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Growth, structure and annealing behaviour of epitaxial ZrO_2 films on Pt(1 1 1)

Klaus Meinel, Karl-Michael Schindler, Henning Neddermeyer *

Fachbereich Physik, Martin-Luther-Universität Halle-Wittenberg, D-06099 Halle, Germany

Abstract

For future investigations of catalytic reactions on sulfated ZrO_2 surfaces by means of scanning tunneling microscopy (STM), ZrO_2 films are prepared on Pt(1 1 1) and characterized by STM and low-energy electron diffraction (LEED). The films are prepared by vapor deposition of Zr in an O_2 atmosphere followed by annealing (also in an O_2 atmosphere). Conditions are searched where well-ordered, continuous and smooth ZrO_2 films are formed. Depositing the films according to literature data at room temperature [Surf. Sci. 237 (1990) 166] yields films with hillock morphology which decay during annealing and loose continuity. The desired film perfection is attained, however, if the films are deposited at 470 K and postannealed at 950 K. Continuous films are obtained displaying large terraces and a clear $p(1 \times 1)$ ZrO_2(1 1 1) LEED pattern. A splitting of the LEED spots reveals that the films are slightly rotated with respect to Pt(1 1 1). However, annealing the films at temperatures >1000 K again yields discontinuous films which indicates the metastable character of the ZrO_2 films on Pt(1 1 1) substrate.

Keywords: Zirconium; Scanning tunneling microscopy; Surface structure, morphology, roughness, and topography; Growth; Epitaxy; Low energy electron diffraction (LEED)

1. Introduction

Sulfated ZrO_2 catalysts are extremely active in the low temperature isomerization of *n*-alkanes [1]. However, the mechanism of the reaction, in particular the specificity and role of surface active centers, are unknown up to now. A deeper understanding of the activation of alkanes on the ZrO_2 surface is of crucial relevance as alkanes are the chemical raw materials of the future. STM investigations of the ZrO_2 surface during reaction are very promising for elucidating details of the reaction mechanism [2]. For such studies, it is suitable to prepare the insulating ZrO_2 as a thin film on a conducting substrate before sulfation for preventing charging effects [3,4]. The films, however, should display a well-ordered structure and an almost two-dimensional (2D) morphology characterized by large and smooth terraces for having clear conditions for further investigations. In our studies, thin ZrO_2 films are prepared on a Pt(1 1 1) substrate and characterized by STM and LEED. The preparation follows a procedure described by Maurice et al. [5] who reported on the formation of ZrO_2(1 1 1) films on Pt(1 1 1) substrate displaying face centered cubic (fcc) C1

* Corresponding author. Tel.: +49-345-55-25560; fax: +49-345-55-27160.
E-mail address: neddermeyer@physik.uni-halle.de (H. Neddermeyer).

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(calcium fluoride like) structure. The films showed a ($8/3 \times 8/3$) periodicity with regard to the Pt(1 1 1) substrate as deduced from LEED which was assigned to a p(2×2) reconstruction induced by missing O atoms. From the results of integral techniques of surface analysis, the authors deduced a 2D film morphology of the ZrO_2 films. The films have been prepared by evaporating Zr onto Pt(1 1 1) at room temperature in an O_2 atmosphere of about 10^{-6} mbar and by postannealing (also in an O_2 atmosphere of about 10^{-6} mbar) at temperatures between 900 and 1100 K. However, we found that the films prepared according to the same procedure described in [5] display a hillock or even a discontinuous morphology as revealed by STM. We have therefore increased the temperature of deposition for ameliorating the film quality. Similar as in previous studies of the growth of other oxide films [4], best conditions for preparing high-quality films were found for deposition temperatures around 470 K. After annealing, such films display the desired well-ordered structure and an almost 2D film morphology. However, annealing the films at temperatures above 1000 K induces the beginning of film decay which demonstrates the metastable character of the ZrO_2 films.

2. Experiments

The experiments have been performed in an UHV chamber (base pressure 10^{-10} mbar), housing a room temperature STM and a high-resolution LEED system for spot profile analysis (SPALEED). In addition, the chamber is equipped with facilities for sample heating, Ar^+ ion bombardment, defined gas inlet and Zr evaporation. The Pt(1 1 1) substrate (miscut $< 0.1°$) was cleaned in-situ by cycles of Ar^+ ion bombardment, UHV heating at temperatures of about 1300 K and heating in an O_2 atmosphere at 800 K as described elsewhere [6]. Temperature was measured by means of a pyrometer. The final surface showed a bright LEED pattern and STM revealed clean and large terraces (width > 100 nm) separated by monoatomic steps. For preparing the ZrO_2 layers, Zr was evaporated in an O_2 atmosphere (O_2 pressure about 1×10^{-6} mbar) from the ending 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 ZrO_2, respectively. The evaporation rate was restricted to values between 0.1 and 0.2 monolayers (ML)/min due to the low vapor pressure of Zr. After deposition of the film, the sample was postannealed at temperatures between 470 and 1150 K (also in an O_2 atmosphere of 1×10^{-6} mbar) and finally characterized by LEED and STM. In the LEED experiments, the usual electron energy was 66 eV. The STM studies were performed in the constant current mode with tunneling currents between 0.1 and 1 nA and positive sample biases between 0.1 and 4 V.

3. Results and discussion

In a first series of experiments, we prepared the films according to the procedure described by Maurice et al. [5], i.e. the Zr was deposited at room temperature and the sample postannealed up to temperatures where ZrO_2 LEED spots appear. Fig. 1(a) shows the STM image of a 4 ML thick ZrO_2 film taken after deposition. A high density of small hillocks is revealed which is obviously induced by multilayer growth where several layer levels are simultaneously developed. Annealing the film at temperature above 900 K induces film smoothing. However, the hillock morphology remains even if the film is annealed up to 1000 K as demonstrated by the STM image of Fig. 1(b). About four different layer levels are identified formed by islands and terraces, the width of which does not exceed 10 nm. Increasing the postannealing temperature to about 1050 K does not yield the desired completion of the film smoothing. Instead, the film gets a discontinuous character. First, deep holes are formed ranging down to the substrate as shown by the STM image of Fig. 1(c) (see arrow). Continuation of the heating completely destroys film connection and induces the formation of three dimensional aggregations of ZrO_2 sitting on the free lying Pt(1 1 1) substrate (Fig. 1(d)).

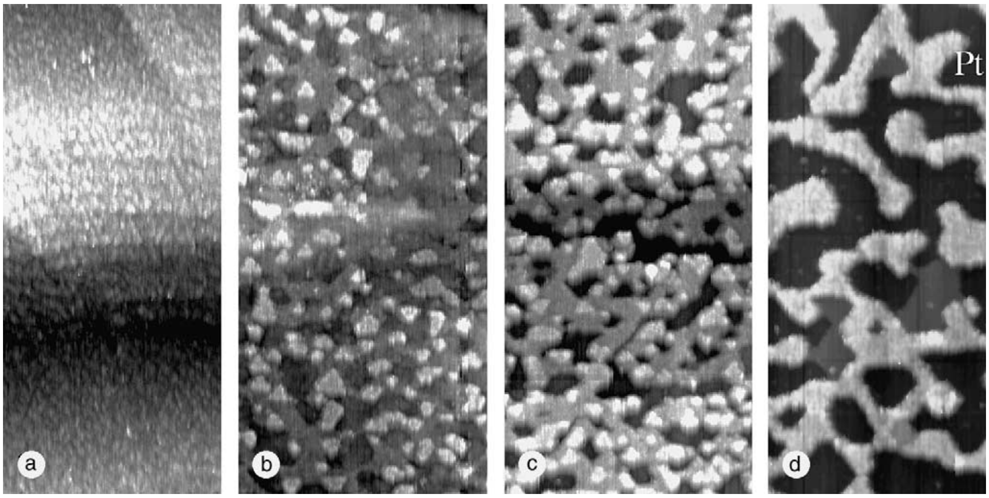

Fig. 1. STM images of 4 ML thick ZrO_2 films on Pt(1 1 1) deposited at room temperature taken after deposition (a) and after postannealing at 1000 K (b) (annealing time 20 s) and 1050 K (c,d; annealing time 20 and 60 s, respectively). Image size 75 nm × 150 nm.

In another series of experiments, the films (mean thickness also 4 ML) have been deposited at a temperature of 470 K where in our group best conditions were found for a 2D film formation for other oxides [4]. The 470 K deposition of ZrO_2 films also yields a hillock morphology induced by multilayer growth as shown by the STM image of Fig. 2(a). The films, however, display already immediately after deposition a weak $p(1\times1)$ ZrO_2(1 1 1) LEED pattern. It is observed together with the $p(1\times1)$ LEED pattern of the Pt(1 1 1) substrate which is yet visible at film thicknesses below 5 ML. The reciprocal unit vectors (shortest distance between two spots) of the $p(1\times1)$ Pt LEED pattern correspond to a 0.28 nm distance between neighboring Pt atoms in real space. In contrast, the ZrO_2 LEED pattern indicates a (1 1 1) lattice with a mesh size of about 0.36 nm, which

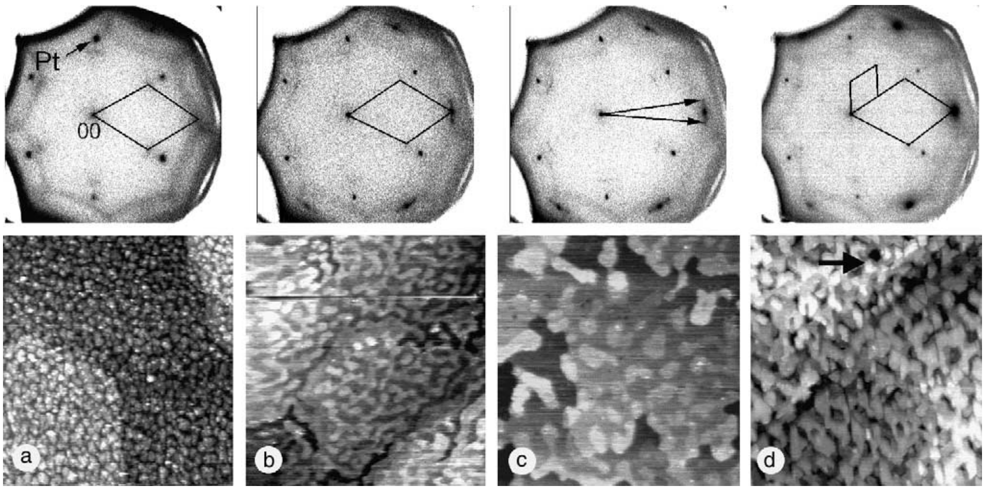

Fig. 2. STM images and LEED patterns of 4 ML thick ZrO_2 films on Pt(1 1 1) deposited at 470 K taken after deposition (a) and after postannealing at 950 K (b,c; annealing time 10 and 20 min, respectively) and 1020 K (annealing time 20 min). Image size 150 nm × 150 nm. LEED energy 66 eV. In the LEED patterns the unit cells of the $p(1\times1)$ and $p(2\times2)$ structures are indicated.

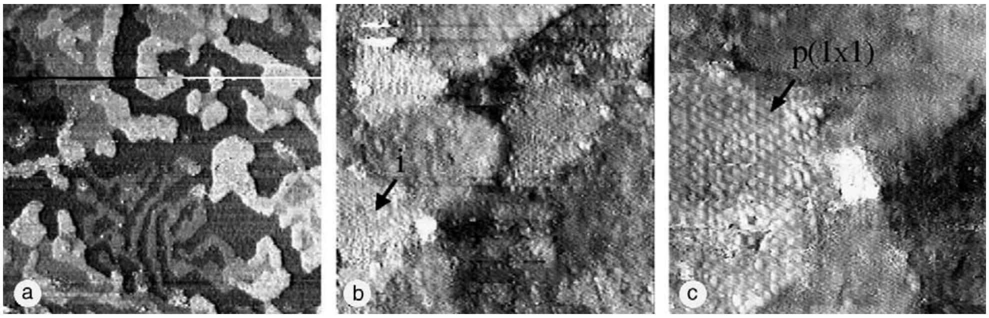

Fig. 3. STM images of continuous and smooth ZrO_2 film on Pt(1 1 1). Mean thickness 4 ML. 470 K deposition, postannealing at 950 K. Image size 100 nm × 100 nm (a), 20 nm × 20 nm (b), and 8 nm × 8 nm (c). For explanation see text.

corresponds to the (1 1 1) planes of fcc C1 ZrO_2 having a calcium fluoride like structure [2,7]. For such a film, postannealing at temperatures around 950 K results in a morphology which is nearly 2D as shown by the STM images of Fig. 2(b) and (c). 2D ZrO_2 islands are observed residing on large terraces. The island size is increased with annealing time (compare Fig. 2(b) and (c)). Simultaneously, the LEED spots of the $p(1 \times 1)$ ZrO_2 become sharper. No indications of a $p(2 \times 2)$ superstructure are found. The LEED spots are partly splitted by ±5.5° (Fig. 2(c)) which indicates the presence of domains slightly rotated with respect to the Pt(1 1 1) substrate. This slight film rotation may ameliorate film/substrate accommodation as observed for other systems [8]. However, the preparation of perfect ZrO_2 films presupposes that the temperature does not essentially exceeds 1000 K. Fig. 2(d) shows the STM image of a 4 ML thick ZrO_2 film, which was annealed at 1020 K immediately after the 470 K deposition. Obviously, the film quality is reduced at such a high annealing temperature. Again a hillock morphology is observed where at least four levels are developed. In addition, small holes are formed ranging down to the substrate (see arrow in Fig. 2(d)), which can be interpreted as an indicative of beginning film decay. In the LEED pattern, weak spots of a $p(2 \times 2)$ structure are perceivable, similar as described by Maurice et al. [5].

In Fig. 3, STM images are displayed showing the surface of smooth ZrO_2 films at higher resolution. Measuring the apparent heights of the 2D islands and of the terrace steps, respectively, we found different values (i.e. 0.14, 0.24, 0.32 and 0.45 nm). For some of the islands, an atomic resolution of the $p(1 \times 1)$ structure was achieved (e.g. in Fig. 3(c) where island i of Fig. 3(b) is imaged at high resolution). These differences of island height and imaging of the surface structure of the islands, respectively, may indicate that different island types are present on the surface. It is quite possible that different surface terminations are established on top of the different islands. In the fcc C1 structure of ZrO_2 (calcium fluoride like), the (1 1 1) plains contain either O atoms or Zr atoms. The stacking sequence is two O planes for one Zr plane. Hence, three different terminations (one Zr and two different O terminations) are in principle possible. Recent calculations of the phase diagram of surface termination of fcc C1 ZrO_2(1 1 1) suggest the coexistence of different terminations for low O vapor pressures, partly induced by H [9].

4. Conclusions

In our endeavors of preparing well-ordered epitaxial ZrO_2 layers on Pt(1 1 1), we obtained best results for a 470 K deposition of Zr in an O_2 atmosphere followed by 950 K annealing (also in O_2 atmosphere). The films display large terraces covered by 2D islands. Bright LEED spots evidence the excellent ordering of the films. According to the LEED pattern the films are formed by stacks of (1 1 1) planes of fcc C1 ZrO_2 without displaying any superstructure. Indications are found for different terminations of the islands and terraces of the film, respectively. The films are slightly rotated which is probably induced by film /substrate interaction. Hence, films are now available which are very suitable for future STM investigations of catalytic reactions on sulfated ZrO_2 surfaces. Due to the assumed lateral differences in surface termination, one has to expect also lateral variations of the catalytic activity. However, we have to emphasize that well-ordered ZrO_2 films on Pt(1 1 1) display a metastable character and become discontinuous if the preparation temperature is increased above 1000 K.

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