Growth of Ce on Rh(111)

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Abstract

We have studied the growth of cerium films on Rh(111) using STM (scanning tunneling microscopy), LEED (low energy electron diffraction), XPS (X-ray photoelectron spectroscopy) and AES (Auger electron spectroscopy). Measurements of the Ce films after room temperature deposition showed that Ce is initially forming nanoclusters in the low coverage regime. These clusters consist of 12 Ce atoms and have the shape of pinwheels. At a coverage of 0.25 ML (monolayer, ML) an adatom layer with a (2×2) superstructure is observed. Above 0.4 ML, Rh is diffusing through pinholes into the film, forming an unstructured mixed layer. Annealing at 250 °C leads to the formation of ordered Ce–Rh compounds based on the bulk compound CeRh$_3$. At a coverage of 0.1 ML, small ordered (2×2) surface alloy domains are observed. The exchanged Rh atoms form additional alloy islands situated on the pure Rh(111) surface, showing the same (2×2) superstructure as the surface alloy. At a coverage of 0.25 ML, the surface is completely covered by the surface alloy and alloy islands. The (2×2) structure is equivalent to a (111)-plane of CeRh$_3$, contracted by 6%. Annealing a 1 ML thick Ce layer leads to a flat surface consisting of different rotational domains of CeRh$_3$(100). The Rh needed for alloy formation comes from 50 A deep pits in the substrate. Finally we show that LEIS (low energy ion scattering) is not suitable for the characterization of Ce and CeRh films due to strong effects of neutralization.

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1. Introduction

Rare earth metal based materials exhibit a variety of physical properties that are of technological importance.

In the past, most of the studies concerning the Ce–Rh-system were made to understand the electronic properties of Ce metal and of Ce in Ce based compounds. The metal Ce has different stable phases with different valences. At low pressures and room temperature trivalent Ce is stable. In intermetallic compounds Ce is so called “mixed valent”. The 4f states of Ce hybridize with the conduction states of the alloying element. The valence is between trivalent (γ-like) and tetravalent (α-like), depending on the strength of hybridization. The appropriate description of the interaction of the 4f state and the conduction bands is discussed in different works. Extensive studies using X-ray photoelectron spectroscopies (XPS), X-ray absorption spectroscopy (XAS) or resonant photoemission (PE) of the α-like compounds

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CeRh$_3$ and CeRh$_2$ have been performed to investigate these effects [1–7].

The Ce–Rh-system is also of special interest in catalysis, as far as 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 favorable factors has been ascribed to the promoting role of ceria [8]. Because of the importance of ceria based catalysts studies of Ce film growth are a matter of particular interest.

Several studies of cerium thin films on transition-metal substrates showed that cerium forms an epitaxial overlayer on substrates where no stable bulk alloys are known, e.g. V and W [9,10]. On substrates where bulk intermetallics with Ce are known, e.g. Pt [11–13], Cu [14], Al [15], Pd [16], Ce reacts and is intermixing with the substrates forming interdiffusion layers already at room temperature. Annealing leads to the formation of ordered surface structures.

The Ce–Rh bulk phase diagram [17] includes seven stable Ce$_x$Rh$_y$ phases. Therefore intermixing is expected when Ce is deposited on Rh. Photoemission studies of Ce layers on polycrystalline Rh foils [16,18,19] and on a Rh(100) single crystal [20] prove this assumption. Ce is intermixing at room temperature and forms an ordered alloy film after annealing when deposited on Rh. Warren et al. [18] concluded from AES measurements of heated Ce overlayers on Rh foils an alloy stoichiometry of Ce$_3$Rh$_2$.

Schneider et al. [1] reported the formation of a surface compound with a (2×2) superstructure at 6.6–13.2 ML thick Ce film deposited on Rh(111) at room temperature and subsequently annealed to 827 °C. LEED and AES measurements suggested that the ordered surface structure was corresponding to the (111) surface of CeRh$_3$. Valence-band angle-resolved photoemission data of the films are in good agreement with LDA-LCAO band structure calculations of CeRh$_3$.

Tang, Lawrence and co-workers [12] have defined empirical rules for predicting which intermetallic compound will be generated by annealing a rare earth film deposited on a transition-metal substrate, with which intermetallic compounds are known. They state that at low coverages the stoichiometry of the intermetallic compound can depend on the initial coverage, but at higher coverages the compound formed at a specific annealing temperature is independent of the coverage. Secondly, the symmetry and orientation of the resulting compound has to be closely related to the symmetry of the substrate. Additionally, the lattice mismatch of the compound and the substrate should be small. For thicker films of rare earths a small mismatch can be accommodated at the interface and a stable compound can be grown on top of the mismatch region. If the structure is not determined by interfacial constraints, annealing will force the formation of the most stable compound with the highest free energy of formation. Furthermore, the compound with the higher transition-metal concentration shall be favored, in case that two compounds have similar free energies of formation.

In this work we report on the structure of Ce on Rh(111). We show that Ce is intermixing with the substrate at room temperature at coverages above 0.4 ML. Below 0.4 ML, Ce stays on top of the substrate. Annealing at 250 °C enforces alloying and leads to the formation of ordered surface structures based on the Ce–Rh compound CeRh$_3$.

2. Experimental

STM, AES, XPS, LEIS and LEED measurements were performed in an UHV-chamber with a base pressure below 5×10$^{-11}$ mbar. The STM measurements were performed using a customized commercial STM (Omicron μ-STM) with an electrochemically etched W-tip. All STM images were obtained in constant current mode with the sample negative. The Rh sample was prepared by 2 keV Ar$^+$ sputtering and annealing at 800 °C in a separate chamber (base pressure in the low 10$^{-10}$ mbar range). At this stage no impurities could be detected by AES and a sharp p(1×1) LEED pattern was obtained. Ce was deposited from a liquid nitrogen cooled electron beam evaporator after careful outgassing. The deposition rate, calibrated with a quartz crystal microbalance, was
0.1 ML/min (1 ML is defined here as the amount of atoms in one Rh(111) layer). During Ce evaporation, the pressure in the preparation chamber remained below $1.6 \times 10^{-10}$ mbar. For the XPS experiments we used a water cooled 300 W MgK$_\alpha$ source (15 kV anode voltage). LEIS measurements were carried out with 1 keV He$^+$ ions and 1 keV Ne$^+$ ions at a scattering angle of 90° and a current density of about 10 nA/cm$^2$, keeping the Rh crystal at RT. The LEIS measuring time was limited to 50 s for each spectrum in order to avoid modifying the surface by sputtering.

The Rh standard for calibrating the Rh LEIS signals was taken of the clean Rh(111). As we did not have a pure Ce crystal the Ce standard used was a 45 Å thick Ce film deposited on V(110), where no intermixing is occurring [9]. Detection of ions for LEIS and electrons for XPS was performed with a hemispherical energy analyzer.

3. Experimental results

3.1. Room temperature deposition

The growth mode of Ce on Rh(111) at room temperature was studied by coverage dependent AES measurements of up to 4 ML thick Ce layers. For these measurements the coverage was increased stepwise and the AES spectrum was taken after every deposition.

The roughly linear decrease of the Auger peak-to-peak-height (APPH) of the Rh$_{301\text{eV}}$ signal (Fig. 1a) and the increase of the APPH of the Ce$_{664\text{eV}}$ signal (Fig. 1b) indicate the growth of an adatom layer up to 0.4 ML. Above 0.4 ML, the tendency of the signals continues, but the slope decreases. The decrease of the Rh signal is very slow and shows a deviation from exponential decay. Even after deposition of 4 ML Ce the Rh signal has decreased by 44% only.

STM images of the Ce films show the following evolution of the surface structure. In the lower submonolayer range statistically distributed Ce clusters consisting of 12 Ce atoms, marked “1”, “2” and “3” in Fig. 2a, are visible. The clusters have the shape of pinwheels and the rotational direction is clock- or anticlockwise. We consider it likely that these clusters are pinned by defects or impurities. Furthermore, vacancies of seven Rh atoms, marked “4” in Fig. 2a, are produced. We also find a seam at the step edges (Fig. 2b). Although disordered, this seam has similar height as the pinwheels and is thus also attributed to a Ce layer. Increasing the Ce coverage up to 0.15 ML results in a higher density of the clusters but does not affect the small Ce seam. Simple counting of the Ce atoms on the STM images shows that about 35–55% of the overall coverage is bound in pinwheels. The seam at the step edges binds at maximum 5% of the remaining Ce. The linear increase of the Ce AES signal with Ce coverage in the range up to 0.4 ML shows that Ce does not diffuse into subsurface sites. We therefore conclude that the
rest of the deposited Ce atoms are mobile, either forming a 2D adatom gas or invisible due to a repulsive interaction with the tip [21]. Sometimes the remaining Ce is visible as scratches in STM images. LEED measurements at this coverage do not show any superstructures. Approaching 0.25 ML, diffuse \((2 \times 2)\) superstructure spots show up in LEED and also the STM images indicate an adatom layer with a \((2 \times 2)\) superstructure (Fig. 2c). With increasing coverage the clusters agglomerate and the whole surface is covered by a loosely bound \((2 \times 2)\) superstructure. Because of the weak binding of the adatom layer the Ce atoms of the \((2 \times 2)\) superstructure are mobile and can be moved by the STM tip. Therefore the Rh substrate lattice periodicity can be imaged in some places (Fig. 2c).

In the coverage regime above 0.25 ML the LEED spots of the superstructure are disappearing and the Rh\((111)\) substrate LEED pattern becomes weaker. At 1 ML no maxima, not even the Rh \(p(1\times1)\) spots, are visible. STM images at this coverage show a rough unstructured surface with 5 Å deep pits (Fig. 3).

### 3.2. Annealed films

The influence of annealing to 250 °C was investigated for coverages of 0.05, 0.1, 0.25 and 1 ML. In the submonolayer range, annealing leads to the formation of a surface alloy. The Ce clusters disappear completely. At 0.05 ML single embedded Ce atoms are visible in STM as higher features (Fig. 4a). By counting these atoms it can be shown that after annealing also the Ce atoms that were invisible before can be imaged. The embedded atoms are randomly distributed and in LEED no superstructure can be seen. With increasing coverage, a diffuse \((2 \times 2)\) superstructure shows up in

![Fig. 2. (a) and (b) STM images of 0.1 ML Ce deposited on Rh\((111)\) at room temperature. (a) Atomically resolved image \((71\times71\text{ Å}^2, 9 \text{ mV}/0.5 \text{ nA})\) showing the Rh substrate, a vacancy \((4)\) and Ce clusters having the shape of pinwheels with a rotational direction clockwise \((1,2)\) and anticlockwise \((3)\). The scratches are attributed to mobile 2D Ce adatoms. (b) Atomically resolved image \((45\times75 \text{ Å}^2, -2 \text{ mV}/1 \text{ nA})\) showing the disordered Ce seam at a step edge of the Rh\((111)\) substrate. (c) Atomically resolved STM image \((100\times100 \text{ Å}^2, -5 \text{ mV}/0.8 \text{ nA})\) of 0.25 ML Ce deposited on Rh\((111)\) at room temperature. In part of the surface the Rh substrate is visible because the Ce atoms of the \((2 \times 2)\) superstructure are weakly bound and can be moved by the STM tip.

![Fig. 3. STM image \((1000\times1000 \text{ Å}^2, -75 \text{ mV}/2.9 \text{ nA})\) of 1 ML of Ce deposited on Rh\((111)\) at room temperature. The surface is rough and a few pits are visible. The section profile is taken over one pit.](image-url)
LEED and also STM images illustrate the ordering at the surface (Fig. 4b). The surface alloy atoms are forming small areas with a local $(2 \times 2)$ superstructure. In addition, islands with the same $(2 \times 2)$ superstructure are forming, which consist of the Rh atoms expelled by the alloying process and those Ce atoms that are not incorporated in the substrate (Fig. 4b). The formation of these islands is a clear indication of surface alloying [22], while the absence of islands after deposition at room temperature without annealing tells us that the surface alloy does not form at room temperature. By counting the atoms it can be shown that all Ce atoms are visible in the topmost layer and therefore the pure Rh substrate has to be beneath the $(2 \times 2)$ alloy islands. At 0.25 ML (Fig. 4c) the whole surface is covered by the $(2 \times 2)$ surface alloy and the $(2 \times 2)$ alloy islands. At this stage the LEED pattern shows very sharp $(2 \times 2)$ superstructure spots. The binding energies in the XPS-spectrum of the $f^0$, $f^1$ and $f^2$ configurations [23,24] correspond to those of the XPS spectrum of CeRh$_3$ [5,6], as marked in Fig. 4d. 

Starting from a 1 ML thick Ce film, which exhibits a rough unstructured surface with 5 Å deep pits after room temperature deposition, the result of annealing at 250 °C is demonstrated in Fig. 5. The STM image in Fig. 5a shows a smoothed surface with 40 Å deep pits. The step height of the smooth surface is 2 Å, as shown in Fig. 5b. In atomically resolved STM images domains of a square superstructure with a side length of 4 Å are visible. The domains are randomly distributed (Fig. 6a). Fig. 6b shows a LEED
pattern of this surface. The LEED pattern indicates that three domains of the square structure rotated by 60° to each other are preferred (Fig. 6c).

The LEED maxima of these main domains are sharp in radial direction, but different rotational angles of the domains lead to a circular smearing

Fig. 5. STM images of 1 ML Ce deposited on Rh(1 1 1) at room temperature annealed at 250 °C. (a) 3000×3000 Å², −1 mV/0.7 nA. The insert shows a profile over three pinholes along the line. (b) 1000×1000 Å², −1 mV/0.7 nA. Domain boundaries are white. The section along the black line shows the interlayer distance of 2 Å.

Fig. 6. 1 ML Ce deposited on Rh(1 1 1) at room temperature annealed at 250 °C. (a) Atomically resolved STM image (100×200 Å², −5 mV/3.19 nA) showing the square structure in four domains with different orientations. The domain boundaries appear dark. (b) LEED pattern at 64 eV incident electron energy. (c) Reciprocal unit cells of the three main domains of the square structure. Small full circles indicate the resulting LEED maxima.
of the LEED maxima. The Auger signals of Ce\textsubscript{664 eV} and Rh\textsubscript{301 eV} show that the Rh concentration at the surface increases during annealing to 250 °C. While the Rh APPH increases by one third, the Ce APPH decreases by 13%. The change occurs abruptly when annealing at 250 °C and the signal does not change with longer annealing time.

3.3. Low-energy ion scattering experiments

As LEIS is widely used as a technique to determine the surface composition [25] we have also tried LEIS experiments to determine the surface composition of the different structures [26]. Unfortunately this undertaking was far from straightforward. The effects of neutralization were too strong and additionally varied for the different investigated surface structures. So these measurements did not give additional information regarding the surface composition for our system.

At first we investigated the Ce films with He\textsuperscript{+} projectile ions, for which we could not detect any Ce signal. So we tried to quantify the Ce concentration at the surface by looking at the decrease of the peak area of the Rh LEIS signal (Fig. 7a). It turned out that the decrease of the Rh signal was very strong, even for low Ce coverages, and not linearly depending on the amount of Ce (Fig. 7a). We attribute this to a strong neutralization of the He\textsuperscript{+} ions in the vicinity of Ce atoms, similar to the trajectory-dependent neutralization by Pb [27], but even more pronounced.

For the following experiments we used Ne\textsuperscript{+} ions, which are neutralized less efficiently. With 1 keV Ne\textsuperscript{+} ions it was possible to obtain a very weak Ce standard signal. Although the geometrical cross section of Ce is larger than the one of Rh, the Ce standard signal was less than 1% of the Rh standard signal (Fig. 7b).

Fig. 7c shows LEIS spectra of Ce on Rh(111). While the LEIS signal of 1 ML Ce at room temperature is identical to the Ce LEIS standard, the LEIS signal of 1 ML Ce after annealing to 250 °C is six times bigger than the Ce LEIS standard. This is surprising, as STM and AES measurements show that after annealing Rh is diffusing to the surface. Another unexpected result was the fact that the Ce signal of 0.25 ML Ce at room temperature was bigger than the Ce LEIS standard. In other words, the strength of the Ce signal is heavily
dependent on the local environment. These results can be explained by both strong resonant neutralization and by a change in the valence of the Ce. The probability for neutralization of the scattered ions by Ce atoms is high because the work function of Ce is only 2.9 eV [28] and so resonant neutralization can take place [29]. A similar case of valence-dependent neutralization was observed for Yb on Ni(1 0 0) by Andersen et al. [30]. Similar to the strong reduction of the Rh LEIS signal with He\(^+\) ions, we also attribute the disappearance of the Rh peak (Fig. 7c) with Ne\(^+\) ions to neutralization by neighboring Ce atoms on the incoming and outgoing trajectories [27].

We have to conclude that LEIS is not a suitable technique to determine the composition of the first layer if a material with extremely high neutralization, like Ce, is present. Our results indicate, however, that LEIS can be used to detect changes in the electronic structure of the Ce atoms.

4. Discussion

Concerning growth at room temperature, coverage dependent AES and STM measurements indicate that at low coverages, up to 0.25 ML, Ce is staying on top of the substrate, which is in agreement with the lower surface free energy of Ce compared to Rh [31]. For higher coverages the deviation from exponential decay of the APPH of the Rh\(_{301}\text{eV}\) signal is indicating either Stranski Krastanov growth or Rh diffusing to the topmost layers. As STM images of this coverages show a rough unstructured surface with 5 Å deep pits, but no islands corresponding to the coverage, Stranski Krastanov growth can be excluded. The pits are deeper than the thickness of the Ce layer and so they must be excavated by Rh diffusion into the film [32]. Thus, it can be concluded that, as the coverage is increased, a mixed interface is formed. The Rh substrate is diffusing through pinholes in the film and mixes with the Ce atoms, leaving pits in the substrate. The driving force for the interdiffusion is the tendency to form Ce–Rh bonds rather than Ce–Ce bonds, in other words the high enthalpy of alloy formation. The interdiffusion layer at room temperature is not ordered, however.

The monolayer alloy with a (2×2) superstructure, which evolves as very low Ce coverages are annealed to 250 °C, is geometrically equivalent to the (1 1 1)-plane of CeRh\(_3\), compressed by 6%. The XPS-measurements of these coverages shows that the electronic structure of Ce in this surface alloy is the same as in CeRh\(_3\) (Fig. 4d). Combining the STM, LEED and AES measurements of the annealed 1 ML thick Ce film indicates the formation of a stable Ce–Rh intermetallic compound with a square unit cell and an interlayer spacing of 2 Å. By comparing the planes of the bulk Ce–Rh phases with the square superstructure we can identify the structure as CeRh\(_3\) too. The (1 0 0)-plane of CeRh\(_3\) has a side length of the unit cell of 4.02 Å, which corresponds perfectly to the STM measurements. In [1 0 0]-direction the CeRh\(_3\) crystal has a stacking sequence of a mixed Ce–Rh-plane and a pure Rh plane in every other layer. The distance between two layers is 2.01 Å, which corresponds to the measured interlayer spacing (Fig. 5b). The fact that all domains look the same in STM, implies that always the mixed Ce–Rh layer is the topmost layer, with antiphase domain boundaries at the 2 Å-steps.

The formation of CeRh\(_3\)-like compounds is according to the empirical rules of Tang et al. [12]. First, the cubic AuCu\(_3\)-type compound CeRh\(_3\) has symmetry close to the fcc Rh crystal. From the symmetry point of view also the cubic MgCu\(_2\)-type compound CeRh\(_2\) would be a possible resulting compound. Since the thermodynamical data for the two intermetallic compounds are incomplete, an interpretation can be done with the help of the binary phase diagram [17]. CeRh\(_3\) is the intermetallic compound with the highest congruent melting point, which indicates that it is the most stable compound. Furthermore, the transition-metal coordination is higher and the Ce–Rh bonds are shorter for CeRh\(_3\). Therefore it has to be expected that CeRh\(_3\) is formed. The best fitting orientation of CeRh\(_3\) on a Rh(111) surface is the (111) plane, because it fits symmetrically and the lattice mismatch is minimal.

Indeed, our results prove that at very low Ce coverages annealed to 250 °C, a surface alloy, equivalent to the (1 1 1)-plane of CeRh\(_3\), is formed. Also at higher Ce coverages after annealing to 250 °C the intermetallic compound CeRh\(_3\) is formed,
but for the thicker films the most favorable plane is the (1 0 0)-plane of CeRh$_3$. We can understand this by considering the balance between the strain, interface energy and surface energy. In the ultra-thin films, the strain energy of a single epitaxial CeRh$_3$ layer is low enough to allow the formation of such a layer in spite of its misfit. The situation changes for thicker CeRh$_3$ films, where the strain energy of the film does not allow a commensurate interface. In this case, the difference between the interface energies of CeRh$_3$(1 1 1)/Rh(1 1 1) and CeRh$_3$(1 0 0)/Rh(1 1 1) becomes smaller, and the minimalization of the surface energy determines the orientation of the CeRh$_3$ film. Given the significantly lower surface energy of Ce as compared to Rh, the Ce–Rh-terminated CeRh$_3$(1 0 0) surface with 50% Ce in the surface layer is more favorable than CeRh$_3$(1 1 1) with 25% Ce and 75% Rh in the surface. The strong tendency towards formation of Ce–Rh bonds and, thus, ordered Ce–Rh alloys, prevents the formation of a pure Ce surface, however. This is a common phenomenon in systems with strong ordering tendency [33].

5. Conclusions

The growth of Ce on Rh(1 1 1) and the structures after annealing have been studied by using STM, AES, XPS and LEED. We find that Ce has a strong tendency to intermix with the substrate. Only at room temperature at coverages in the low submonolayer regime no intermixing occurs. In this case, Ce is forming nanoclusters that grow together and at 0.25 ML an adatom layer with a (2×2) superstructure is observed. At Ce coverages above 0.4 ML Rh is diffusing through pinholes and forms an unstructured mixed Ce–Rh layer. After annealing to 250 °C surface structures on the basis of the stable intermetallic compound CeRh$_3$ are formed. Strong valence-dependent neutralization of noble gas ions by Ce atoms prevents detection of the surface composition low-energy ion scattering.

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References
