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Thermally induced formation of vacancy-islands on the atomic terraces of $TiO_2(1\,1\,0)$ surface covered by Pt

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Abstract

Thermal stability of ultrathin Pt layers deposited onto $TiO_2(1\,1\,0)$-$(1 \times n)$ surface was studied by scanning tunneling microscopy in the temperature range of 300–1200 K. Besides the formation of 3D particles and the gradual sintering of the initial clusters, a unique morphological feature—one monolayer (ML) deep vacancy-islands (pits)—developed as a result of annealing above 1000 K. This appeared on the atomic terraces of the substrate covered by Pt of a few percent monolayer. The edge of these pits were typically decorated by Pt nanoparticles grown during the annealing procedure, showing that the bonding between the admetal and the substrate is the strongest at these sites. The formation of the vacancy-islands can be explained by the decoration process activated by the thermal treatment above 500 K. Depending on the Pt coverage, two types of morphological states can be distinguished: (1) at very low coverages (<0.05 ML) one pit contains one Pt nanoparticle; (2) in the case of higher coverages (>0.15 ML) few Pt nanoparticles are localized in a particular vacancy-island of round shape, typically at the perimeter of the pit.

Keywords: Scanning tunneling microscopy; Platinum; Titanium oxide; Surface structure, morphology, roughness, and topography

1. Introduction

One of the characteristic properties of noble metals deposited on reducible oxides is their decoration by the support material on the effect of high temperature reduction [1–3]. In the last few years several authors reported that the investigation of the so called two-dimensional (2D) model systems (metal epitaxy on oxide surfaces) may deliver a lot of new and detailed information about the decoration process [3–8]. For example, Dulub and his coworkers demonstrated by atomically resolved scanning tunneling microscopy that a well ordered decoration layer is formed on the top of the supported Pt crystallites as a result of annealing in UHV at 1000 K [8]. In the present study we provide some further interesting observations about the structural changes of the $TiO_2(1\,1\,0)$ terraces nearby the supported Pt particles. In contrast to the experiments performed by Dulub et al., the results described in this study relate to low Pt coverages (a few percent of monolayer). The formation of nanopits (vacancy-islands) around the Pt nanoparticles is probably connected with the decoration phenomenon observed earlier in several cases [3–8]. The possibility for tailored fabrication of pits by this process may be of

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importance in the further work with the 2D model catalysts (2DMC).

2. Experimental

The experiments were performed in an UHV apparatus equipped with Ar^+-gun, AES-LEED analyzer, quadrupol mass spectrometer and scanning tunneling microscope. The UHV-compatible transfer system served for introducing the sample from air to vacuum and for positioning of it for the different treatments in the vacuum chamber. The $TiO_2(1\,1\,0)$ crystals (one side polished) were purchased from PI-KEM (England). A special sample holder was developed for annealing of the crystals: a resistively heated W-filament was painted by high temperature ceramic adhesive (AREMCO Products Inc.) and the sample was sticked to this assembly. In this way a very low electric power (approx. 10 W) needed to achieve the sample-temperature of 1200 K.

The cleaning procedure of the $TiO_2(1\,1\,0)$ crystals consisted of a few hours annealing at 800 K in UHV followed by several cycles of Ar^+ bombardment (10 min, 1 keV, 10^{-6} A/cm^2) at 300 K and annealing at 1100 K for 10 min in UHV. The cleanliness of the sample were checked by Auger-electron spectroscopy and by STM-detection of the (1×1) terraces formed after a longer annealing at 900 K in UHV. The amount of Pt deposited was controlled by adjusting the current flowing through a Pt-filament (99.95%) spotwelded to thicker Ta rods. The surface concentration of the deposited metal is given in monolayer equivalent (ML) which corresponds to 1.5×10^{15} Pt atoms/cm^2. The calculation of this value was based on the appearing volume of 3D Pt crystallites observed on the STM images taken off after annealing the sample at 1200 K (see more details in [9]). During Pt-dosing, the distance between the evaporator and the sample was approximately 20 mm, in this way the warming of the probe was negligible. The STM pictures were typically recorded with a sample-tip voltage of +1.5 V and a tunneling current of 0.2 nA.

3. Results and discussion

Fig. 1 shows the characteristic STM images recorded on the pure $TiO_2(1\,1\,0)$–$(1 \times n)$ surface (n varies between 2 and 5). It can be seen on the large scale image (200 nm $\times$ 200 nm) that the sample used in the present study exhibits rather large terraces referring to an accurate orientation of the sample (Fig. 1A). The average size of the terraces was approximately 80 nm $\times$ 150 nm. The step edges oriented in $[1\,\bar{1}\,2]$ are slightly rippled by short steps in the [0 0 1] direction. The one-dimensional (1D) strands running in the crystallographic orientation of [0 0 1] exhibit a statistically uniform distribution on the (1×1) arranged terraces (Fig. 1B). The formation and the structure of

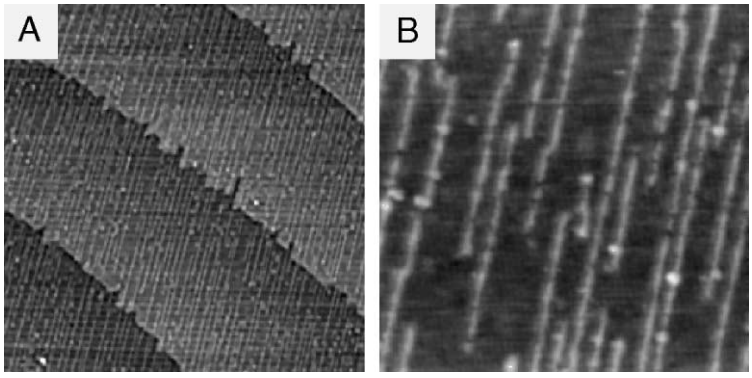

Fig. 1. Characteristic STM pictures detected on the clean $TiO_2(1\,1\,0)$-$(1 \times n)$ surface used as substrate in this work. The size of the images: (A) 200 nm $\times$ 200 nm; (B) 50 nm $\times$ 50 nm. The parameters of the tunneling: $U_t = +1.5$ V (sample positive); $I_t = 0.2$ nA.

the outrising added rows were precisely characterized in several recent papers and they were identified as an 1D epitaxial Ti_2O_3 phase [10–16]. It is worth remarking that on the smaller scale images the (1×1) arrangement of the terraces (the region between the added rows) can be readily detected.

In the following experiments, the effect of thermal treatments of the sample exposed to Pt at 300 K in UHV is studied by STM. The initial Pt coverage was approximately 0.08 ML (with an error of approximately 25%) calculated from the volume of the outrising new features (see more details in [9]). The STM images of 100 nm × 100 nm reveal the characteristic localization of the Pt nanoparticles formed already at 300 K and sintered at higher temperatures (Fig. 2A–D). A general feature of the images presented in Fig. 2 is that the outrising round shape features (identified as Pt particles) are uniformly distributed on the terraces without any preferential decoration of the step edges. It can be also seen that the 1D added rows are not favourite sites in the particle formation. At higher magnification, however, it appeared that the end of the rows exhibits some preference for bonding the metal particles of 1–2 nm. All these observations provide further evidencies for the site selective nucleation of Pt clusters on mixed (1×1) and (1×2) surface reported recently by Gan et al. [17]. At the same time smaller clusters (<1 nm) are also formed on the (1×1) terraces in clear separation from the outrising rows even after annealing at 500 K for 10 min (Fig. 2A). This behaviour is substantially determined by the local oxidation state of the surface. Accordingly, the oxygen vacancies on the (1×1) terraces and the oxygen deficient sites at the end of the outrising 1D rows exhibits the highest activity in bonding of the admetal atoms or nanoparticles [8,13,14,17]. The thermal treatment at 700 K results in a clear increase both the concentration and the size of the appearing particles (Fig. 2B). This tendency can be explained by a gradual sintering of the smaller (partially unresolved few-atom nanoparticles) by the so called Ostwald-ripening where the growth of the particles is determined by the size-dependent sublimation heat. It is also possible that a fraction of support material is diffusing on the top of the Pt crystallites (decoration) over 500 K contributing to further increase of the average particle-size [4,8].

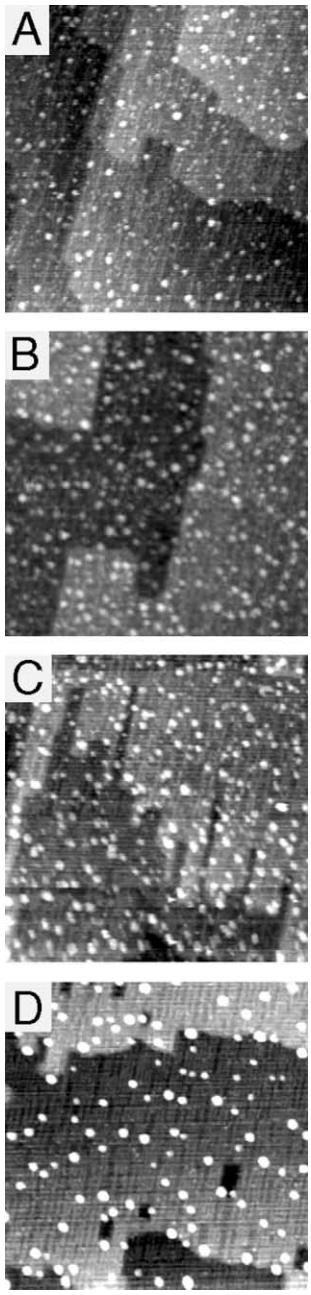

Fig. 2. Effects of thermal treatment of the $TiO_2(1\,1\,0)$-$(1 \times n)$ surface deposited by 0.08 ML of Pt at 300 K. STM images taken after subsequent annealing at (A) 500 K; (B) 700 K; (C) 900 K; (D) 1100 K for 10 min. Image size: 100 nm × 100 nm.

Nevertheless, the volume-enhancement of the ad-particles caused by the decorating oxide layer (maybe self-limiting) becomes obviously less important for larger particles. The particles, however, show a relative wide range (1–4 nm) size-distribution, although the Ostwald-ripening predicts basically a quite uniform and narrow particle-size distribution. This contradiction suggests that other mechanism may also contribute to the restructuring of the $Pt/TiO_2(1\,1\,0)$ surface. In a recent study Frenken et al. [18,19] concluded that the collective particle diffusion plays an important role in the formation of Pd epitaxy on $TiO_2(1\,1\,0)$ surface (especially at low coverages). In addition we think that in the present case the decoration process has also some effect on the diffusion of admetal and it may cause strong deviation from the classical Ostwald-ripening mechanism.

The STM image of the surface annealed at 900 K shows a very surprising feature, namely that the steps running in the direction of $[1\,\bar{1}\,2]$ are very strongly rippled by narrow channels in the orientation of [0 0 1] (Fig. 2C). The vicinity of these channels are definitely decorated by metal particles. This behaviour may be explained by an Pt-activated diffusion of the substrate material in the preferred [0 0 1] orientation. Our earlier study on the reordering of a slightly Ar^+ bombarded TiO_2-(1 1 0) surface has shown that small Ti_xO_y dots with a characteristic diameter of 1 nm are the typical mobile species in the diffusion process [20]. The characteristic vacancy-islands appearing on the terraces detected after annealing at 1100 K strongly support this idea (Fig. 2 D). It can be also seen that the average particle size increased substantially (4–5 nm), and at the same time, the ordering of the terraces improved to a high degree.

As shown in Fig. 3A, some of the pits are well shaped: they are elongated in the [0 0 1] direction and contain at least one nanoparticle. The Pt particles (may be decorated) appearing inside the pits sink also in the support terraces. By variation of the initial coverage of Pt deposited onto the substrate at 300 K followed by annealing at 1100 K in UHV, two different characteristic morphologies can be observed for the pit-crystallite feature: (i) at low coverages (<0.10 ML), the one-pit/one-particle arrangement is the typical form (Fig.

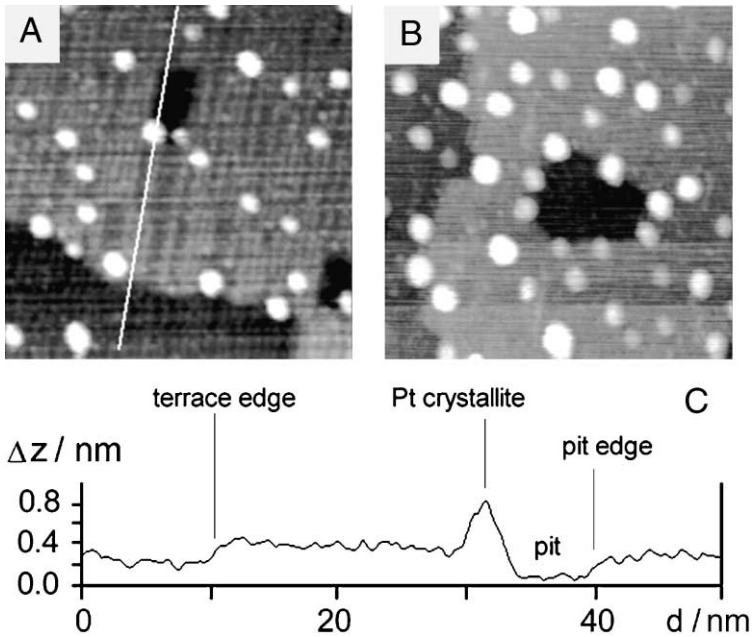

Fig. 3. Characteristic vacancy-island regions for two different initial Pt coverage: (A) 0.08 ML; (B) 0.15 ML. The size of the images: 50 nm × 50 nm. (C) Height-profile along the characteristic line indicated on the STM image A.

3A); (ii) at higher Pt coverages (>0.15 ML) one vacancy-island contains more than one crystallites which typically decorate the edge of the pit (Fig. 3B). The z-profile spectra show the variation of the local height along the lines indicated on the picture A. The characteristic step height for the pit edge is the same as that for the terrace edge (0.19 nm). It means that the depth of the vacancy-island is exactly one monolayer in the substrate terrace. The Pt crystallites localized at the pit-edges are sitting both on the lower or upper terrace, at the same time the position of the crystallites inside the pits varies randomly. It is important to note that any type of imaging failure caused by the so called tip-convolution effects can be totally excluded.

The experimental results presented above clearly suggest that the thermal treatment of the Pt-deposited $TiO_2(1\,1\,0)$ surface causes a reordering of the upper atomic layer of the support oxide. It is worth mentioning that in the case of the metal-free TiO_2 $(1\,1\,0)$-$(1 \times n)$ surface, the same thermal treatment never resulted in formation of any vacancy-islands, although these features readily appear for an Ar^+-prebombarded (at 300 K) surface. The development of a pitted morphology is quite general property in the ordering of oxide surfaces [21]. We may suppose that in our case the supported Pt activates the separation of some Ti_xO_y species from the top layer of the support, and these zero-dimensional (0D) dots can easily diffuse on the surface. During this process the metal particles became also decorated by these species. Naturally, it can not be excluded, that individual Ti and O ions are also migrating species and some Pt–Ti alloy may form above 1000 K [22]. Nevertheless, our results suggest that the mass transfer from the deeper layers is less intensive than the mass transfer in the surface layer.

By comparing our results to those obtained in other laboratories we can conclude that although the decoration was observed in all cases for Pt-covered the $TiO_2(1\,1\,0)$ surface, however, the formation of the terrace-pits is reported only in this work [3–8,23]. This deviation suggests that the phenomenon mentioned above is well detectable only at an optimal Pt coverage (approximately 10% ML). At the lower Pt coverages the metal crystallites are not sufficiently large to cause appreciable changes of the atomic terraces of the oxide support, however at higher Pt coverages (several monolayers) the density and the height of the Pt crystallites prevent the clear detection of the modified oxide terraces.

4. Conclusions

(i) Formation of vacancy-islands was observed on $TiO_2(1\,1\,0)$-$(1 \times n)$ atomic terraces containing a few procent monolayer of Pt following the annealing at 1100 K in UHV.
(ii) The local geometry of the vacancy-islands and the relating Pt crystallites depended on the initial Pt coverage.
(iii) The formation of the pits in the terraces is explained by the decoration process where the supported Pt activates the evolution of some easily diffusing 0D oxide dots by disrupting of them from the top layer of the support.

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