Growth and thermal properties of ultrathin cerium oxide layers on Rh(111)

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Abstract

Ultrathin layers of cerium oxide have been deposited on a Rh(1 1 1) surface and their growth morphology, structure, and thermal stability have been investigated by LEED, STM, XPS, and valence band resonant photoemission. STM and LEED indicate that the ceria grows epitaxially in form of ordered CeO$_2$ islands at elevated substrate temperature (250–300 °C), with (1 1 1) faces parallel and orientationally aligned to the main azimuthal directions of the substrate. The ultrathin ceria films contain significant amounts of reduced Ce$^{3+}$ species, which appear to be located predominantly at the ceria–Rh interface. For thicker films (>6 equivalent monolayers) stoichiometric CeO$_2$ is detected in XPS. Vacuum annealing produces morphologically well-defined hexagonal islands, accompanied by partial reduction and the formation of oxygen vacancies at the ceria surface. The thermal stability and the degree of reduction is a function of the oxide layer thickness, with thinner layers being thermally less stable. At temperatures >800 °C, the ceria decomposes and Ce–Rh alloy phases are identified.

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1. Introduction

Cerium oxide and Rh are important components of the three-way catalyst used in commercial catalytic converters for automotive emission control. The addition of ceria improves the performance of the group VIII metals of the catalyst and a combination of various favourable factors has been ascribed to the promoting role of ceria [1]. One outstanding property of ceria is certainly its reversible oxygen storage capacity, which provides oxygen to the gas mixture during fuel-rich cycles and absorbs oxygen in the fuel-lean cycles. The key factor for the latter property is the Ce$^{4+}$ ↔ Ce$^{3+}$ redox pair, which allows for an easy release or uptake of oxygen by providing a source or sink of electrons. Also, the interactions at the interface between the ceria and the noble metal may add to the promoting role of ceria by enhancing the catalytic activity for CO oxidation [1], perhaps via the creation of active sites at the oxide–metal boundary [2].

In order to understand these interactions at a fundamental level a number of surface science studies of cerium oxide films on single crystal surfaces of group VIII noble metals, such as Ni(1 1 1)
[3], Pd(111) [4], Pt(111) [5,6], Ru(0001) [3], and Rh(111) [7] surfaces, have been performed. A common result in these studies is that the formation of well-ordered cerium oxide overlayers has been detected, which are rotationally aligned by the orientation of the substrate [3–6]. This epitaxial growth is surprising in view of the overall large lattice mismatch between the oxide and the metals (e.g. ~39% in the case of Pd(111)). The cerium oxide phases displaying hexagonal LEED patterns are generally associated with fluorite-type CeO$_2$(111) structures, although defective CeO$_2^{1-x}$ surfaces, with the Ce$^{3+}$/Ce$^{4+}$ ratio depending on preparation and annealing conditions, have been reported.

We have fabricated thin cerium oxide overlayers on Rh(111) with the aim to elucidate the role of the metal–oxide interface in the defect formation process on Ce oxide surfaces and in the creation of active sites at the metal–oxide phase boundary. Here we report the general growth characteristics of Ce oxide, the structures, and the temperature stability of the oxide phases on Rh(111) as investigated by scanning tunneling microscopy (STM), LEED, and X-ray photoelectron spectroscopy of core and valence states. A microscopic study of the defect formation process will be the subject of a subsequent publication [8].

We find that Ce oxide on Rh(111) grows initially in form of double layer islands which percolate, and, as on other group VIII metal (111) surfaces, develops well-ordered rotationally aligned crystallites of CeO$_2^{1-x}$; for nominal layer thicknesses >6 equivalent monolayers (MLE) stoichiometric CeO$_2$ is formed under the deposition conditions employed. The surface phase diagram of ceria on Rh(111) as investigated by scanning tunneling microscopy (STM), LEED, and X-ray photoelectron spectroscopy of core and valence states. A microscopic study of the defect formation process will be the subject of a subsequent publication [8].

2. Experimental

The experiments have been performed in two different ultrahigh vacuum (UHV) systems, with base pressures $\sim 1 \times 10^{-10}$ mbar in both systems. The STM experiments were carried out in a custom-designed three-chamber UHV system equipped with a room temperature STM (Omicron micro-STM), sample preparation and LEED/AES facilities as described previously [9]. The STM was operated in the constant-current mode, with sample biases between $-2$ and $+2$ V and tunneling currents 1–1.5 nA. Typically, higher biases were used for imaging thicker oxide films, whereas biases $<1$ V were employed for high-resolution imaging of the thin ceria layers. The Rh crystal was mounted on a Mo sample plate and was heated indirectly by electron bombardment from the back side. The crystal temperatures were determined by thermocouple readings in separate calibration experiments and preset heating powers were used subsequently. The temperatures given in the STM experiments are accurate to $\pm 20$ °C.

The photoemission spectra were measured in a multi-chamber custom-designed high-resolution electron spectrometer, with a Scienta SES 200 analyser and a preparation chamber containing sample cleaning, evaporation and LEED facilities as reported elsewhere [10]. The photoelectrons of core levels (Ce 3d) were excited with a conventional laboratory X-ray source (Mg K$_\alpha$). The valence band spectra were recorded with photon energies around the Ce 4d–4f resonance, i.e. with 125 eV for on-resonance spectra and 110 eV for off-resonance spectra, at the synchrotron radiation facility ELETTRA in Trieste, Italy. For this purpose the Scienta spectrometer was attached to the Materials Science beamline, operated by the Czech Academy of Sciences in cooperation with ELETTRA, and a combined energy resolution (SX 700—type monochromator plus spectrometer) of $\sim 150$ meV has been employed. The photoelectron spectra were taken in normal-emission geometry with photons incident at 47° with respect to the surface normal. Both on-resonance and off-resonance spectra are in the broad Cooper minimum region of the Rh 4d emission cross-section. The Rh sample in this system was also heated by electron bombardment from the back side. However, the crystal temperatures were measured directly with a chromel–alumel thermocouple spot-welded to the edge of the crystal. The
temperatures given in the XPS experiments are therefore accurate to ±5 °C.

The clean Rh(111) substrate surface was prepared by Ar⁺ ion bombardment and annealing at 1000 °C, and heating cycles in O₂ followed by a final anneal at 1100 °C. The cleanliness of the Rh(111) surface was checked by XPS, AES and LEED. Cerium oxide overlayers were deposited by reactive evaporation of cerium metal in 2 × 10⁻⁷ mbar O₂ onto the Rh(111) surface at a temperature of 250 °C. The cerium evaporation rate was monitored by a quartz crystal microbalance and a typical evaporation rate was ~0.5 monolayer·min⁻¹. Since the actual oxide coverage depends on the morphology and oxidation state of the oxide overlayer, which in turn varies as a function of coverage, only relative cerium oxide coverages will be given in this paper in terms of MLE, which correspond to the evaporated amount of Ce as referred to the density of Rh(111) surface atoms (1.59 × 10⁻¹⁵ atoms cm⁻²). Note that a single monolayer of CeO₂(111) on the Rh(111) surface corresponds to ~0.5 MLE. After careful outgassing of the cerium evaporator contamination-free Ce-oxide/Rh(111) surfaces have been routinely obtained. In the annealing experiments the surfaces were kept for 10 min at the indicated temperatures.

3. Results and discussion

3.1. The surface phase diagram of cerium oxide on Rh(111)

The Ce-oxide/Rh(111) surface phase diagram is shown in Fig. 1(a) as a plot of the regions of stability of the various overlayer phases as observed by LEED and STM. It gives an overview of the stability of various surfaces and oxide structures as a function of oxide coverage and annealing temperature. At the deposition temperature of 250 °C and low oxide coverages (<0.6 MLE) the Ce oxide is disordered and the (2 × 2) structure of chemisorbed oxygen is the only ordered LEED pattern. The Ce oxide remains poorly ordered after evaporation at 250 °C in the coverage range θ_{OXIDE} = 0.6–1.5 MLE, but improvement of order is detected for T > 300–350 °C, where a so-called (1.4 × 1.4) pattern is appearing in LEED. A representative LEED pattern is reproduced in Fig. 1(b), image A. In the region θ_{OXIDE} ~ 0.6–1.9 MLE, T ≈ 300–550 °C, the (1.4 × 1.4) pattern is accompanied by satellite reflexes, which are interpreted in terms of double scattering between the thin Ce oxide islands and the Rh substrate as discussed below in Section 3.3. For T ≈ 550–750 °C, θ_{OXIDE} ~ 0.6–2.5 MLE, the satellites of the (1.4 × 1.4) pattern disappear, which may be understood by the increasing Ce oxide island thickness, as a result of ripening processes at the elevated temperatures as observed by STM.

The (1.4 × 1.4) pattern (Fig. 1(b), A) consists of the Rh(111)1 × 1 reflexes (the outer hexagon) and of the reflections from the ordered Ce oxide island surfaces (the inner hexagon). Obviously, the scattering from the Rh(111) and from the Ce oxide surfaces are superimposed incoherently at this growth stage. The lattice constant of the Ce oxide is measured to 3.85 ± 0.05 Å from the LEED image, which is consistent with both the CeO₂(111) surface lattice (3.89 Å) and the Ce₂O₃(0001) surface (3.82 Å). Thus, the measurement of the surface lattice constant does not allow to distinguish between the two possible CeO₂ and Ce₂O₃ oxide surfaces. However, as argued below, the combined experimental evidence is in favour of the formation of CeO₂(111) surfaces, and we attribute the hexagonal array of the Ce oxide derived (1.4 × 1.4) LEED reflexes therefore to scattering from CeO₂-(111)-type island surfaces. The sharp (1.4 × 1.4) pattern indicates clearly that the CeO₂ crystallites are well ordered and rotationally aligned with the principal azimuth directions of the substrate. For oxide coverages ≥ 3.2–3.8 MLE the CeO₂-(111)1 × 1 spots are observed exclusively (see Fig. 1(b), B), indicating that the Ce oxide islands have reached the coalescence stage.

For T > 700–750 °C the Ce oxide decomposes and Ce–Rh surface alloy structures are formed. The decomposition temperature is a function of the oxide coverage, and oxide islands and surface alloy phases can coexist up to T ≈ 850 °C. For low θ_{OXIDE} ≤ 2.5 MLE and T > 850 °C a (2 × 2) alloy LEED pattern is observed (not shown), but in the region C of the phase diagram of Fig. 1(a) the
Fig. 1. (a) Surface phase diagram of cerium oxide on Rh(1 1 1), showing the stability regions of overlayer phases as a function of oxide coverage and annealing temperature. A–F mark regions where corresponding LEED photographs are given in (b). (b) LEED photographs of: (A) (1.4 × 1.4) pattern, electron energy $E = 84$ eV; (B) CeO$_2$(111)1 × 1 pattern, $E = 84$ eV; (C) CeO$_2$(11 1)1 × 1 + satellites plus (2 × 2) pattern, $E = 44.6$ eV; (D) CeO$_2$(1 1 1)1 × 1 plus (4 × 4) pattern, $E = 33$ eV; (E) (4 × 4) pattern, $E = 45.3$ eV; (F) CeO$_2$(1 1 1)1 × 1 plus (4 × 4) + satellites pattern, $E = 32.6$ eV.
LEED pattern contains the \((1.4 \times 1.4)\) pattern with a complex satellite structure plus the \((2 \times 2)\) pattern (see Fig. 1(b), C), which is indicative of the coexistence of Ce oxide, Rh(1 1 1), and alloy areas. For higher oxide coverages \((\theta_{\text{OXIDE}} > 2.5 \text{ MLE})\) and \(T = 650–800 \, ^\circ\text{C}\) a \((4 \times 4)\) Ce–Rh surface alloy structure coexists with the CeO\(_2\)(1 × 1) pattern (see Fig. 1(b), D; note that the CeO\(_2\) 1st order spots coincide with the \((4 \times 4)\) 3/4th order spots), whereas for \(T > 850 \, ^\circ\text{C}\) the oxide is decomposed completely and the \((4 \times 4)\) alloy pattern solely remains (Fig. 1(b), E). Fig. 1(b), image F, displays a LEED pattern which has been recorded for a 13 MLE oxide coverage at \(\sim 800–850 \, ^\circ\text{C}\), showing both CeO\(_2\)(1 × 1) spots and \((4 \times 4)\) alloy spots with a complicated satellite structure; this again indicates the coexistence of oxide (albeit in a reduced state, see Section 3.3) and alloy phases.

In the following, it is convenient for the purpose of presentation to separate the discussion of the data into three subsections. In Section 3.2 we will investigate the growth pattern of ceria on Rh(1 1 1) as evaporated at 250 \(^\circ\text{C}\), and in Section 3.3 we will discuss the partial reduction of the ceria at elevated temperature, i.e. up to \(T \leq 800 \, ^\circ\text{C}\). In Section 3.4 we will then briefly comment on the oxide decomposition and on the formation of Ce–Rh alloy phases.

### 3.2. The growth of ceria on Rh(1 1 1) at 250 \(^\circ\text{C}\)

The growth conditions of ceria employed in this study have been determined with the objective of obtaining ordered overlayers, which are as fully oxidised as possible. A Rh substrate temperature of 250 \(^\circ\text{C}\) and an oxygen pressure of \(2 \times 10^{-7} \, \text{mbar}\) provided the best compromise for achieving the desired overlayers, although fully oxidised CeO\(_2\) has not been obtained for the first few monolayers (see below). Fig. 2 shows large-scale STM images of cerium oxide on Rh(1 1 1) deposited at 250 \(^\circ\text{C}\). (a) \(\theta_{\text{OXIDE}} = 0.32 \text{ MLE}, \, V = 1.99 \, \text{V}, \, I = 0.81 \, \text{nA}\); (b) \(\theta_{\text{OXIDE}} = 1.3 \text{ MLE}, \, V = 2.03 \, \text{V}, \, I = 1.27 \, \text{nA}\); (c) \(\theta_{\text{OXIDE}} = 2.5 \text{ MLE}, \, V = 1.3 \, \text{V}, \, I = 1.05 \, \text{nA}\); (d) same as (c), \(\theta_{\text{OXIDE}} = 2.5 \text{ MLE}, \, V = 0.8 \, \text{V}, \, I = 1.53 \, \text{nA}\).
of Ce oxide on Rh(111) at various growth stages. In Fig. 2(a) and (b) areas of the Rh crystal surface have been imaged where many monoatomic steps separate terraces of ~200–400 Å width. Many small Ce oxide islands of ~20–50 Å average diameter are observed on the terraces for $\theta_{\text{oxide}} = 0.32$ MLE (Fig. 2(a)), no preferential step edge decoration is seen. For $\theta_{\text{oxide}} = 1.5$ MLE (Fig. 2(b)) the islands have percolated and the Rh surface is essentially covered by the oxide phase. At higher coverage, $\theta_{\text{oxide}} = 2.5$ MLE (Fig. 2(c)), the islands grow three dimensionally and their irregular shapes are clearly apparent. The magnified view of this surface in Fig. 2(d) confirms the irregular island boundaries, but also indicates the existence of some crystalline order within the island structures, in agreement with the observation of the $(1.4 \times 1.4)$ LEED pattern (see Fig. 1). The STM images of Fig. 2 in conjunction with the LEED data thus establish a kind of polycrystalline epitaxial growth [11] of the ceria on Rh(111). The adsorption of CO at room temperature on ceria/Rh(111) has been used to titrate the free Rh metal sites [12]. These experiments have established that the Rh surface is completely covered by the oxide at $\theta_{\text{oxide}} \approx 1$ MLE, which is consistent with the STM observations in Fig. 2(b). Using the areas of the CeO$_2$(111) and Rh(111) unit cells a full monolayer of CeO$_2$(111) on Rh(111) should correspond to $\theta_{\text{oxide}} \approx 0.5$ MLE. The fact that 1 MLE of ceria is necessary to completely cover the Rh(111) surface indicates that the ceria grows initially in form of a double layer oxide.

Fig. 3 presents the analysis of the Ce 3d XPS spectra recorded during the oxide growth process: the total Ce 3d XPS area is plotted versus the oxide coverage as derived from the evaporation rate and this represents the oxide uptake curve of the surface; the coverage regions, where the $(1.4 \times 1.4)$ and CeO$_2$(1 × 1) LEED patterns are observed, are also indicated. The uptake curve is consistent with the island growth mode, and the appearance of the CeO$_2$(1 × 1) LEED structure at ~3.5 MLE coincides with a marked decrease of the gradient of the uptake curve, indicating the point of coalescence of the oxide overlayer. The insert of Fig. 3 gives a plot of the percentage of Ce$^{4+}$ in the Ce 3d signal as a function of oxide coverage. The Ce$^{4+}$ percentage portion in the Ce oxide layer has been evaluated using the intensity (area) of the $f^0$ final state peak of the 3d$3/2$ spin–orbit component [13].

![Fig. 3](image)

Fig. 3. (a) Cerium oxide uptake curve: total area of Ce 3d XPS peaks versus the coverage, as evaluated from the deposition parameters. The range of observed LEED patterns is indicated. (b) Percentage of Ce$^{4+}$ species in the total Ce 3d signal versus oxide coverage.
at 916.5 eV binding energy, with the fully oxidised 13 MLE Ce oxide layer as a calibration point for CeO$_2$. The latter spectrum [12] is very similar to the corresponding published spectra for CeO$_2$ in the literature [7,14].

The data of Fig. 3 indicate that for oxide coverages up to 2.5 MLE significant amounts of reduced Ce$^{3+}$ species are present in the oxide overlayer. Similar observations, i.e. more reduced oxide phases in the proximity of a metal–oxide interface, have been frequently reported in the literature and have been ascribed to, amongst other effects, strong metal–metal bonding at the interface [15]. As an indication for strong metal–metal bonding the affinity to surface alloy formation may be taken, which is clearly strong in the case of the Ce–Rh system [16]. Ce3d spectra characteristic of fully oxidised CeO$_2$ films are obtained for $\theta_{\text{oxide}} \geq 6$ MLE. The fact that the oxide derived reflections of the (1.4 x 1.4) LEED pattern transform continuously into the CeO$_2$-(1 x 1) LEED pattern with increasing oxide coverage suggests that the Ce oxide overlayer grows from the beginning in the CeO$_2$ fluorite structure with the (111) orientation parallel to Rh(111). The Ce$^{3+}$ species may then be associated with oxygen defects, as indeed observed in the STM on the well-ordered Ce oxide islands formed at elevated temperature [8], or with a Ce termination of the oxide phase at the Ce-oxide/Rh interface. Support for the presence of reduced Ce$^{3+}$ atomic species at the interface is obtained from the resonant photoemission measurements as discussed below.

In concluding this section we mention that other oxide overlayer preparation methods, such as evaporation of Ce metal and postoxidation by O$_2$ exposure at various temperatures or oxidation of Ce–Rh alloy phases, formed by annealing of metallic Ce overlayers, have also been tested. Qualitatively similar results, i.e. epitaxially ordered Ce oxide films have been obtained. However, carbon free metallic Ce overlayers are difficult to prepare and the oxide films prepared by the latter methods are more prone to contamination and less completely oxidised than by using the single step reactive evaporation process.

3.3. Partial reduction of ceria on Rh(111) at $T \leq 800 \degree C$

Photoemission spectra of the valence band region of 1.3 MLE Ce oxide as deposited on Rh(111) at 250 °C (curves (a) and (b), “as-laid”) and after annealing at 600 °C (curves (c) and (d)) are displayed in Fig. 4. Spectra (b) and (d) have been excited with a photon energy of $h\nu = 125$ eV, i.e. at the giant 4d–4f resonance of Ce [17], whereas spectra (a) and (c) are the corresponding off-resonance spectra ($h\nu = 110$ eV). The spectra have been normalised at ~12.5 eV binding energy, where the secondary electron background is structureless. The as-laid oxide surface spectra show photoemission intensity from the Fermi energy to a binding energy of 2.5 eV, which is derived from the Rh substrate 4d band. The O 2p valence band extends from 2.5 to ~7.5 eV, whereas the spectral intensity between 15 and 25 eV is due to emission from the Ce 5p and O 2s shallow core states. The O 2p valence band shows different structure in the on-resonance (b) and off-resonance spectra (a): it appears that the peak at ~3.3 eV is enhanced in the on-resonance spectrum. Intensity enhancement is also observed in the Ce 5p region due to the resonance interference process. The O 2p valence band two-peak structure is consistent with the valence band of a bulk sample of CeO$_2$ as reported by Mullins et al. [14]. This supports our conjecture that the cerium oxide as deposited at 250 °C grows in a CeO$_2$ stoichiometry.

Applying reducing conditions to the Ce-oxide/Rh(111) surface by annealing to 600 °C in vacuum (curves (c) and (d)) introduces little changes in the O 2p valence band apart from an overall small shift to higher binding energy (~0.2 eV), however the appearance of the 4f derived emission at 1 eV below $E_F$ indicates reduction of some Ce$^{4+}$ (4f$^0$) to Ce$^{3+}$ (4f$^1$) species in the oxide. Note that the Ce 4f emission intensity in spectrum (d) is greatly enhanced at $h\nu = 125$ eV by the Ce 4d–4f resonance process as compared to the emission of the Rh substrate 4d valence band. This is clearly demonstrated by the off-resonance spectrum (c) from the same surface, where the 4f emission is not visible and only weak Rh 4d emission is observed between $E_F$ and 2.5 eV. The modifications of the
spectral profile of the O2p band between off-resonance and on-resonance spectra indicate that states in the lower binding energy part of the O2p band are coupled to Ce derived states with resonating behaviour at the Ce4d–4f resonance. We propose that the photoemission peak at \( E_{\text{g}} = 3.2–3.5 \) eV is due to O2p states hybridised with Ce valence states. Indeed, Ce derived states have been identified in this energy range of the O2p band in the first-principles electronic structure calculations of Skorodumova et al. [18] for CeO\(_2\).

The absence of 4f photoemission from Ce\(^{3+}\) species in the as-laid 1.3 MLE ceria spectrum of Fig. 4(a) and (b) is at variance with the Ce 3d XPS results in Fig. 3, where a Ce\(^{3+}\) contribution is clearly identified at this coverage. The role of the X-ray beam in reducing the ceria films has been investigated explicitly, but no photon induced reduction effects have been detected. We presume therefore that the different surface sensitivities in the two photoemission experiments are responsible for the different results. In the resonant photoemission experiment the photoelectron escape depth at \( E_{\text{g}} = 125 \) eV kinetic energy should be minimal and the probing depth should be confined to the surface layers of the oxide islands. Conversely, using MgK\(_\alpha\) radiation the Ce 3d photoelectrons have kinetic energies of the order of 350 eV with correspondingly larger escape depths: they can thus originate from both the outer surface of the Ce oxide islands and also from the interface to the Rh. This supports the conjecture that the contribution of reduced Ce\(^{3+}\) species in the as-laid Ce oxide overlayers originates from the ceria–Rh interface, as proposed previously [15]. The appearance of the 4f emission on the heated surface in Fig. 4(b) then testifies that Ce\(^{3+}\) species are formed at the surface of the ceria islands under the reducing conditions of the vacuum annealing process. Indeed, the formation of oxygen surface vacancies upon annealing is observed in the STM (see Fig. 6(d)).

The reduction by vacuum annealing of ceria overlayers on Rh(1 1 1) as followed by Ce 3d XPS spectra is summarised in Fig. 5. Here, the total Ce 3d XPS peak areas and the percentage of reduced Ce\(^{3+}\) are given as a function of annealing temperature for different Ce oxide coverages. The thick 13 MLE ceria film is essentially stable up to \( 800 \) °C (see total Ce 3d area), but reduction of
Ce$^{4+}$ to Ce$^{3+}$ becomes significant beyond 650 °C. At $T > 800$ °C the Ce 3d signal decreases rapidly indicating oxide decomposition, and the formation of Ce–Rh alloy phases and the loss of Ce from surface-near regions due to diffusion into the Rh bulk reduces the Ce content of the surface. The thermal stability of ceria on Rh(1 1 1) is a function of film thickness: the 3.8 MLE film starts to decompose at $\sim$650 °C, whereas for submonolayer coverages (0.9 MLE in Fig. 5) $T \approx 550$ °C marks the decomposition onset temperature. The reduction of Ce$^{4+}$ to Ce$^{3+}$ in the ceria follows the same trend, with the 0.9 MLE submonolayer film being most sensitive to moderate vacuum annealing temperatures. This coverage dependence reflects the influence of the Rh substrate, which enhances the tendency for reduction of the oxide in the proximity of the interface. Similar results have been reported in a previous investigation of ceria particles on Rh(1 1 1) [7]. The present STM observations support the XPS results of Fig. 5: on a 6.5 MLE ceria film no defects at the surface have been observed after annealing to 700 °C. This confirms the dominant influence of the ceria–Rh interface in the reduction process, and indicates that kinetic effects play a less important role in the thickness dependent stability of the cerium oxide overlayers.

The evolution of the morphology of ceria overlayers upon annealing in UHV is illustrated by the STM images of Fig. 6, by way of example for $\theta_{\text{oxide}} = 0.9$ MLE. Fig. 6(a) shows the surface after annealing at $\sim$475 °C. In comparison to the STM image from the as-laid surface (not shown) the 475 °C annealed surface shows first signs of agglomeration. The agglomeration is enhanced on further annealing to $\sim$585 °C (Fig. 6(b)), where larger oxide islands with defined boundaries are formed. After annealing at 680–700 °C well-ordered hexagonal crystallite structures have developed (Fig. 6(c)) with diameters of up to 200 Å. The high-resolution STM images of Fig. 6(d), taken from the top surface of a ceria island prepared similarly as in Fig. 6(c), confirm the crystalline order with a hexagonal lattice constant of 3.85 ± 0.05 Å and reveal a number of dark spots and patches due to oxygen vacancy defects. The latter are partly ordered and the result of reduction as discussed in Fig. 5. The formation of defects and their apparent long-range ordering will be the subject of a forthcoming publication [8]. STM images showing surface defects as in Fig. 6(d), though not
ordered, have been reported recently by Berner and Schierbaum for heated CeO$_2$ island surfaces on Pt(111) [19].

Summarising briefly this section, vacuum annealing of ceria overlayers on Rh(111) leads to a ripening of the oxide islands and to the formation of well-ordered hexagonal crystallite structures. Partial reduction of the oxide surfaces occurs and the concomitant creation of oxygen surface vacancies is confirmed by STM. The amount of reduction and the decomposition temperature of the Ce oxide is a function of the oxide layer thickness, indicating that the Rh(111) surface stimulates the reduction process.

At this point we would like to digress shortly and comment on a region in the phase diagram, between 0.6 and 1.9 MLE oxide coverage after moderate annealing, where a (1.4 × 1.4) LEED pattern with satellite spots is observed (see Fig. 1(a)). Corresponding LEED photographs are reproduced in Fig. 7(a) and (b) along with an STM image of the 0.9 MLE Ce-oxide/Rh(111) surface heated to 470 °C in Fig. 7(c). The STM measurement shows that the Ce oxide island shapes are still mainly random, but STM line profiles across the islands indicate that many islands are bilayer structures. The LEED pattern may then be interpreted in terms of multiple scattering effects between the oxide and the substrate structure, with the double scattering vector $\mathbf{g} = \mathbf{g}_{\text{CeO}_2} + \mathbf{g}_{\text{Rh}}$ generating the satellite spots. The schematic simulation of the LEED pattern in Fig. 7(d) illustrates the Rh(1 × 1) (solid circles) and the CeO$_2$(1 × 1) (open circles) reflections and the double scattering spots (grey circles). The LEED pattern thus reflects the internal order of the Ce oxide islands,
which is difficult to recognise in the STM because stable tunnelling conditions with atomic resolution were difficult to obtain from these surfaces.

3.4. Decomposition of ceria on Rh(111)—surface alloy formation

Ordered Ce–Rh surface alloy phases are formed by decomposition of ceria at \( T \geq 700–800 \) °C. At lower oxide coverages a \((2 \times 2)\), at higher oxide coverages a \((4 \times 4)\) LEED pattern is observed. LEED and O 1s XPS measurements indicate that below \( \sim 800 \) °C the surface alloys coexist with reduced CeO\(_2\), island structures, see e.g. the LEED pictures of Fig. 1(b) C, D, and F, where the CeO\(_2\)(1 \times 1) reflections have still high intensity. Resonance valence band photoemission spectra of 1.3 MLE Ce-oxide/Rh(1 1 1) in the as-laid state (a) and after annealing to \( \sim 850 \) °C ((b) and (c)) are displayed in Fig. 8. The as-laid surface spectrum is identical to Fig. 4(b) and shows Rh4d, O2p, Ce 5p, and O 2s emission bands. The on-resonance spectrum (c) of the annealed surface is significantly different from the as-laid surface spectrum, with an intense Ce4f\(^{1}\) emission at \( \sim 2 \) eV below \( E_F \) and a sharp peak at the Fermi level. The O2p band of ceria is replaced by a feature centred at \( \sim 5 \) eV, which shows no resonance coupling indicating oxygen chemisorbed on Rh sites of the alloy. The presence of oxygen at the surface after this treatment is confirmed by the O 1s XPS spectrum (not shown). The validity of resonance photoemission to probe surface processes becomes apparent by comparing the on-resonance (curve (c)) and off-resonance (curve (b)) spectra. In the latter the Ce4f emission is barely visible and the Rh4d
emission is unaltered with respect to the unannealed surface. The O\textsubscript{2}p emission is dominant in the off-resonance spectrum, but it indicates also that the oxide oxygen of ceria is replaced by a different oxygen species.

The interpretation of the on-resonance spectrum of Fig. 8(c) is straightforward. The formation of the Ce–Rh alloy phase with reduced trivalent Ce\textsuperscript{3+} species is confirmed by the Ce\textsuperscript{4f\textsubscript{1}} peak and the behaviour of the Rh\textsuperscript{4d} emission at the Fermi level. The resonance enhancement near \(E_F\) is the result of the hybridisation of Rh\textsuperscript{4d} states with Ce\textsuperscript{5d} states, and the concomitant coupling to the Ce\textsuperscript{4d–4f} resonance process. The presence of the O\textsubscript{2}p emission indicates that oxygen is still present at the surface at this temperature (see also the O\textsubscript{2}s feature at \(\sim\)22.5 eV), presumably in form of chemisorbed oxygen on Rh sites.

4. Conclusions

The growth morphology and structure and the thermal reduction of ultrathin ceria overlayers on Rh(1 1 1) have been investigated by LEED, STM, XPS, and valence band resonant photoemission with use of synchrotron radiation. The ceria grows in form of ordered CeO\textsubscript{2} crystallites following a Vollmer–Weber island growth mode, with (1 1 1) faces parallel and orientationally aligned to the Rh-(1 1 1) substrate. Ultrathin ceria layers (<6 MLE) contain significant amounts of Ce\textsuperscript{3+} species, which appear to be dominantly located at the ceria–Rh interface. For ceria films thicker than 6 MLE stoichiometric CeO\textsubscript{2} is detected in XPS. Annealing in vacuum leads to the formation of well-defined hexagonal island structures, accompanied by partial reduction and the formation of Ce\textsuperscript{3+} species at the surface with concomitant surface O vacancies. The degree of reduction depends on the oxide layer thickness, suggesting a promoting role of the ceria–Rh interface for the reduction process. At high temperature (>800 °C) the ceria decomposes and Ce–Rh surface alloy phases are detected. The surface alloying process is clearly identified in valence band resonance photoemission spectra.

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References