide. These novel gate oxide layers would allow for further downscaling of field-effect transistors (FET) by simultaneously increasing device performance and lowering power consumption. However, the interface between the silicon substrate and the high-\( k \) gate oxide requires precise engineering since the interface trap densities and the carrier scattering need to be minimized to allow for reliable, high-performance devices.

Therefore, almost perfect epitaxial interfaces between the silicon substrate and the high-\( k \) material are required. Yet, achieving a well-defined epitaxial interface has so far been considerably impeded by RE-promoted silicon oxidation, resulting in amorphous silicon oxide and RE silicate formation.

To overcome these challenges given by the high reactivity of the REOx-silicon interface different approaches have been employed, ranging from influencing the growth kinetics by varying the REOx growth rate and substrate temperature to introducing surface active agents as, e.g., hydrogen. Since hydrogen limits the growth temperature to 450°C due to its relatively low desorption temperature, other adsorbates, which allow for higher growth temperatures, would in principle be more favorable because at given interface stability higher growth temperatures directly translate into an increased crystallinity of the deposited REOx film. In this respect, chlorine presents a suitable alternative, which is commonly used in semiconductor processing.

Recently, we have suggested the use of chlorine passivation for the growth of well-ordered Ce\(_2\)O\(_3\) adlayers on Si(111) by reactive molecular beam epitaxy (MBE) in ultra-high vacuum (UHV). Here, we widen the scope and test the general concept of REOx growth following substrate pre-passivation, which we will call adsorbate-mediated growth, in an extensive study employing several commonly used surfactant active agents. First, we compare the crystalline quality, interface composition and oxidation state of ultrathin cerium oxide films deposited on chlorine, silver, and gallium passivated silicon(111) by employing X-ray standing waves (XSW) and hard X-ray photoelectron spectroscopy (HAXPES). For Cl passivation, which yields the cerium oxide films of the highest quality, we also perform XSW-HAXPES with O1\(_s\) photoelectrons in a chemically sensitive manner, thereby shedding light on the atomic interface structure of silicon oxide and silicate species.

In the second part of the manuscript, we test the transferability of the concept of Cl passivation to other REOx by investigating its influence on the growth of lanthana films on bare and chlorine passivated Si(111), again by utilizing XSW and HAXPES to quantify the crystallinity of ultrathin lanthana films and the interface composition. XSW also allows monitoring of the Cl binding sites during the growth process, again by employing XSW and XPS. Together with the cerium oxide results, this analysis unambiguously confirms the beneficial effect of Cl preadsorption with respect to REOx crystallinity and in-
interface sharpness.

Finally, in the last part we demonstrate that the adsorbate-mediated growth concept enables the realization of well-defined ultrathin REOx multilayers, i.e., a well-ordered, ultrathin cerium oxide layer on top of a highly crystalline, ultrathin lanthanum film that was grown on Cl-passivated Si(111). By using XSW we are able to selectively probe and quantify the crystallinity of each REOx layer, while HAXPES serves to elucidate the chemistry at the lanthana-silicon interface and to determine the oxidation state of each REOx layer.

II. EXPERIMENTAL

All experiments were performed at the Hamburg Synchrotron Radiation Laboratory (HASYLAB), which is located at the Deutsches Elektronensynchrotron (DESY) in Hamburg, Germany. At the undulator beamline BW1, the samples were prepared and characterized in situ under UHV conditions employing XSW, XPS, and low-energy electron diffraction (LEED). The XSW experiments were performed in a nondispersive setup employing a water-cooled Si(111) double-crystal monochromator with an asymmetrically cut second crystal for enhanced phase contrast. As inelastic secondary signals, photoelectrons were recorded at photon energies of 2.6 keV and 3.35 keV while x-ray fluorescence data was collected at primary energies of 5.9 keV. The HAXPES measurements were conducted at photon energies of 3.35 keV and 2.6 keV.

Sample preparation started from polished, RCA-cleaned Si(111) crystals, which were introduced into the UHV chamber and degassed at a temperature of 630°C for at least 12 h. The Si(111) crystals were then annealed to 880°C to remove the protective silicon oxide from the RCA treatment and to achieve a (7×7) reconstruction, which was verified by LEED. In the case of Si(111) surface passivation chlorine, silver, and gallium were used to saturate silicon dangling bonds prior to REOx growth. In reference experiments, REOx films were directly deposited onto the (7×7) reconstructed Si(111) surface. In the case of Cl passivation we followed our recipe published earlier. Passivation with Ag was achieved by saturation exposure of Ag from a knudsen cell at 500°C substrate temperature leading to a (√3 × √3)R30° reconstruction as witnessed by LEED (data not shown). Ga passivation was achieved by evaporating metallic Ga using an electron-beam evaporator at 625°C substrate temperature, yielding a surface that exhibited a LEED pattern indicating the presence of a prevailing (√3 × √3)R30° reconstruction together with a faint contribution of an incommensurate (6.3×6.3) phase. The very existence of the latter domains ensures that essentially all dangling bonds of the Si substrate are saturated because the (6.3×6.3) phase is known to only form after the completion of the (√3 × √3)R30° phase in this temperature range. The RE oxides were then deposited at the same conditions by evaporating the RE metal using an electron-beam evaporator in a preset oxygen ambient of 5 × 10⁻⁷ mbar partial pressure and a substrate temperature of 500°C. Typical growth rates were in the range of 2 Å/min as determined from complementary x-ray reflectometry (XRR) measurements.

In an XSW experiment, the sample reflectivity and the intensity of an element-specific inelastic signal, e.g., x-ray fluorescence or photoelectrons, are recorded simultaneously while tuning the sample through the (hkl) Bragg condition. By fitting the reflectivity and the respective yield of the inelastic secondary signal within the framework of the dynamical theory of x-ray diffraction, the modulus f_c ("coherent fraction") and the phase φ_c ("coherent position") of the (hkl) Fourier component of the spatial distribution function of the contributing atoms may be determined with high precision. In general, for photoelectrons as inelastic secondary signal non-dipole effects may occur depending on the selected core level and the experimental conditions. But, due to our measurement geometry these non-dipole effects are minimized. A comparison between CeLα fluorescence and Ce3d photoelectrons of a crystalline, one monolayer thin cerium oxide film (data not shown) indicates non-dipole contributions of less than 8% in the coherent fraction. In the following, whenever fluorescence and photoelectrons as inelastic secondary signals from rare-earth atoms are compared in an effort to quantify film crystallinity, we will correct for non-dipole effects in the coherent fraction by taking into account an 8% difference.

As we have shown in our previous publication XSW is highly suitable for studying the epitaxial quality of ultrathin REOx films on silicon. A quantitative measure for the crystallinity of a REOx film of known thickness is the coherent fraction. After correction for thermal vibrations, its value can directly be compared to the theoretical value of the coherent fraction calculated for given crystal structure and film thickness.

III. RESULTS AND DISCUSSION

In the following sections, we present our experimental results for rare-earth oxide growth on passivated Si(111) surfaces. We will first discuss the influence of different passivating agents (Sec. IIIA) on the epitaxial film quality of ultrathin ceria films by employing HAXPES as well as XSW–HAXPES, which complements and further enhances our previous study. In Sec. IIIB we then also demonstrate the improved crystallinity of ultrathin lanthanum films due to chlorine passivation. Finally, again employing a combination of chemically sensitive XSW and hard x-ray photoelectron spectroscopy (HAXPES) we assess the crystallinity and interface composition of ultrathin rare-earth multilayers up to a few nanometers on Cl-passivated Si(111) in Sec. IIIC.
A. Ceria growth on passivated Si(111)

We begin our discussion by comparing the oxidation state of cerium oxide grown on Si(111) crystals passivated by Cl, Ag, and Ga as well as cerium oxide grown on non-passivated Si(111). Since all oxide films were grown at a substrate temperature of 500°C and an oxygen background pressure of 5 \times 10^{-7} \text{ mbar} we introduce a short hand notation for improved readability as follows: The preparation conditions will be labeled by "(5)" , "(5-Cl)" , "(5-Ag)" and "(5-Ga)" identifying the oxygen partial pressure (divided by 10^{-7} \text{ mbar}) and the passivating agent used in the respective experiment. In Fig. 1 we present Ce3d photoemission spectra of cerium oxide films for the growth recipes (5), (5-Cl), (5-Ag) and (5-Ga) for a nominal film thickness of 6 Å. Qualitatively, the four spectra show the same peak structure and exhibit the typical shape that is attributed to a single Ce^{3+} (Ce_2O_3) oxidation state. Quantitatively, all four yields are the same within the errorbar and on average amounts to \Phi_c = 1.065. Since the coherent position is independent of the passivating agent applied prior to cerium oxide growth and all cerium oxide films exhibit the same film thickness, the coherent fraction \Phi_c is a direct measure of the crystalline order of the film. For the preparation conditions (5), (5-Cl), (5-Ag), and (5-Ga) the coherent fractions amount to \Phi_c(5) = 0.74, \Phi_c(5-Cl) = 0.86, \Phi_c(5-Ga) = 0.75 and \Phi_c(5-Ag) = 0.35, respectively. Therefore, we conclude that chlorine passivation of Si(111) prior to cerium oxide growth leads to the highest crystalline quality of ultrathin ceria films while passivation with silver drastically impedes crystallinity and leads to much worse ordering than found for cerium oxide films deposited without passivation. Gallium preadsorption does not seem to have any effect on the crystalline order of the ceria film since the difference in the coherent fraction compared to the ceria film grown on non-passivated Si(111)-(7 \times 7) is within the error bar.

In quantitative XSW simulations as described earlier, we assumed a laterally fully strained Ce_2O_3 film of two O_{0.75}-Ce-O_{0.75} trilayer (TL) thickness with a relative spacing of 3.32 Å as derived from continuum elasticity theory based on elastic constants for CeO_2. This model predicts a coherent fraction of f_c(sim.) = 0.925, which only differs by \Delta f_c = 0.065 from the experimental result of f_c(5-Cl) = 0.86 for the Cl-passivated cerium oxide film. Within the error bar of our XSW measurement, this deviation can be fully attributed to thermal vibrations. Even when taking into account non-dipole contributions in the order of a few percent, we conclude that the cerium oxide film grown on Cl passivated Si(111) is very highly ordered.

After having discussed the influence of the passivating...
FIG. 3. (Color online) O1s photoemission spectra of ceria films with a film thickness of 6 Å grown on non-passivated Si(111) and Cl, Ag and Ga passivated Si(111) at 500°C substrate temperature and an oxygen partial pressure of 5 × 10⁻⁷ mbar (preparation conditions: (5), (5-Cl), (5-Ag), (5-Ga)). The spectra were recorded at photon energies of 3.35 keV for (5), (5-Cl) and (5-Ga) and 2.6 keV for (5-Ag) and have been deconvoluted into three species: CeO₂, Si-O-Ce, SiOₓ using Voigt profiles.

FIG. 4. (Color online) Chemical-sensitive XSW data (data points) and theoretical fit according to the dynamical theory of x-ray diffraction (solid lines) using O1s photoelectrons which belong to the Si-O-Ce and SiOₓ species obtained in the case of Cl passivation. The coherent fractions of the interfacial species in the case of Cl passivation seem to be very highly ordered, probably due to several inequivalent binding sites. A thick ceria films grown at 500°C substrate temperature and an oxygen partial pressure of 5 × 10⁻⁷ mbar on non-passivated Si(111)-(7 × 7) and Cl passivated Si(111) (5-Cl) are depicted in Fig. 4. As expected for amorphous phases, the coherent fractions of Si-O-Ce (5) = 0.12 and of SiOₓ (5) = 0.20 obtained for the silicate and silicon oxide species for the growth on bare Si(111) are very small indicating a very poor ordering, probably due to several inequivalent binding sites. A direct result of the low concentration of SiOₓ species (Fig. 4 (5-Cl)) as compared to the Si-O-Ce and CeO₂ species, suggesting that only a small portion of the interface exhibits silicon oxide species, which are incorporated in an almost perfectly ordered fashion. Although the coherent fraction of the Si-O-Ce species, which represent the majority of the interfacial species, is more than tripled as compared to the recipe (5), a suggestion of a structural model would be speculative at best since at least a bimodal atomic distribution function would have to be considered to satisfactorily explain its (111) Fourier component. Nevertheless, our XSW results for both the SiOₓ and the Si-O-Ce interface species offer a suitable benchmark within a combined analysis using XSW and theoretical calculations, e.g., within the framework of density functional theory, which could provide further insight into the complex chemistry at the REOₓ-silicon interface.
Si(111), from our XSW and HAXPES investigations we can unambiguously infer that chlorine is the superior passivating agent for the realization of highly ordered, epitaxial cerium oxide films on silicon accompanied by a very low amount of ordered silicate and silicon oxide species at the interface. In the following section, we test the transferability of the Cl passivation recipe for the growth of ultrathin lanthana films.

B. Lanthana growth on Cl passivated Si(111)

To study the influence of Si(111) surface passivation on other rare-earth oxides besides ceria we prepared a 1.8 nm thin lanthana film on both bare Si(111)-(7 × 7) and Cl/Si(111)-(1 × 1). In analogy to the previous experiments, these lanthana films were grown at 5 × 10^{-7} mbar oxygen background pressure and a substrate temperature of 500°C, again denoted by (5) and (5-Cl). Fig. 5 shows a representative La3d photoemission spectrum and Si1s spectra for preparation conditions (5) and (5-Cl). As is visible from Fig. 5(a) the films were grown as La2O3 since the spectrum exhibits the typical double peak structure known for lanthana. The effect of chlorine passivation is clearly documented by the comparative Si1s HAXPES data for the recipes (5) and (5-Cl) (see Fig. 6(b)), which depending on passivation exhibit an apparent intensity modulation in the range of higher binding energies, i.e., ∼2−6 eV shifted relative to the Si1s main peak. In the (5-Cl) case, this part of the spectrum only consists of inelastically scattered electron background and is almost perfectly flat otherwise while the same region in the case of (5) exhibits substantial integral intensity. This intensity can be attributed to the presence of various silicon oxide species in different oxidation states at the interface, e.g., silicon oxide and silicate. Hence, from our spectroscopic investigations we conclude that chlorine adsorption prior to lanthana growth strongly reduces silicon oxidation at the interface.

By employing XSW in (111) Bragg reflection (Fig. 6(a)), we are able to assess and compare the epitaxial quality of the lanthana films grown on passivated and non-passivated silicon. The LaLα fluorescence yields (see Fig. 6(b)) were recorded at an incident photon energy of 5.9 keV. For the fluorescence data, the coherent position Φc amounts to Φc = 0.99 for both preparation conditions. The coherent fraction f_c for the lanthana film grown after Cl passivation amounts to f_c(5-Cl) = 0.57 while the lanthana film grown on Si(111)-(7 × 7) (5) only possesses a coherent fraction of f_c(5) = 0.42, yielding a significant difference of Δf_c = 0.15 in the coherent fractions. Therefore the XSW fluorescence results reveal a higher crystallinity for the lanthana films grown on chlorine passivated Si(111) as compared to lanthana deposited on bare Si(111)-(7 × 7). This is in agreement with our XPS Si1s investigation, which points toward a substantial concentration of silicate and silicon oxide species.
species at the interface for the growth without passivation.

To perform an analogous quantitative XSW simulation for lanthana films as in the case of cerium oxide, the crystallographic nature of the sesquioxide has been elucidated by other experimental approaches. Grazing incidence x-ray diffraction studies of lanthana films grown on Cl-passivated silicon (data not shown) reveal that La2O3, just like Ce2O3, crystallizes in the so called C-type bixbyite structure and that the formation of the well-known hexagonal phase is suppressed. In quantitative XSW simulations for a 1.8 nm thick bixbyite lanthana film with a lattice constant of a = 11.36 Å (Ref. 37), we assumed a laterally fully strained La2O3 film of five O0.75-LaO0.75 trilayer thickness with a trilayer spacing of 3.45 Å as derived from continuum elasticity theory again based on elastic constants for CeO2 (Ref. 32). This model predicts a coherent fraction of \( f_c(\text{sim.}) = 0.614 \). If we assume an isotropic Debye-Waller factor of \( D(111) = 0.95 \), then the simulated coherent fraction lies within the error bar of the experimental value of \( f_c(5-\text{Cl}) = 0.57 \). This result clearly indicates an almost perfect crystalline order of the lanthana film grown on chlorine passivated Si(111).

Further information on the atomic arrangement of the lanthanum atoms perpendicular to the Si(111) diffraction planes in the lanthana film (5-Cl) is gained by performing XSW measurements in (111) geometry employing La3d5/2 photoelectrons as secondary signal, which were recorded at a photon energy of 3.35 keV (see Fig. 6(b)). Because generally the escape depth of photoelectrons in a certain material (in the order of Ångströms to nanometers) is far less than the escape depth of photons (in the order of several µm), the XSW photoelectron measurement is more sensitive to the atomic ordering of the uppermost lanthana layers while the x-ray fluorescence measurement equally probes the entire film. The coherent fraction employing La3d5/2 photoelectrons amounts to \( f_{\text{La3d5/2}}(5-\text{Cl}) = 0.70 \) and is substantially higher than the corresponding coherent fraction \( f_{\text{LaL3}}(5-\text{Cl}) = 0.57 \). Extrapolating from the previous discussion for cerium oxide 3d photoelectrons, this difference cannot be solely explained solely by non-dipole effects and suggests a structural origin. This finding is a first indication for the lanthana film exhibiting a higher crystalline order in the upper layers than near the interface. However, this difference is still relatively small if one takes into account non-dipole effects on the order of about 8%. Furthermore, the coherent fraction deduced from the fluorescence data is close to the simulated value of \( f_c(\text{sim.}) = 0.614 \), the partial derivative of the crystalline order of the lanthana film in the vertical direction is close to zero, i.e., the variation in crystallinity along the vertical direction is almost negligible. Concluding this discussion, we note that the overall crystallinity of the lanthana film is very high, underlining the beneficial effect of chlorine passivation on oxide crystallinity.

To study the behavior of chlorine in the lanthana growth process we employed XPS and XSW on the Cl1s core level before and after lanthana deposition. Lanthana was deposited at 500°C and on oxygen background pressure of 5 × 10⁻⁷ mbar. Fig. 7(a) shows the XSW data, which are normalized Cl1s photoemission spectra recorded at 3.35 keV photon energy. The Cl1s photoemission intensity after lanthana growth is only slightly decreased. Since the Cl1s photoelectrons exhibit a kinetic energy of about 528 eV, the inelastic electron mean free path in La2O3 is approximately 1 nm as derived from the TPP2M formula. Therefore, Cl1s photoelectrons originating from chlorine atoms bound at the interface of the 1.8 nm thick lanthana film should be attenuated by a factor of \( e^2 \). From this analysis of the Cl1s spectra we infer that the chlorine atoms almost completely segregate to the surface of the La2O3 film during growth. These findings are supported by the Cl1s XSW data, which are displayed in Fig. 7(b). While the yield collected before lanthana deposition essentially describes the expected Cl on-top site identified in previous investigations we note a drastic change in the overall shape of the inelastic secondary signal after lanthana growth, which quantitatively results in variations from \( f_{\text{Cl1s}} \) from 0.72 to 0.30 and \( \Phi_{\text{Cl1s}} \) from 0.78 to 0.45 after oxide growth. The strong decrease in the coherent fraction together with the change in the coherent position prove a binding site change of the chlorine atoms during growth, in total agreement with the XPS results. Therefore we conclude that chlorine acts as surfactant and that the interface passivation appears to be less stable. This finding is in contrast to the role of chlorine during ceria growth at the same preparation conditions, where chlorine was shown to mainly remain at the interface, thereby act-

FIG. 7. (Color online) (a) Cl1s photoemission spectra of chlorine-terminated Cl/Si(111)-(1 × 1) recorded at 3.35 keV photon energy and after deposition of 1.8 nm of lanthana grown at 500°C substrate temperature in an oxygen background pressure pressure of 5 × 10⁻⁷ mbar. (b) XSW data (open symbols) obtained in Si(111) Bragg reflection using Cl1s photoelectrons and theoretical fit according to the dynamical theory of x-ray diffraction (solid lines) for the two preparation steps described in (a).
In conclusion the presented data for lanthana films grown at preparation conditions (5-Cl) and (5) clearly show higher crystallinity with strongly decreased silicate formation at the interface for the chlorine passivated growth. Furthermore, a detailed analysis of the (5-Cl) lanthana film proves that chlorine segregation during growth is an intricate interplay between the RE metal and the adsorbate.

In this section we present first results for the growth of REOx multilayers on chlorine-passivated Si(111) using the example of cerium oxide growth on lanthana de-passivated growth experiment (Sec. III A), the cerium oxide film was grown at a substrate temperature of 500 °C and an oxygen partial pressure of 5 mbar on Cl-passivated Si(111).

When comparing the coherent fractions and the coherent positions of the LaLo yields of the multilayer film and for the initial lanthana layer on Cl/Si(111)-(1×1), a change of ∆fLaLo = 0.05 is observed in the coherent position while the respective coherent fraction changes only by ∆fCeLo = 0.02, meaning that only the coherent position of the LaLa inelastic signal undergoes a statistically significant, yet rather subtle change. However, the situation is completely different when employing La3d5/2 photoelectrons as secondary signal (Fig. 8(b)), which exhibit a coherent fraction of fCeLa3d5/2 = 0.87 and a coherent position of ΦCeLa3d5/2 = 1.05 after cerium oxide deposition. When compared to the respective values before cerium oxide growth, these findings reveal a substantial increase in the coherent fraction of ∆fLa3d5/2 = 0.17 while the coherent position stays the same within the error bar. Likewise, the difference in the coherent fraction between the fluorescence data and the photoelectron signal of the lanthana film in the rare-earth oxide multilayer is even increased to ∆fLaLo = 0.32, which remains at more than 0.24 even if we again assume non-dipole effects in the order of 0.08. Hence, these differences in the Fourier components for the individual secondary signals can only be related to significant structural changes within their respective sampling depths. This indicates that the top lanthana layers have become very highly ordered, as revealed by the La3d5/2 XSW measurement, as a side effect of the growth of cerium oxide. This “healing” of the topmost La2O3 layers has to be counterbalanced by a respective loss of crystallinity in the lowest layers near the interface, so that the overall epipalxial quality of the lanthana film, which is monitored by the LaLa inelastic signal, may stay the same.

To get an even more detailed insight into this crystallinity gradient of the lanthana film we performed quantitative XSW simulations taking into account the finite escape depth of the La3d photoelectrons with a kinetic energy of 2.5 keV in La2O3. Applying the TPP2M formalism yields a value of λLa2O3 (2.5 keV) = 3.95 nm. The attenuation of the photoelectrons due to the cerium oxide film and the associated change in probing depth can be neglected since the corresponding attenuation factor e−dLa2O3/λCe2O3 is the same for all photoelectrons that are emitted from the lanthana film. Therefore, the existence of the ceria film does not influence the coherent fraction and coherent position of the La3d XSW results. The first result of the XSW simulations shows that the calculated value for λLa2O3 is too high to explain the large difference of ∆fLaLo = 0.24 between the fluorescence and the photoelectron XSW data of a 1.8 nm thick La2O3 film. This is in agreement with the energy range of the experimental data.
accordance with spectroscopic investigations of slightly thicker ceria films grown on Si(111), where we find an inelastic electron mean free path that is about half of the calculated value by the TPP2M formula. Hence, in the following analysis we assume a value of $\lambda_{\text{La}_2\text{O}_3}(2.5\text{ keV})/2$ and additionally take into account the geometry of our experimental setup, where the photoelectrons leave the sample in an off-perpendicular direction to the surface leading to a further attenuation of photoelectrons. Our XSW simulations reveal that the assumption of a laterally fully strained $\text{La}_2\text{O}_3$ film with a trilayer spacing of 3.45 Å also cannot explain the difference in the coherent fractions of the fluorescence and the photoelectron data. In the following estimation we assume a $\text{La}_2\text{O}_3$ film with 6 O-La-O trilayers with a smaller trilayer spacing of 3.23 Å, which corresponds to a vertical lattice constant expansion of 3% compared to the vertical Si(111) lattice periodicity. A simple numerical model, which takes into account a variation of crystalline order in [hkl] direction, is then implemented by associating each trilayer (TL) in the lanthana film with a depth-dependent disorder parameter $C_i \in [0, 1]$, with $i$ representing the TL index as counted from the interface. Within this approach, a quite abrupt crystallinity gradient can be realized in the following way: $C_1 = 0$, $C_2 = 0.05$, $C_3 = 0.5$, $C_4 = 1$, $C_5 = 1$, and $C_6 = 1$. Here, the extremal values 0 and 1 represent total structural disorder and perfect bixbyite crystallinity, respectively. This model leads to coherent fractions of $f^{\text{sim.}}_{\text{La}_2\text{O}_3, \text{TL}_{i+2}} = 0.72$ and $f^{\text{sim.}}_{\text{La}_2\text{O}_3, \text{TL}_{i+3}} = 0.55$, i.e., a difference of $\Delta f^{\text{sim.}} = 0.17$, with an according difference of the coherent position of $\Delta \Phi^{\text{sim.}} = 0.01$, in agreement with the experimental results for $\Delta \Phi^c$.

Although our simulations cannot completely reproduce a difference in the coherent fractions of the photoelectron and fluorescence inelastic secondary signal of $\Delta f^c = 0.24$, it clearly reveals the presence of perfectly ordered bixbyte trilayers in the upper part of the $\text{La}_2\text{O}_3$ film in the rare-earth oxide multilayer structure and essentially disordered layers close to the interface to the underlying silicon. Although $\Delta f^{\text{sim.}}$ does depend on the assumed trilayer spacing as well as trilayer disorder, the result for the crystallinity gradient always shows the following behavior: Few layers at the interface are amorphous, while the upper layers are highly ordered. The transition between total disorder and nearly perfect crystallinity takes place in the regime of one or two trilayers and is therefore very sharp.

From the quantitative XSW simulations of the $\text{La}_2\text{O}_3$ film we conclude that upon the growth of cerium oxide at elevated temperatures of 500°C and an oxygen background pressure of $5 \times 10^{-7}$ mbar the lanthana trilayers closer to the silicon interface lose crystalline order while the upper trilayers in the film become perfectly ordered. This result is corroborated by the O1s HAXPES data displayed in Fig. 9(a) and (b), which were recorded at 3.35 keV incident photon energy for the lanthana film grown on Cl/Si(111)-(1×1) and for the cerium oxide on lanthana REOx multilayer, respectively. The experimental spectra were fitted with three Voigt line shaped oxygen species: an oxygen species in a REO$_x$ chemical environment (REO$_x$), a silicate species (Si-O-RE), and an silicon oxide species (SiO$_x$). In the fitting procedure, the relative binding energies as referred to the REO$_x$ species were assumed to be shifted by 1.0 eV (Si-O-RE) and 2.1 eV (SiO$_x$), resulting in only slight deviations from the values published for ceria grown on Si(111) previously. The Lorentzian width was set to 0.15 eV while the Gaussian width was adapted to fit the experimental resolution.
species to 1, the integrated intensity of each species is 0.61 (REO₂), 0.29 (Si-O-RE), and 0.10 (SiO₂) for the O1s spectrum recorded prior to ceria growth (Fig. 1(a)). After cerium oxide deposition (Fig. 1(b)), the integrated intensities amount to 0.65 (REO₂), 0.22 (Si-O-RE), and 0.14 (SiO₂). Since the total film thickness is increased by a factor of 4/3 from 1.8 nm to 2.4 nm due to the deposition of the cerium oxide film, one would expect the following integrated intensities if the amounts of Si-O-RE and SiO₂ species were not altered during cerium oxide deposition and intensity attenuation due to a finite escape depth of the O1s photoelectrons: 0.68 (REO₂), 0.24 (Si-O-RE), 0.09 (SiO₂). Although the deconvolution of the O1s spectrum results in an error of the normalized intensity of approximately ±0.01, the deviations of the actual intensities of the oxygen species after growth from the expected intensities are significant and would be even larger if taking into account the attenuation of the photoemission signal of the interface species. This means that we do observe a ripening process at the interface that is mainly accompanied by silicon oxide formation during cerium oxide deposition due to elevated substrate temperatures (500 °C) and the exposure to oxygen at partial pressures of $5 \times 10^{-7}$ mbar. Hence, the increase of amorphous silicon oxide species at the interface inferred from the HAXPES data is in very good agreement with the decrease in crystalline order of the lanthana layers at the interface, which is deduced from the analysis of the coherent fraction of our XSW results. In addition, the increased coherent position ($\Delta \Phi_x = 0.05$) of the fluorescence XSW data displayed in Fig. 2 and Fig. 3 suggests that the lanthana film is pushed slightly outwards as compared to the Si(111) diffraction planes, which could be a side effect of the oxidation of the silicon substrate.

After having discussed the epitaxial quality and the ripening of the interface of the rare-earth multilayer we finally discuss the spectroscopic investigation of the Ce3d core level in Fig. 4(c) of the ceria film, which is striking, because it also reveals a Ce³⁺ oxidation state. As it is known ultrathin ceria films on silicon exhibit the Ce³⁺ oxidation state. The transition from the Ce³⁺ to the Ce⁴⁺ oxidation state is supposed to take place with increasing film thickness while the interfacial layers stay in the Ce³⁺ oxidation state. Since Ce catalyzes the formation of silicon oxide and silicate, it can be understood why ceria on silicon exhibits the Ce³⁺ oxidation state at the interface and oxidizes with increasing film thickness. But here, we present data of ultrathin epitaxial ceria in the Ce³⁺ oxidation state grown on La₂O₃, which should decouple the cerium oxide film from the silicon support. Intriguingly, at the same preparation conditions and for ceria islands up to 2 nm, we find that ceria on Ru(0001) can easily be oxidized. Hence, the question arises why ceria on lanthana exhibits the Ce³⁺ oxidation state. While we cannot provide a definitive answer, a possible driving force could be the very small lattice mismatch of C-type Ce₂O₃ ($a = 11.16$ Å) and C-type La₂O₃ ($a = 11.36$ Å) which would constrain the ultrathin ceria film to pseudomorphic growth in the Ce₃O₃ phase.

To summarize this section, we have shown that ceria can be grown on lanthana deposited on chlorine passivated Si(111) with comparable epitaxial quality. Furthermore, it could be revealed that the lanthana film becomes almost perfectly ordered in the upper layers during ceria deposition, while the layers at the interface show crystalline order due to the ripening of silicon oxide species. Finally, we demonstrated that ultrathin ceria films also grow in the Ce³⁺ oxidation state on lanthana.

IV. CONCLUSION

We have presented a detailed study on the adsorbate-mediated growth of rare-earth oxides on Si(111). Based on synchrotron-based x-ray photoemission and x-ray standing wave investigations we have demonstrated that the specific type of chemical passivation of the silicon substrate appears to be crucial in obtaining high-quality, epitaxial rare-earth oxide films in molecular beam epitaxy. Among the passivating agents (Cl, Ag, Ga) tested, chlorine yielded the highest degree of REOₓ film crystallinity combined with a well-ordered oxide-semiconductor interface exhibiting only a very low concentration of silicon oxide and silicate species. Quite surprisingly, gallium preadsorption yields the same degree of oxide crystallinity compared to cerium oxide growth on the bare Si(111) surface, whereas passivation with silver even drastically decreases the crystalline order of the cerium oxide film.

Furthermore, the HAXPES and XSW results illustrate that the quality of the cerium oxide films achieved is always tied to the structural and chemical properties of the oxide-silicon interface. Only in the case of Cl, it is sharp and well-ordered with suppressed silicon oxide and silicate species while in the other cases it was shown to comprise considerable amounts of amorphous silicon oxide and silicate species.

The use of Cl passivation was also shown to be essential in obtaining high-quality films of ultrathin lanthana on Si(111). In this case, the Cl segregates to the surface of the lanthana film, rendering the lanthana-silicon interface very susceptible to ripening during further thermal treatment. Hence, the role of chlorine as growth modifier depends on the specific rare-earth oxide that is grown via molecular beam epitaxy: Only in the case of cerium oxide the Cl atoms mostly remain at the interface, hence acting as interfacant. However, for both lanthana and praseodymia the Cl changes its adsorption site and takes on the role as surfactant.

The results for the cerium oxide on lanthana multilayer reveal that both rare-earth oxide films exhibit comparable crystallinity with very limited intermixing. Furthermore, despite the coupling from the substrate cerium oxide grows in the Ce³⁺ oxidation state. Detailed X-ray standing wave simulations of the rare-earth oxide multi-
layer show that a ripening process occurs at the interface between lanthana and silicon, which is documented by an increase in amorphous silicon oxide species and which leads to a vertical crystallinity gradient in the lanthana film. However, cerium oxide growth is also concomitant with an almost perfect ordering of the upper lanthana bixbyite trilayers.

The superior crystallinity of rare-earth oxide films when grown on Cl-passivated Si(111) is accompanied with a sharp and ordered interface with suppressed silicate and silicon oxide species. In terms of application, this way of tuning the structural properties of an epitaxial oxide-silicon interface might represent an important step toward low interface trap densities and minimized carrier scattering, eventually allowing for their integration as high-\(k\) gate oxides.

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