

Available online at www.sciencedirect.com



Surface Science 562 (2004) 204-218



www.elsevier.com/locate/susc

STM, LEED, and DFT characterization of epitaxial ZrO_2 films on Pt(111)

K. Meinel^{a,*}, A. Eichler^b, K.-M. Schindler^a, H. Neddermeyer^a

^a Fachbereich Physik, Martin-Luther-Universität Halle-Wittenberg, D-06099 Halle, Germany ^b Institut für Materialphysik und Center for Computational Materials Science, Universität Wien, Sensengasse 8/12 A-1090 Wien, Austria

> Received 30 January 2004; accepted for publication 26 May 2004 Available online 19 June 2004

Abstract

Thin epitaxial ZrO_2 insulator films on a Pt(111) substrate have been studied by means of scanning tunneling microscopy (STM), low-energy electron diffraction (LEED), and density functional theory (DFT) calculations. The films have been prepared by Zr vapor deposition in an O₂ atmosphere followed by post-annealing also in an O₂ atmosphere. The process of film formation was investigated from the island state up to film thicknesses where the films completely cover the substrate. Continuous $ZrO_2(111)$ films of high quality with smooth surfaces and high structural order are obtained for film thicknesses above 3 monolayers (ML) and temperatures of deposition and post-annealing of 470 and 950 K, respectively. A carpet like growth mode is observed which corresponds to the relatively weak film/ substrate interaction found in DFT calculations. The investigations reveal a clear $p(1 \times 1)$ surface structure, which rotates during annealing with respect to the substrate. Based on DFT calculations, the possibility of different surface terminations is discussed. Annealing the samples at temperatures >950 K induces a three-dimensional restructuring of the ZrO₂ films which destroys the film continuity. Imaging discontinuous ZrO₂ films at small tunneling voltages yield a characteristic contrast reversal for local film thicknesses >2 ML indicating the retarded formation of the insulator gap of ZrO₂ during film growth which has been proven also by DFT calculations.

Keywords: Zirconium; Scanning tunneling microscopy; Insulating films; Growth; Surface structure, morphology, roughness, and topography; Density functional calculations

1. Introduction

Sulfated ZrO_2 catalysts have been found to be very active in the low temperature isomerization of *n*-alkanes, the anticipated raw materials of the future [1]. Up to now, the mechanism of the reaction is almost unknown, despite the tremendous economic importance of the isomerization process. For getting insights into the molecular events occurring on the ZrO_2 surface, an STM investigation during reaction is very promising as has been impressively demonstrated for other catalysts [2]. In the case of ZrO_2 , however, charging effects may impede an STM inspection as the material is insulating. Therefore it is

^{*}Corresponding author. Tel.: +49-345-55-25579/25382; fax: +49-345-55-27160/27017.

E-mail addresses: meinel@physik.uni-halle.de, meinel@ ep3.uni-halle.de (K. Meinel).

suitable to prepare the ZrO_2 as a thin film on a conducting substrate. By studying the ZrO_2 surface in such a thin film arrangement, charging effects can be avoided as has been shown for other insulating materials [3,4]. The ZrO_2 films, however, should possess a high structural order with an almost two-dimensional (2D) morphology characterized by large and smooth terraces for having well-defined conditions for the reactions.

In literature, one finds numerous studies of ZrO₂ films which have been induced by their increasing technological application (see e.g. [5] and the references therein). ZrO₂ films are used as hard and high-temperature protective coatings e.g. for tools, turbine wheels, magnetic media, and the like. In addition, they have been successfully applied as insulating buffer layers for capacitors and high-temperature superconductors in microelectronic devices. However, most work on ZrO₂ films deals with polycrystalline layers. Investigations of monocrystalline high-quality films are scarce. About 10 years ago, Maurice et al. [6] reported on the formation of face centered cubic (fcc) C1 (calcium fluorite like) ZrO₂-(111) films on a Pt(111) substrate where the Zr atoms form an fcc lattice. LEED revealed that a $p(2 \times 2)$ reconstruction is present on the surface which was attributed to missing O atoms. Based on results of integral techniques of surface analysis, the authors deduced a 2D film morphology of the ZrO₂ films. The films have been obtained by evaporating Zr onto Pt(111) at room temperature in an O_2 atmosphere of about 10^{-6} mbar and by post-annealing (also in an O₂ atmosphere) at temperatures around 1000 K. Encouraged from this work, we also chose the $ZrO_2/Pt(111)$ film/substrate system for the intended reaction experiments. In a first study performed by STM and high resolution LEED [7], we reexamined the ZrO_2 film formation on Pt(111). However, we found that the films prepared according to the procedure described in Ref. [6] display a multilayer or even a discontinuous morphology. So we tried to ameliorate the film quality by changing the temperatures of deposition and post-annealing. As a result, we found conditions for preparing high-quality ZrO₂ films by increasing the

deposition temperatures to about 470 K. After post-annealing at a temperature of 950 K, such films developed the desired well-ordered structure and an almost 2D film morphology for film thicknesses >3 monolayers (ML). LEED gave a $p(1\times1)$ diffraction pattern indicating that no surface reconstruction is present. A splitting of the ZrO₂ LEED spots by ±5.5° implies a slight rotation with respect to the Pt(111) substrate. However, post-annealing the films at temperatures >950 K induced a restructuring of the films into 3D islands which demonstrated the metastable character of 2D ZrO₂ films on Pt(111).

In the present study, the ZrO_2 film formation on Pt(111) is studied in more detail. In addition, density functional theory (DFT) calculations are performed to support, interpret, and explain the experimental findings. After introducing into the setup of the experiments and the calculations (Chapter 2), we first describe the initial stages of perfect ZrO₂ film formation from the submonolayer range to a thickness of about 3 ML where the films gain continuity (Chapter 3.1). Here, we also demonstrate the weak film/substrate interaction yielding a carpet like growth mode and discuss a possible interface structure. In Chapter 3.2, previously presented suggestions for the surface structure of the ZrO₂ films are compared with DFT calculations of the surface termination and the stability of the films during high temperature annealing is discussed. Finally, the electronic nature of the ZrO₂ films is investigated by studying the voltage dependence of the STM contrast (Chapter 3.3). Comparing STM images taken at high and small bias voltages (typical 3 and 0.2 V) a characteristic contrast reversal is observed for discontinuous ZrO₂ films which demonstrates the presence of an electronic band gap. This contrast reversal, however, is revealed only for a local film thickness above 2 ML which indicates that the gap formation is retarded during the ZrO₂ film growth. This agrees with DFT calculations which demonstrate the complexity of band structure development during ZrO_2 film growth on Pt(111). In Chapter 4, the main issues of the present work are summarized.

2. Method and setup

2.1. Experiments

The experiments have been performed in a UHV chamber (base pressure 10^{-10} mbar) housing a room temperature STM, a high-resolution LEED system for spot profile analysis (SPA-LEED) which we use for conventional LEED, and an analyzer for Auger electron spectroscopy (AES). In addition, the chamber contains facilities for sample heating, Ar⁺ ion bombardment, defined gas inlet and Zr evaporation. Details of the experimental setup are published elsewhere [8]. The Pt(111) substrate (miscut $< 0.1^{\circ}$) was cleaned in situ by cycles of Ar⁺ ion bombardment, UHV heating at a temperature of 1300 K and heating in an O₂ atmosphere at 800 K as described in [9]. Temperatures were measured by means of a pyrometer and a Ni/CrNi thermocouple attached to the sample heater. The final surface showed a bright LEED pattern and STM images revealed clean and large terraces (width > 100 nm) separated by monoatomic steps. For preparing the oxide layers, Zr was evaporated in an O₂ atmosphere (pressure about 1×10^{-6} mbar) from the tip of a Zr wire (purity 0.9995) heated by electron bombardment. The evaporation rate was measured by means of a quartz microbalance and by STM measurements of the volume of deposited submonolayers of clean Zr (UHV deposition) and ZrO₂, respectively. The evaporation rate was limited to values of 0.1-0.2 monolayers (ML)/min due to the low vapor pressure of Zr. After deposition of the film, the sample was post-annealed at temperatures between 470 and 1150 K also in an O₂ atmosphere (pressure about 1×10^{-6} mbar) and finally characterized by LEED and STM. In the LEED experiments, the typical electron energy was 66 eV. The STM studies were performed in constant current mode (CCM) with tunneling currents between 0.1 and 1 nA and positive sample biases between 0.1 and 4 V.

2.2. Calculational

The calculations are performed using the Vienna ab initio simulation package VASP [10,11]

which is a density functional theory (DFT) code, working in a plane wave basis set. Electron-ion interactions are described using the projector augmented wave method [12,13] with plane waves up to an energy of $E_{\text{cut}} = 250 \text{ eV}$. Increasing E_{cut} to 350 eV changes absolute energies by about 60 meV per formula unit; relative energies, as surface energies change by less than 10 mJ/m². For exchange and correlation, the functional proposed by Perdew and Zunger [14] is used, adding (semilocal) generalized gradient corrections (GGA) [15]. With this setup and a k-point sampling on a grid of $9 \times 9 \times 9$ k-points a lattice constant of 5.164 Å (compared to the experimental value of 5.0858 Å [16]) was determined for ZrO_2 in the cubic fluorite structure. The heat of formation for this structure (neglecting zero point energies) is calculated to 10.26 eV (compared to an experimental value of 11.40 eV [17]). Depending on the size of the unit cell, the k-point sampling was adapted for the surface calculations: the (2×2) Pt supported ZrO₂ film was sampled by $5 \times 5 \times 1$ k-points and for the (4×4) cells used for the determination of the 2D phase diagram only a single off symmetry k-point at (0.25, 0.25, 0) was used. A similar setup was applied in previous studies on tetragonal ZrO₂ for the description of the bulk [18] and surface properties [19], as well as for the characterization of the ZrO₂/Pt interface [20].

3. Results and discussion

3.1. Initial stages of growth and mode of film formation

The STM images of Figs. 1–3 illustrate the development of the ZrO_2 film morphology from island state to complete substrate coverage. The films are imaged immediately after deposition at 470 K in O₂ atmosphere and after post-annealing at 950 K, also in an O₂ atmosphere. We start in discussion by considering the film states obtained after the first preparation step, i.e. the deposition. At low coverages, 2D islands are observed (density about 2×10^{12} cm⁻²) sitting on the clean Pt(111) substrate (Fig. 1a). With growing thickness, the islands increase in size (compare Figs. 1a,b and



Fig. 1. Initial stages of ZrO_2 film formation on Pt(111) imaged by STM. The STM images where taken immediately after 470 K deposition (left) and after 950 K post-annealing (right). Film thickness: 0.3 ML (a,f), 0.7 ML (b, g), 1.1 ML (c,h), 1.7 ML (d,i) and about 3 ML (e,j). Image size 50×25 nm². Besides ZrO_2 islands small dots of C induced impurities (C) are observed as indicated in a, f, g by small arrows. Note that the STM images (a,d) are influenced by sample drift.

2a). On the top of the islands, islands of the second layer level develop (see large arrows in Figs. 1a,b and 2a) which are observed already at coverages of 0.3 ML. At substrate steps as imaged in Fig 3a (step is indicated by "S"), the number and the size of the islands are locally increased indicating that the steps promote nucleation (this holds also for the islands on top). During longer lasting measurements (some hours), small protrusions (C) became visible (small arrows in Figs. 1a and 3a, see also small arrows in Fig. 1f and g) the number of which gradually increases with time. According to AES analyses yielding a growing C signal, we attribute these protrusions to carbon induced impurities coming from the residual gas pressure. They are observed only on areas of the clean Pt(111) substrate and can be removed by annealing the sample in O_2 atmosphere. In contrast, a



Fig. 2. High resolution STM images and LEED patterns of a 0.7 ML thick ZrO_2 film on Pt(111) taken after 470 K deposition (a,b) and 950 K post-annealing (c). Image size 20×20 nm². Bias voltages 3 V (a) and 0.15 V (b,c). LEED energy 66 eV. Note the sample drift of (a,b) causing a shift of the islands (i). In the LEED pattern of (a), the unit mesh of $p(1 \times 1) ZrO_2(111)$ is indicated. For explanation see text.

growing C contamination is not observed by means of AES and STM for continuous ZrO_2 films completely covering the Pt(111) substrate.

The structure of the ZrO₂ islands is revealed in more detail in Fig. 2a where the STM image of a 0.7 ML thick ZrO_2 film is shown together with the observed LEED pattern. The island edges display a tendency of an alignment along [110] like directions. At a tunneling voltage of 0.15 V, almost atomic resolution is achieved. Atomic rows are partly visible and also regular arrangements of small protrusions and depressions (arrows in Fig. 2b) probably induced by individual atoms. The depressions may be caused by O atoms as O atoms on surfaces are usually measured by STM as depressions (see, e.g., the systems O/Cu(100) [21], O/Ru(1000) [22]). In LEED, patterns of a slightly rotated $p(1 \times 1)$ fcc ZrO₂(111) structure are observed together with the diffraction pattern of the Pt substrate (see inset of Fig. 2a). All in all, the ZrO₂ islands appear slightly bumpy, probably because neighboring atoms of the film rest above different substrate sites, e. g. hollow, bridge and on top positions of the substrate. Increasing the coverage to about 1.1 ML (Fig. 1c) yield not only a general increase of the island size but also the formation of islands of the third layer level on top of the islands of the second layer level (arrows in Fig. 1c). Obviously, a multilayer or hillock mode of growth is established where higher layer levels start to grow before the underlying ones are completed similar as observed for other film/substrate systems or even in homoepitaxial film growth [23,24]. In addition, the island shape becomes more irregular. Due to the multilayer mode of growth and the irregular island shape, the film gets a rough and irregular appearance which is reinforced with growing film thickness (compare Fig. 1a–e). Nevertheless, the $p(1 \times 1)$ pattern of an fcc (C1) $ZrO_2(111)$ structure is clearly revealed in LEED even for film thicknesses >3 ML [7].

We now describe the results of the second step of the film preparation, i.e. the post-annealing at 950 K in an O₂ atmosphere of 1×10^{-6} mbar. Comparing the islands found after deposition and after post-annealing (Figs. 1a–c, 2a and Figs. 1f–h, 2b) one perceives a reduction of island density of about a factor of 2. Obviously, the post-annealing



Fig. 3. STM images of ZrO_2 islands around substrate steps (S) taken after 470 K deposition (a) and post-annealing (b) with scheme of possible step influences on film structure (c). Mean film thickness 0.6 ML (a) and 1.1 ML (b). Image size 75×50 nm². In the scheme, the differently tinted layers represent the differently composed layers of a compound.

induces a drastic material rearrangement. The area of uncovered Pt as well as the mean size of the islands is increased. Characteristically, the islands appear as small slabs with almost smooth surfaces having different heights. In Fig. 2b, where a 0.7 ML thick ZrO_2 film is imaged, the apparent island heights are 2, 3, and 4 Å. The islands are revealed in almost atomic resolution in Fig. 2b indicating that their structural perfection is ameliorated during post-annealing. The increase of structural order is also indicated by the island edges which run now more pronounced along [110] like directions. Amazingly, the ZrO₂ LEED spots vanished during the annealing (see inset of Fig. 2c), despite the increase of structural order and size of the individual ZrO₂ islands.

An other interesting item is the role of substrate steps. The island population of the post-annealed film is almost unaffected by the steps (see Fig. 3b) and the decoration effect is reduced. Instead, the islands simply lay over the step edges. Obviously, a carpet like mode of growth is established for the post-annealed films as it has also been observed for other compounds (e.g. NaCl films on Ge(100) [25] and CoO films on Ag(100) [4,26]). Due to the carpet mode of growth, only a slight film bending is induced at the steps and the formation of antiphase boundaries at steps is avoided as visualized by the schemes of Fig. 3. Such a carpet like growth behavior implies a strong lateral interaction within the film and a weak interaction between the film and the substrate. The latter corresponds to our observation that for special conditions of STM imaging we were able to sweep aside the relatively weakly sticking ZrO₂ islands and to clean up the surface of the Pt(111) substrate by simple tip action. This is demonstrated by Fig. 4 showing a sample area (A) which was measured before with higher imaging velocity (5 min/image instead of 20 min/image) and decreased tunneling voltage (2 V instead of 3 V) where the tip came closer to the islands. This area is completely free of ZrO2 islands displaying only the almost smooth surface of the Pt(111) substrate. On the left side, the removed ZrO_2 material is visible as marked by (B) which was obviously swept into a pile by the tip; a similar pile of ZrO₂ material is found for the right side of the area not visible in Fig. 4. On the cleaned area, the C induced contamination typical for clean Pt(111) is restarted and a growing number of (C) protrusions is again revealed.

The physical reason of the relative weak interaction between the ZrO_2 film and the Pt(111) substrate may lie in the specificity of the ZrO_2/Pt interface. The most probable interface structure in which the oxide matches with the metal surface



Fig. 4. STM image of a 1.7 ML thick ZrO_2 film on Pt(111) post-annealed at 950 K. Area (A) was imaged before with a sample bias of 2 V and increased scanning velocity which sweeped away the ZrO_2 islands. The removed ZrO_2 material is heaped up at the left and right part of (A) in piles (B). On the cleaned Pt(111) C induced impurities (C) are formed again.

was presented in a recent DFT study [20]: a (2×2) unit cell can be brought in almost perfect registry with a $(\sqrt{7} \times \sqrt{7})$ cell of the underlying Pt support. In that way, the effective mismatch can be reduced from about 30% to only 2.2%. In such a structure, the interface energy (defined as the energy necessary to form the interface from bulk material) is calculated to 1.68 J/m² for a five layer oxide film supported on four layer of platinum. Comparing this value to the (calculated) surface energies of ZrO₂(111) and Pt(111) of 0.90 and 1.50 J/m² which have to be raised upon separation, the interface is stabilized by an adhesive energy of only 0.72 J/m^2 . This would explain the aforementioned carpet-like grow mode and the weakness of the sticking of the ZrO₂ islands on Pt(111), respectively, as observed in the STM measurements. The proposed interface structure is further in line with LEED and STM results, revealing the formation of a $8/3 \times 8/3$ (where $8/3 \sim \sqrt{7}$) or p(2×2) superstructure, respectively, which have been observed by Maurice et al. [6] and also in our previous experiments for specific preparation conditions [7].



Fig. 5. STM images (a,c) and LEED pattern (b) of a continuous ZrO_2 film on Pt(111). Film thickness about 4 ML. Image sizes $125 \times 80 \text{ nm}^2$ (a) and $5 \times 5 \text{ nm}^2$ (c). In (b,c) the unit mesh of $p(1 \times 1) ZrO_2(111)$ is indicated.

Continuing our study of ZrO₂ film morphology, we observed that the post-annealed ZrO₂ islands increase in size and height with growing film thickness. They start to coalesce at a film thickness around 1.5 ML (see Fig. 1i) which is accompanied by the reappearance of a ZrO_2 LEED pattern (not shown here, see Chapter 3.3, Fig. 8a). Increasing the film thickness to more than 3 ML, the Pt substrate remains completely covered (see Fig. 1j) and an almost 2D morphology of ZrO₂ is obtained [7]. The post-annealed ZrO_2 film now displays large terraces populated by 2D islands. In LEED, a sharp $p(1 \times 1)$ diffraction pattern of $ZrO_2(111)$ is revealed which is rotated by $\pm 5.5^{\circ}$ indicating that the film is slightly twisted with respect to the substrate ([7], see also Fig. 5). Similar to other film/ substrate systems, the film twisting may ameliorate film substrate accommodation [27,28]. All in all, almost perfect films are obtained as wanted for the future experiments of catalytic processes on ZrO₂ surfaces.

3.2. Surface terminations and film stability

According to the $p(1 \times 1)$ LEED pattern observed in the experiments [7], the surface of the continuous ZrO_2 films corresponds to that of a non-reconstructed (C1) $ZrO_2(111)$ surface. This structure was also revealed by means of STM. However, atomic resolution was achieved only for specific 2D islands on top of the ZrO₂ films (see Fig. 5c). In addition, we found that the island heights are not uniform. For a 4 ML thick ZrO₂ film a detailed inspection yield apparent heights of 2D islands and steps amounting to approximately 1, 2, 3, and 4 Å. From both observations, i.e. (i) the different heights of 2D islands and (ii) the different imaging behavior of 2D islands of continuous films, we came to the suggestion that the islands may display different terminations [7]. According to the structure of fcc (C1) $ZrO_2(111)$ [29], three different terminations are generally possible depending on the stacking sequence of the O and Zr layers, respectively, i.e. one Zr and two different O terminations. Such a variety of surface terminations would also explain the different heights of post-annealed ZrO₂ islands, measured in the submonolayer stage (Fig. 2c), which are not a multiple of a complete O/Zr/O layer (~ 3 A). Partly, these different terminations may be stabilized by atoms of the residual gas (O_2, H_2, H_2O) , ...) as discussed for other oxides, e.g. for NiO where the $(1 \ 1 \ 1)$ surface is assumed to be stabilized by OH⁻ [30].

In order to gain further insight into the stability of different surface terminations of the oxide, we employed ab initio thermodynamics as described in detail in Ref. [31], which combines simple thermodynamic considerations with results from ab initio calculations. This allows us to construct the surface phase-diagram of cubic $ZrO_2(111)$ (neglecting the influence of the metal underneath) as a function of the chemical potentials of H and O (coming from the residual gas), which is shown in Fig. 6. To allow for a gradual variation between different phases, a $p(4 \times 4)$ surface cell was used in the calculations, which makes coverage variations in steps of 1/16 ML possible. For further details on the setup we refer the reader to Ref. [19], where the same method and setup was employed to calculate the surface phase diagram for tetragonal ZrO₂.

All chemical potentials are referenced to $1/2E(O_2)$ and $1/2E(H_2)$, i.e. the energy zero is chosen such that O_2 and H_2 molecules have zero energy. Using these energy zeros, the following restrictions



-3

-2

T for $p(O_2) = 10^{-9}$ atm: 1000 500

E

-5

-4

-6

16 O

600

apply for the chemical potentials μ (which are marked as grey dashed lines in the phase diagram): the chemical potentials have to be negative; otherwise O_2 or H_2 would move from the particle reservoirs to the surface and would start to condensate there. A similar condition-preventing water to condensate at the surface—is given by $\mu(O) + 2\mu(H) < E(H_2O)$, with $E(H_2O)$ being the zero Kelvin formation energy of water, which is calculated to be -2.64 eV. Finally, there exists also a lower bound for the oxygen chemical potential, which is determined by the complete reduction of the oxide to metallic Zr and hence is given by the heat of formation of ZrO_2 (per O atom): $\mu(O) > -5.13$ eV. However, such low chemical potentials are no longer reachable by increasing the temperature or reducing the pressure; e.g. even

-3

-2

0

, (eV)

T for

 $p(H_2) =$

10⁻¹³atm

1000

500

OK

0

-1

at 1000 K a partial pressure of less than 10⁻⁷ mbar is necessary, to reach an O chemical potential of -2 eV. Only under highly reductive conditions (e.g. under atomic H atmosphere) or in non-equilibrium situations (e.g. by applying an electric field or during growth) the left part of the phase diagram could become accessible. The interrelation between partial pressure, temperature and chemical potentials (see. e.g. Ref. [31]) is illustrated by the inset in Fig. 6. To make a direct comparison to our experimental results easier, we included temperature scales at the axes for the O and H chemical potentials, which are valid for the partial pressure ranges of interest: for O₂ 10⁻⁶ mbar and for H₂—which is the main component of the residual gas at UHV conditions-a partial pressure of 10^{-10} mbar.

In its general features, the phase diagram is very similar to that published recently for tetragonal ZrO_{2} [19]. The stoichiometric O-termination (16O) dominates the phase diagram. This is the phase which is stable under the conditions corresponding to the annealing phase. However, at lower temperatures at which the oxide is deposed, a second phase is stable and covers up to half of the surface. This phase consists of neighboring OH-molecules adsorbed at different heights, which are interconnected via a hydrogen bond. A sketch of this structure at a sixteenth monolayer coverage is given as inset in the phase diagram. Another way of interpreting this phase is the adsorption of H₂O on the O terminated ZrO₂ surface. This structure merits additional attention, since at atmospheric conditions (normal pressure and room-temperature with 200 mbar O₂ partial pressure and a partial pressure of 10^{-4} mbar for H₂), the chemical potentials of O and H are -0.29 and -0.35 eV, respectively. These values fall into the high-coverage regime of this doubly OH terminated phase. For the growth of the oxide this doubly OH termination might play the role of a surfactant leading to a smooth layer by layer growth. The annealing process finally leads the system into the regime, where only the O termination is stable.

However, in the construction of the presented phase diagram it is implicitly assumed, that the bulk oxide below the surface serves as a thermodynamic reservoir fixing the chemical potential of the bulk oxide. This holds of course only for thicker oxide layers and not in the initial stages of oxide growth. In the beginning of the growth process it is therefore well possible, that many kinds of surface oxides develop, which differ from the bulk oxide in structure and stoichiometry. A wealth of such novel 2D oxide structure was recently discovered for the growth of vanadium oxide on the (111) surface of Pd [32,33].

We now turn to the stability of the ZrO_2 films on Pt(111) during annealing which is another essential item. As already emphasized in our previous study [7], 2D $ZrO_2(111)$ films on Pt(111) display a thoroughly metastable character. Annealing the films to temperatures above 950 K results in a drastic 3D material rearrangement where the film continuity is lost. At the beginning, holes of the ZrO_2 film are formed reaching down to the Pt(111) substrate. During the annealing, the holes become larger and the film is gradually transformed in coalesced 3D islands residing on the clean Pt(111) substrate as described in our previous work [7] and shown in the STM images of Fig. 7.

3.3. Electronic nature of ZrO_2 films on Pt(111)

Discontinuous ZrO₂ films as depicted in Fig. 7 are ideal samples for demonstrating the electronic nature of ZrO₂ films on Pt(111) by means of simple STM imaging. For large sample biases $(\geq \pm 2 \text{ V})$, the holey ZrO₂ film is measured in the usual way as protrusion with respect to the Pt(111) substrate visible at the bottom of the film holes. This is demonstrated by the STM image of Fig. 7a taken with a tunneling voltage of 3.1 V. For small tunneling voltages (e.g. 0.15 V), however, the film appears depressed (see Fig. 7b). For intermediate tunneling voltages (e.g. 1.6 V), the film contrast almost vanishes (Fig. 7c) and the steps of the Pt(111) substrate (S) became more prominent. In the diagram of Fig. 7d, the general course of this characteristic contrast reversal is visualized by the apparent height of the ZrO₂ film obtained for different tunneling voltages. Similar as for other discontinuous insulator films on metallic substrates [4,26,34-36], the contrast reversal can be attributed to the electronic gap present



Fig. 7. STM images of a decayed ZrO_2 film (post-annealed at 1050 K) displaying free lying substrate areas. Film thickness 4 ML. Image size $150 \times 150 \text{ mm}^2$. Sample bias 3.1 V (a), 0.15 V (b), and 1.6 V (c). Depending on bias voltage, the film appears as protrusion (a) or depression (b) or becomes even transparent (c). In the diagram (d), this change of contrast is quantified by measuring the apparent film height in dependence on sample bias.

in the insulating films. For large sample biases, the tunneling electrons pass via a normal electronic transport through the insulating film by moving within its valence or conduction band, respectively, on their course from the tip to the metal substrate or vice versa depending on polarity. Any charging of the film by the injected electrons is prevented if the film thickness is small in comparison to the electron mean free path (typical in the 10 nm range). In such a thin film situation, similar tunneling currents and film contrasts, respectively, are obtained as for a metal film. For small sample bias voltages, however, the energy of the passing electrons is within the band gap of the insulating film. In such a case, electron transport through the film is only possible by a tunneling

process. In other words, for small sample bias voltages besides the vacuum barrier an additional barrier is present for the tunneling electrons. The spatial width of this barrier corresponds to the film thickness. Hence, the transmission probability is decreased which reduces the tunneling current. As an immediate response, the tip moves closer to the sample since the imaging system strives to yield the tunneling current constant during CCM imaging. As a result, the apparent height of the film is decreased and the film becomes invisible or even appears depressed with respect to the neighboring areas of metal substrate. This characteristic change of contrast can always be considered as a clear signature of the presence of an electronic band gap.

A contrast reversal, however, was not observed for the submonolayer regime where the surface is also composed by ZrO_2 islands and clean $Pt(1\ 1\ 1)$ areas. Here, the ZrO_2 islands do not display a contrast reversal neither after deposition nor after post-annealing. They always appear as protrusions even at bias voltages as low as 0.15 V (see Fig. 2b and c). Obviously, there are still states in this energy range of the submonolayer islands. So the question arises, how the formation of the band gap proceeds in dependence on film thickness.

For studying the formation of the band gap, we have analyzed films with a mean film thickness of 1.7 and 2.5 ML (Fig. 8). In the contrast analysis, we exclusively used the post-annealed films since a gap analysis of non-annealed films is hampered by their roughness (Chapter 3.1). In addition, we assumed that structure and stoichiometry of postannealed films would better correspond to perfect ZrO₂ film samples. Clear contrast reversals were already observed for the 1.7 ML thick film after post-annealing at 980 K. The STM image of Fig. 8b shows the topography of the film (bias voltage 3.1 V). The film is formed by coalesced ZrO_2 islands. LEED yields a weak $p(1 \times 1)$ ZrO₂(111) diffraction pattern (indicated in Fig. 8a by black arrows). Imaging the film at small sample bias of 0.15 V (Fig. 8c) yields that some parts of the islands (indicated by arrows in Fig. 8b) appear in the reversed contrast as depression. Surprisingly, the brightest and highest areas of the islands imaged in Fig. 8b (apparent local film thickness ≈ 10 A) show no contrast reversal. A clear classification of the nature of the film, however, is problematic. The post-annealing temperature (980 K) was relatively high in this case. Hence, a substantial 3D material rearrangement was induced which possibly yield also a modification of film composition. Therefore, we have decreased the post-annealing temperature to about 900 K for the 2.5 ML thick ZrO_2 film. At this reduced temperature, the hillock morphology formed during film deposition was not completely destroyed during post-annealing as indicated by the blurred LEED pattern of Fig. 8d and revealed by the STM image of Fig. 8e showing the film topography (bias 3.2 V). Four layer levels (a,b,c,d) are observed. The lowest level (a) appears as holes, the next level (b) is formed by coalesced islands, level (c) is represented by islands sitting on level (b), and on top of some of the (c) islands, additional islands form level (d) belonging to the tops of the highest hillocks. The depth of the holes and the height of the islands, respectively, is 3 Å as measured by STM. This corresponds to the mean height of a complete $ZrO_2(111)$ ML composed of two O layers enclosing one Zr layer (3 Å). We therefore assume, that the ZrO₂ film displays a unique surface termination in this case. (For observing multiple terminations as discussed in Chapter 3.2, higher post-annealing temperatures are probably necessary.) For assigning the local film thickness of the different height levels, we have to speculate about the film thickness of the deepest level, i.e. the hole areas (a). Assuming there film thicknesses of 0, 1, and 2 ML, we obtain from the relative areas of the different levels visible in the STM image (a: 0.08, b: 0.47, c: 0.33, d: 0.06) mean film thicknesses of 1.38, 2.38 and 3.38 ML, respectively. As the highest and the lowest thickness values deviate by more than 25% from the mean thickness expected according to the calibrated deposition rate, we are sure that the actual mean thickness is 2.38 ML and that the local film thickness within the holes (a) amounts to 1 ML. Consequently, we ascribe for the following height levels (b,c,d) a local film thickness of 2, 3, and 4 ML. In Fig. 8f the film is imaged with a small bias voltage of 0.2 V. A complete change of contrast is obtained. The terraces of the Pt(111) substrate with their steps (S) become more perceivable and the contrast between the height levels a and b vanishes, i.e. the holes (a) are no longer visible. The height of the islands of level (c) is reduced to 1 A. In addition, the top areas (level d) of the highest and largest hillocks mostly found at the Pt(111)steps (s) appear in a reversed contrasts, i.e. 4 A depressed with respect to level (c). From this contrast behavior, we can conclude that a clear gap is already present in the second ML-otherwise the holes at level (a) would be visible in Fig. 8d. Moreover, it seems that the process of gap formation proceeds over several layers. At least 4 ML are apparently necessary for getting a perfect ZrO₂ band gap completely free of electronic states-otherwise there would be no contrast reversal of the level (d) areas.



Fig. 8. LEED patterns and STM images of 1.7 ML (a,b,c) and 2.5 ML thick (d,e,f) ZrO_2 films on Pt(111) post-annealed at 970 K (a,b,c) and 900 K (d,e,f). Image size 50×50 nm². Sample bias 3.1 V (b,e) and 0.15 V (c,f). For explanation see text.

For investigating this complex process of gap formation, DFT calculations for ZrO_2 films with increasing thickness are performed. On top of a four layer film of Pt gradually 1–5 ML of ZrO_2 are

adsorbed. The system is modelled in a $\sqrt{7} \times \sqrt{7}$ cell at the (theoretical) lattice constant of Pt ($a_{\rm Pt} = 3.99$ Å) and the structure of the oxide and of the two uppermost Pt layer is optimized. As



Fig. 9. Calculated local density of states for ZrO_2 films of increasing thickness (1–5 ML shown in column 1–5) on a four layer Pt support. Shown are the projected density of states per layer (metal/oxide) for the two uppermost metal layers (first two rows) and the adsorbed ZrO_2 layers (rows 3–8).

mentioned already above, in that superstructure, a $p(2 \times 2)$ cell of ZrO₂ fits with a mismatch of only 2.2% almost perfectly onto the metal support.

In Fig. 9, the density of states projected onto individual Pt/ZrO_2 layers is displayed. The second Pt layer below the interface is almost independent

of the oxide above and exhibits an electronic structure very similar to bulk Pt. The Pt layer at the interface, however, shows some distinct features, which depend even on the thickness of the adsorbed oxide layer. Most pronounced changes can be found in the region of the lower part of the O 2p band between 4 and 6 eV below the Fermi edge. Correspondingly, these states are modified quite substantially at the oxide layer at the interface, as well. However, the most important change happens in the former gap of the oxide. Independent of the number of adsorbed ZrO₂ layers, the gap in the lowermost layer is filled by metal induced states making the oxide metallic. From the second layer on a gap starts to develop. While the gap at the surface of \sim 3.5 eV is already converged after the third layer, it takes up to five layers, until the band gap in the middle of the film has reached its bulk value of close to 4 eV.

Thus the calculations generally confirm the complexity of band structure formation of growing ZrO₂ films found in the experiment. In particular, the metallic character of the first ZrO₂ layer is confirmed. They also corroborate that from the second layer on a gap is formed. However, no indications of the existence of additional states within the gap region were found for film thicknesses >2 ML. Hence, according to the calculations, the gap formation process seems to be completed already for the second ML which is in contrast to the experiments. However, the real process of gap formation may be proceeding in an even more complicated way. Specific interface effects not included in calculations as e.g. misfit induced film bending or interdiffusion may interfere and additionally retard the full band structure development.

4. Summary

Applying STM, LEED, and DFT studies, we investigated the formation of ZrO_2 films on Pt(111). We have demonstrated that epitaxial $ZrO_2(111)$ films with high structural perfection are obtained by deposition of Zr in O₂ atmosphere and sample post-annealing (also in O₂ atmosphere). The films grow in the carpet mode and display already in the submonolayer stage a high structural order.

For film thicknesses >3 ML, the films become continuous displaying an almost 2D morphology after annealing at temperatures around 950 K. A sharp $p(1 \times 1)$ LEED pattern is observed which reveals that ZrO_2 (111) films are formed possessing an fcc (C1) structure. The LEED pattern is rotated by $\pm 5.5^{\circ}$ which shows that the films are slightly twisted with respect to the $Pt(1 \ 1 \ 1)$ substrate. Based on DFT calculations, the possibility of different surface terminations are discussed. However, the 2D grown ZrO₂ films are metastable. Post-annealing the films at temperatures >950 K induces the formation of 3D ZrO₂ islands. Studying discontinuous and ultrathin (<3 ML) films reveals a specific contrast reversal in STM imaging which demonstrates together with DFT calculations the presence of an electronic gap, the formation of which proceeds over several layers.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft through the priority programme 1091 "From ideal to real systems: bridging the pressure and material gap in heterogeneous catalysis". Helpful discussions with members of the Forschergruppe "Oxidic interfaces" at the Martin-Luther Universität Halle-Wittenberg are gratefully acknowledged.

References

- [1] K. Arata, Adv. Catal. 37 (1990) 165.
- [2] J.A. Jensen, K.B. Rider, Y. Chen, M. Salmeron, G.A. Somorjai, J. Vac. Sci. Technol. B 17 (1999) 1080.
- [3] H.-J. Freund, H. Kuhlenbeck, V. Staemmler, Rep. Prog. Phys. 59 (1996) 283.
- [4] I. Sebastian, T. Bertrams, K. Meinel, H. Neddermeyer, Faraday Disc. 114 (1999) 20.
- [5] M. Rühle, Adv. Mater. 9 (1997) 195.
- [6] V. Maurice, M. Salmeron, G.A. Somorjai, Surf. Sci. 237 (1990) 116.
- [7] K. Meinel, K.-M. Schindler, H. Neddermeyer, Surf. Sci. 532–535 (2003) 420.
- [8] Th. Berghaus, A. Brodde, H. Neddermeyer, St. Tosch, Surf. Sci. 184 (1987) 273.
- [9] M. Hohage, T. Michely, G. Comsa, Surf. Sci. 337 (1995) 249.

- [10] http://cms.mpi.univie.ac.at/vasp/.
- [11] G. Kresse, J. Furthmüller, Phys. Rev. B 54 (1996) 11169, Comput. Mater. Sci. 6 (1996) 15.
- [12] P. Blöchl, Phys. Rev. B 50 (1994) 17953.
- [13] G. Kresse, D. Joubert, Phys. Rev. B 59 (1999) 1758.
- [14] J.P. Perdew, A. Zunger, Phys. Rev. B 23 (1981) 5048.
- [15] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, Phys. Rev. B 46 (1992) 6671.
- [16] C.J. Howard, R.J. Hill, B.E. Reichert, Acta Crystallogr., Sect. B: Struct. Sci. 44 (1988) 116.
- [17] Handbook of Chemistry and Physics, 84th ed., CRC Press LLC, 2003–2004.
- [18] A. Eichler, Phys. Rev. B 64 (2001) 174103.
- [19] A. Eichler, G. Kresse, Phys. Rev. B 69 (2004) 045402.
- [20] A. Eichler, Phys. Rev. B 68 (2003) 205408.
- [21] D.J. Coulman, J. Winterlin, R.J. Behm, G. Ertel, Phys. Rev. Lett. 64 (1990) 1761.
- [22] C. Stampfl, S. Schwegmann, H. Over, M. Scheffler, G. Ertel, Phys. Rev. Lett. 77 (1996) 3371.
- [23] K. Meinel, M. Klaua, H. Bethge, J. Cryst. Growth 89 (1988) 447.
- [24] J. Vrijmoeth, H.A. vander Veight, J.A. Meyer, E. Vlieg, R.J. Behm, Phys. Rev. Lett. 72 (1994) 3843.

- [25] C. Schwennike, J. Schimmelpfennig, H. Pfnür, Surf. Sci. 293 (1993) 57.
- [26] I. Sebastian, Thesis, Halle, 2000.
- [27] J.C. Hamilton, S.M. Foiles, Phys. Rev. Lett. 75 (1995) 882.
- [28] Ch. Ammer, K. Meinel, H. Wolter, A. Beckmann, H. Neddermeyer, Surf. Sci. 375 (1997) 302.
- [29] P. Villars, L.D. Calvert (Eds.), Person's Handbook of Crystallographic Data for Intermetallic Phases, American Society for Metals, Metals Park, OH, 1986.
- [30] D. Cappus, M. Haßel, E. Neuhaus, M. Heber, F. Rohr, H.-J. Freund, Surf. Sci. 337 (1995) 268.
- [31] K. Reuter, M. Scheffler, Phys. Rev. B 65 (2002) 035406, refs. therein.
- [32] S. Surnev, G. Kresse, M.G. Ramsey, F.P. Netzer, Phys. Rev. Lett. 87 (2001) 086102.
- [33] S. Surnev, J. Schoiswohl, G. Kresse, M.G. Ramsey, F.P. Netzer, Phys. Rev. Lett. 89 (2002) 246101.
- [34] I. Sebastian, H. Neddermeyer, Surf. Sci. 454–456 (2000) 771.
- [35] J. Viernow, D.Y. Petrovykh, A. Kirakosian, J.-L. Lin, F.K. Men, M. Henzler, F.J. Himpsel, Phys. Rev. B 59 (1999) 10356.
- [36] C. Hagendorf, R. Shantyr, K. Meinel, K.-M. Schindler, H. Neddermeyer, Surf. Sci. 532–535 (2003) 346.

218