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STEP REARRANGEMENT UPON LOW PRESSURE OXIDATION OF THE $Pt_3Ti(510)$ SURFACE: A STUDY BY SCANNING TUNNELING MICROSCOPY

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The oxidation of the single crystal stepped $Pt_3Ti(510)$ surface at oxygen pressures below 10^{-5} mbar and at a temperature of 770 K was studied by means of X-ray photoelectron spectroscopy (XPS), low energy ion scattering (LEIS) and low energy electron diffraction (LEED). Scanning tunneling microscopy (STM) was used to follow the evolution of the surface morphology on the atomic scale. The clean surface studied in ultrahigh vacuum conditions was found by LEIS to be composed of platinum only in the outermost surface plane. LEED and STM indicate that the clean $Pt_3Ti(510)$ surface consists of (100) terraces separated by double atomic steps. The exposure of the clean surface to oxygen at pressures in the range of 10^{-7}–10^{-5} mbar leads to the growth of a titanium oxide layer (with a composition close to TiO) which covers completely the substrate surface. The TiO film has long range order and exhibits complex LEED patterns. The STM measurements indicate that the ordered array of steps is kept in the early stages of the oxide film growth, whereas a change of the step morphology and step orientation is observed during the oxidation process.

Keywords: Platinum; titanium; alloy; oxidation; stepped surface; STM.

1. Introduction

The interest in the study of titanium oxide films on Pt and Pt–Ti alloy surfaces is mainly related to the fact that they mimic the situation resulting when platinum supported on titania catalysts is heated at high temperature. In these conditions, a thin layer of titanium oxide may migrate onto the surface of the platinum crystallites and cover completely or in part the surface of the platinum particles. The presence of reduced titanium oxides on the platinum clusters is thought to be responsible for the changes in the catalytic activity when the catalyst is reduced at high temperature.[1,2]

Ultrathin films of titanium oxides on platinum surfaces can be prepared either by vapor deposition

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of titanium and subsequent oxidation[3] or by oxidizing a platinum–titanium alloy.[4–6] It has been shown that exposures at relatively low O_2 pressures (below 10^{-5} mbar) and high temperatures (700–1000 K) of Pt_3Ti alloy surfaces lead to the formation of titanium oxide films with a thickness limited to a few atomic layers only.[4,5] Most of the studies performed so far on single crystal samples in this area have been performed on flat, low-Miller-index surfaces. Nevertheless, in the effort of modeling the properties of real catalysts there would be interest in examining instead stepped surfaces which can be obtained by cutting a single crystal along a high-Miller-index plane. The use of a stepped surface could be a way to prepare titanium oxide films with nanometric size not only in the direction perpendicular to the surface but also laterally, since the ordered array of steps can work as a template for the growth of a nanostructured oxide phase. However, the oxygen adsorption can lead to a modification of the step structure (for instance step bunching) and induce a faceting of the surface, as shown by the studies of stepped Cu surfaces.[7,8] Nucleation and growth of the oxide films are expected to influence even more drastically the morphology of the surface. Hence, it is of fundamental importance for the preparation of ordered nanonostructures to check how the array of steps is modified during the oxidation.

These phenomena have been examined in early studies of titanium oxide films grown on the stepped (510) surface of Pt_3Ti.[4,5] In these studies, low energy electron diffraction (LEED) provided useful information about the evolution of the step structure evolution and faceting induced by oxygen adsorption and oxide growth. However, scanning probe techniques such as scanning tunneling microscopy (STM) and atomic force microscopy (AFM) can give a direct image of the surface morphology on the atomic scale and permit one to follow the evolution of the step morphology during the oxidation process. In the present work, we re-examined the oxidation process of the $Pt_3Ti(510)$ surface using STM to obtain real space images of the growth of the titanium oxide layers prepared by exposing to O_2 the $Pt_3Ti(510)$ surface.

2. Experimental Details

The experiments were performed in an ultrahigh vacuum system with a base pressure in the low 10^{-10} mbar range. The system consists of two connected chambers — one used for sample preparation and characterization, the other for the STM measurements. The analytical/preparation chamber was equipped with a sample manipulator, a hemispherical electron/ion analyzer for XPS and LEIS measurements, a nonmonochromatized Al/Mg X-ray source, an ion gun used for surface cleaning, and LEIS and LEED optics. The STM chamber was equipped with a microscope produced by Sigma-scan (model GPI-300).[9–11] The sample could be moved from the manipulator in the analytical chamber to the microscope by means of a transfer system.

The $Pt_3Ti(510)$ sample is the same one used in previous studies.[5] The surface was prepared by cycles of Ar ion sputtering (500 eV) and annealing up to 1000 K until no contaminants could be detectable by XPS and LEIS. In these conditions a sharp LEED pattern characteristic of the clean surface was observed.[5] XPS spectra were measured at normal electron emission, using the Mg K_α as excitation radiation. The spectra were collected with a constant pass energy of 44 eV. The LEIS spectra were measured using a He^+ beam with an energy of 1 keV and at a scattering angle of 135°. STM measurements were performed at room temperature. Tungsten tips sharpened *in situ* by Ar ion bombardment were used in the STM experiments.

3. Results and Discussion

3.1. *The clean $Pt_3Ti(510)$ surface*

The presence of an ordered array of steps on the $Pt_3Ti(510)$ surface can be observed in LEED by the characteristic splitting into doublets of the spots corresponding to the terraces.[5] These terraces are unreconstructed (100) planes. From the energy dependence of the splitting of the $(0, 0)$ spot we found an average step height of 3.9 Å. This is in agreement with the bulk-truncated structure of the (510) surface consisting of (100) terraces separated by double atomic steps [i.e. steps whose height corresponds to two interlayer spacings of the (100) surface]. Terraces separated by double atomic steps have the same composition. For the $Pt_3Ti(510)$ two terminations of the unreconstructed (100) terraces are possible. One termination is a plane of pure platinum whereas the other is mixed, containing 50 atomic % of

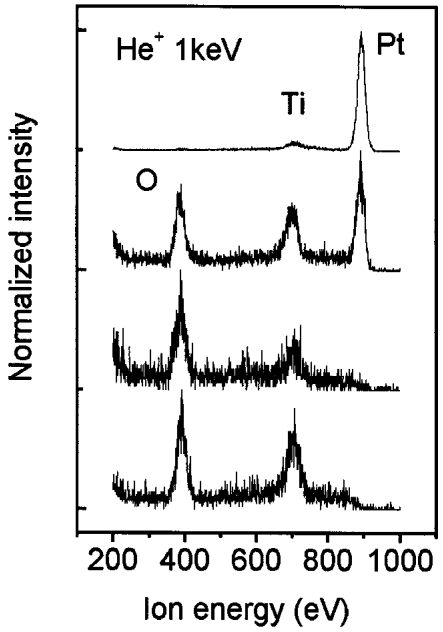

Fig. 1. LEIS spectra measured for the clean $Pt_3Ti(510)$ surface and for increasing exposures to oxygen at 770 K: (a) 150 s, pO_2 2×10^{-7} mbar; (b) 150 s, pO_2 1×10^{-6} mbar; (c) 300 s, pO_2 7×10^{-6} mbar. The intensities are normalized to the maximum in each spectrum and offset for a better reading.

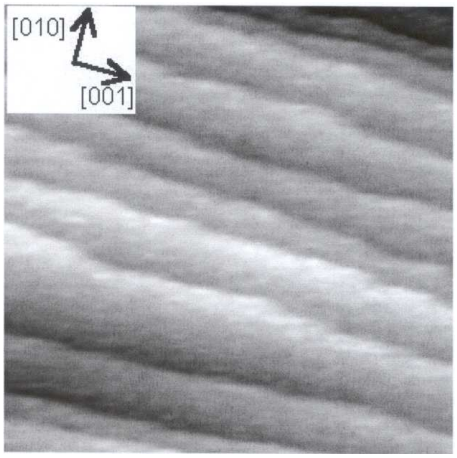

Fig. 2. STM image of the clean $Pt_3Ti(510)$ surface. 13.9 nm × 13.50 nm, tunneling current 0.2 nA, sample bias −0.5 V.

platinum and titanium. LEIS spectra measured for the $Pt_3Ti(510)$ indicate that the (100) terraces are terminated by a layer of pure Pt (Fig. 1). The LEIS results are consistent with the findings of a quantitative LEED analysis of $Pt_3Ti(100)$ showing that the stable termination of this surface is the pure platinum plane.[12]

A typical STM image of the clean surface is shown in Fig. 2. The lack of atomic resolution can be attributed to the narrowness of the terraces since close steps produce a disturbance to the image. The other reason may be the adsorption of gas from the residual atmosphere during the time needed for the sample to cool to RT after annealing. We found that the quality of the images got rapidly worse with time during the measurements due to adsorption of carbon monoxide and hydrogen, as indicated by XPS, LEIS and thermal desorption mass spectrometry.

The STM measurements confirm that the surface consists mainly of terraces separated by steps having an average height of 3.9 Å, i.e. is double atomic steps. However, there exists a clear statistical distribution of the terrace width around the mean value of approx. 20 Å, the width expected for terraces separated by double atomic steps. A fraction of the surface (estimated to be around 20%) shows also monoatomic steps. The residual titanium signal observed in the LEIS spectra may be due to these termination defects.

3.2. *Oxidized surface*

The oxidation was carried out by exposing the sample held at 770 K at oxygen pressures in the $10^{-7} - 10^{-6}$ mbar range. These conditions are close to those used in previous studies of Pt_3Ti surfaces.[4,5] The LEIS spectra measured at various stages of the oxidation process are shown in Fig. 1. After oxygen exposures higher that approx. 500 s and at an oxygen pressure of 2×10^{-7} mbar, the whole surface is covered by a layer containing only oxygen and titanium since the platinum signal is not detectable in the LEIS spectrum. Ti 2p XPS spectra measured for increasing oxygen exposures are shown in Fig. 3. Upon oxygen exposure an increase of the Ti2p peak intensity and a decrease of the Pt 4f intensity are observed. During oxidation, the component at 455.5 eV (corresponding to the clean surface) gradually disappears while the component at BE of 456.2 eV grows and becomes the main peak in the Ti $2p_{3/2}$ peak, as indicated by the curve fitting analysis. The latter value corresponds well to the Ti $2p_{3/2}$ BE measured for titanium ultrathin layers formed by oxidation of Pt_3Ti surfaces and attributed to Ti(II).[6] The curve fitting

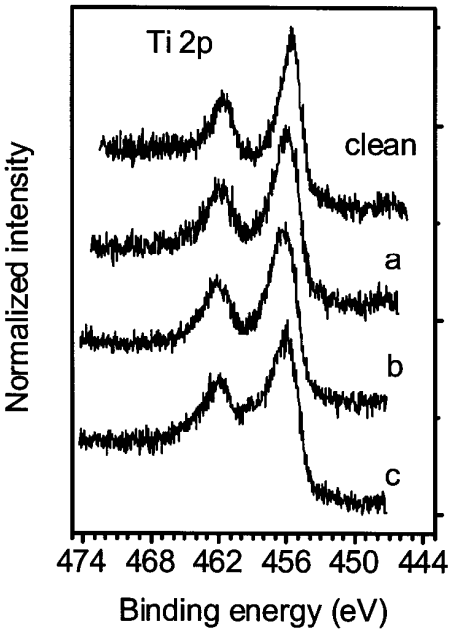

Fig. 3. XPS spectra measured for the clean $Pt_3Ti(510)$ surface and for increasing exposures to oxygen at 770 K: (a) 150 s, pO_2 2×10^{-7} mbar; (b) 150 s, pO_2 1×10^{-6} mbar; (c) 300 s, pO_2 7×10^{-6} mbar. The intensities are normalized to the maximum in each spectrum and offset for a better reading.

analysis of the Ti2p spectra indicates the presence of an additional component (at approx. 459.0 eV) corresponding to Ti(IV) for the highest oxygen exposure. The area of this component is about 10%–20% of the area of the main peak. On the basis of the LEIS and XPS data we can conclude that for oxygen exposures at a pressure in the 10^{-7} mbar range, the substrate surface is covered by an ultrathin layer having a composition close to TiO. For exposures at higher oxygen pressures TiO_2 begins to form.

The appearance of extra spots in the LEED pattern indicates the growth of an ordered epitaxial film of titanium oxide formed by exposing the Pt_3Ti surface to oxygen. The complex LEED patterns observed in the present case are similar to those found for the TiO films formed by oxidation of the $Pt_3Ti(100)$ surface.[4] In that case the diffraction patterns were interpreted in terms of several domains of a titanium oxide phase with a hexagonal (or oblique) unit cell. The presence of double diffraction spots suggests the formation of flat titanium oxide islands with a thickness of a few atomic layers.[4] Upon increasing the exposure to oxygen, the doublets due to

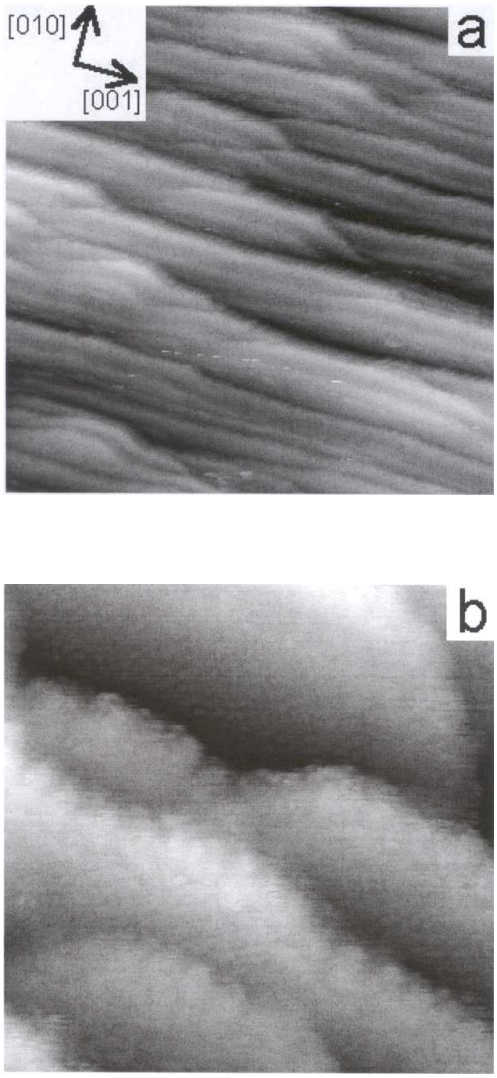

Fig. 4. STM images collected after an exposure of 150 s (a) and 300 s (b) at pO_2 of 2×10^{-7}, T 770 K. (a) 97 nm $\times$ 101 nm, tunneling current 0.2, sample bias -0.3 V; (b) 27.7 nm $\times$ 26.9 nm $\times$ 1.7 nm, tunneling current 0.2 nA, sample bias -0.3 V.

the steps gradually vanish and are replaced by single spots corresponding to the (100) terraces.

STM images collected after an oxygen exposure at a pressure of 2×10^{-7} mbar are shown in Fig. 4. It is evident that the terraces are wider here than in the case of the clean surface. Kinks can also be observed developing along the step edges. The STM images show that oxidation of the $Pt_3Ti(510)$ induces a partial bunching of steps and an enlargement of the terraces in accordance with the disappearance of the

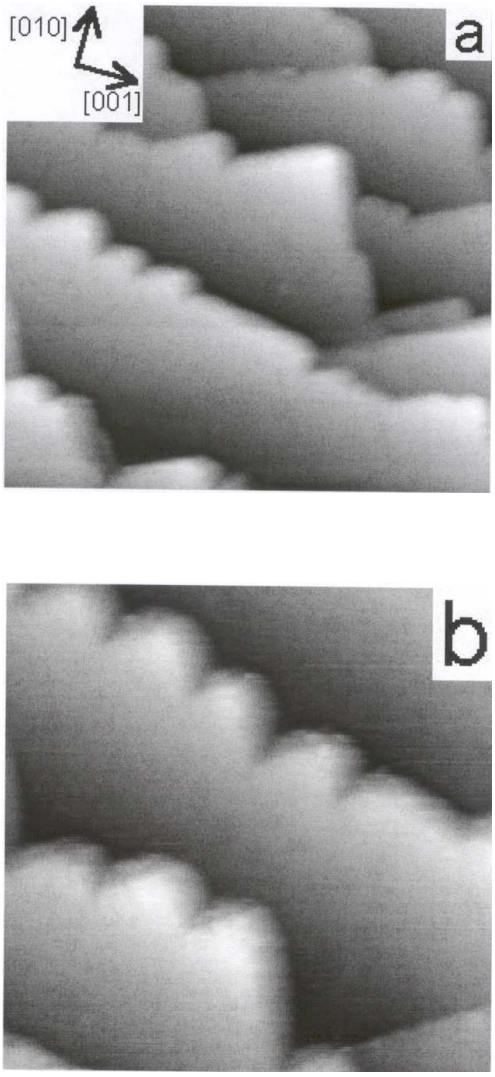

Fig. 5. STM images acquired after an exposure of 150 s with a pO_2 of 1×10^{-6} mbar, T 770 K. (a) 48.5 nm × 47.2 nm, unneling current 0.2 nA, sample bias −0.2 V; (b) 30.2 nm × 30.0 nm, tunneling current 0.2 nA, sample bias −0.1 V.

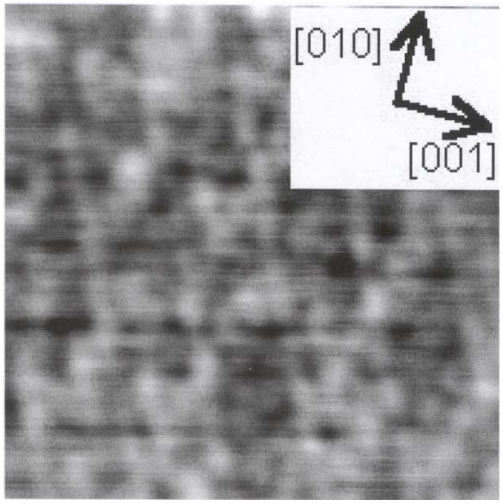

Fig. 6. Two-dimensional STM image measured on the large terraces of the oxide film prepared under the conditions reported in the caption of Fig. 5: 0 nm × 4.8 nm, tunneling current 0.2 nA, sample bias −0.2 V.

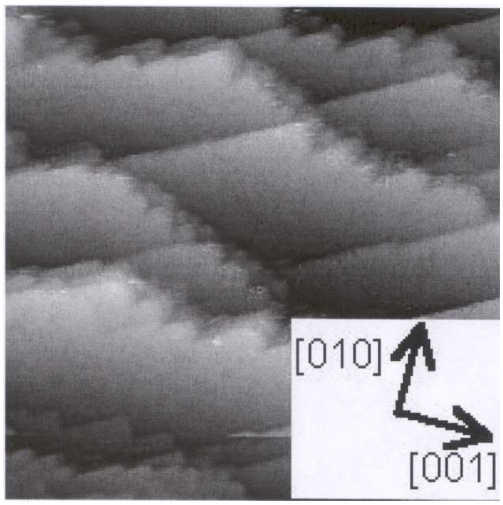

Fig. 7. STM image acquired after an exposure of 300 s with a pO_2 of 7×10^{-6} mbar, T 770 K: 92 nm × 94 nm, tunneling current 0.2 nA, sample bias −0.9 V.

spot splitting observed in LEED patterns. Double atomic steps characteristic of the clean surface coexist with multiatomic steps with an average height of 1 nm separating terraces as large as 4 nm.

Oxidation carried out at higher oxygen pressures leads to a significant modification of the step morphology [Figs. 5(a) and 5(b)]. The steps are more regular and higher than in the case of lower oxygen exposures. The average size of the terraces is of the order of 15 nm, separated by steps 2 nm high. Hence, the disappearance of the spot splitting observed in the LEED pattern upon oxidation is due to the increase of the terrace size rather than to a bunching of the steps. At this stage, the growth of the titanium oxide film induces the formation of kinks in the steps. The steps form angles of 45° one to the other, i.e. they are oriented along the [011] and [01$\bar{1}$] directions.

On the larger terraces, rows of bright features can be observed (see Fig. 6). The bright features can be interpreted as titanium atoms in the oxide layer, as suggested for the case of TiO films encapsulating Pt clusters deposited on $TiO_2(110)$.[13,14] A more detailed discussion on these structure will be presented in a forthcoming paper.[15]

The STM images collected after oxidation at the maximum pressure used in this work (7×10^{-5} mbar) show an array of steps similar to those observed in the previous oxidation stages (Fig. 7).

4. Conclusions

By means of XPS and LEIS we found that exposures to oxygen at a pressure below 1×10^{-5} mbar and at 770 K of the $Pt_3Ti(510)$ surface lead to the formation of a TiO film that is a few atomic layers thick. The LEED patterns observed after oxidation indicate that the oxide film grows epitaxially on the alloy surface. The formation of the oxide film induces a substantial modification of the step morphology. In the early stages of oxidation, irregular kinks develop along the steps, but the main orientation of the step along the [001] direction is maintained. After oxidation at an oxygen pressure of 2×10^{-6} mbar, the terraces become wider and multiatomic steps oriented preferentially along [011] directions form. The STM results reveal that the growth of the titanium oxide layer does not induce a step bunching, but an ordered array of steps with preferential orientations is present even after oxidation.

Acknowledgment

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