PERGAMON

Vacuum 61 (2001) 317–322

VACUUM
SURFACE ENGINEERING, SURFACE INSTRUMENTATION & VACUUM TECHNOLOGY

www.elsevier.nl/locate/vacuum

Self-organization of oxide nanodots generated by low energy Ar^+ bombardment on $TiO_2(1\,1\,0)$–(1×2)

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Abstract

Defect sites generated by low energy Ar^+ bombardment (0.5–1.5 keV) at room temperature and the effect of subsequent annealing were studied on a $TiO_2(1\,1\,0)$–(1×2) surface by STM. It was found that, due to the effect of ion bombardment, the row structure of the reconstructed $TiO_2(1\,1\,0)$–(1×2) surface transforms into a granular structure where the 0D nanodots exhibit a rather narrow size-distribution at about the diameter of 2 nm. The ordering of these dots can be induced by a slight thermal treatment at 500–700 K resulting in 1D strings along the crystallographic orientation of [0 0 1]. In this stage the surface terraces show (1×1) structure. Due to the effect of further annealing at 900 K the surface converts into a (1×2) reconstructed arrangement. The latter process is accompanied by the dissolution of the out-rising dots and strings formed in the previous treatments. It is assumed that the composition of the uniform nanodots is probably $(Ti_2O_3)_n$ where n varies between 4 and 6.

Keywords: Low energy Ar^+ bombardment; $TiO_2(1\,1\,0)$–(1×2); Self-organization of nanodots on oxide surfaces; Anisotropic surface diffusion; Scanning tunnelling microscopy

1. Introduction

Ion bombardment of solid materials is a widely used method for surface-selected machining and it is applied extensively in different high technology procedures [1,2]. Besides the cleaning and sputtering treatments, which are the most important applications in this field, there are numerous other possibilities for the usage of low energy noble gas ion radiation: (i) formation of microscale structures by focussed ion beams (litography); (ii) modification of the adhesive properties of the surfaces for better sticking of thin films; (iii) hardening of the epitaxial thin layers and; (iv) induced formation of quasi-periodic surface nanostructures. In the case of oxide surfaces, it is well known that the ion sputtering usually results in a preferential removal of the oxygen content of the surface and sub-surface layers [3,4]. Although this process was studied in detail for different materials by photoelectron spectroscopy measurements, the nanoscale structures formed in the process could not be resolved. Some recent studies show, however, that the application of STM and AFM can deliver detailed information about the nanostructures generated by ion bombardment [4,5].

The characteristic reconstructions appearing on the surface of different TiO_2 single crystals exhibit a direct correlation with the oxidation state of the top layers [5–10]. In recent work, Benett et al.

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0042-207X/01/$ - see front matter
PII: S0042-207X(01)00136-1

demonstrated by STM-movie experiments that the reactivity of the $TiO_2(1\,1\,0)$–(1×2) surface depends very sensitively on the oxygen content of the subsurface layers [7]. They have found that cyclic oxidative epitaxial growing starts only on highly reduced oxide crystals which contain a large number of oxygen defects. The authors concluded that the diffusion of Ti atoms is responsible for this process and it leads to the formation of reduced epitaxial oxide nanostructures with characteristic morphology. It can be expected that the typical nano-objects formed in the different treatments (oxidation, annealing, bombardment) of the TiO_2 surfaces have well-defined chemical composition and structure. Assuming this connection, the probable structure of the nanodots presented in this paper can also be suggested by considering the results of some earlier studies [4–11].

In this work, the effect of the Ar^+ bombardment and the subsequent annealing of the ion treated $TiO_2(1\,1\,0)$–(1×2) surface is studied by STM. The main point emphasized in the present paper is the formation and structure of the nanodots found as a characteristic uniform feature observed during the phase transitions on the TiO_2 single-crystal surfaces.

2. Experimental

The experiments were performed in an UHV system equipped with an STM-head, a quadrupole mass spectrometer and a LEED-AUGER analyser [6]. The Ar^+ beam (incidence angle of 60° relative to the surface normal) in the energy range of 0.5–1.5 keV with the current density of 10^{-5} A cm^{-2} was produced by an ion gun. The polished $TiO_2(1\,1\,0)$ sample was clipped on a Ta plate and mounted on a transferable sample cartridge. An ohmically-heated W filament, positioned just below the Ta plate, served for the annealing of the probe. The temperature was checked by a thin chromel–alumel thermocouple attached to the side of the sample. The cleaning procedure of the $TiO_2(1\,1\,0)$ surface consisted of a few hours annealing at 800 K in UHV, some cycles of Ar^+ ion bombardment (10 min, 1.5 kV, 10^{-5} A cm^{-2}) at room temperature and annealing at 1200 K for 10 min in order to produce a well-ordered 1×2 reconstructed structure [6]. The purity of the surface was checked by AES measurements.

The STM imaging was performed by a chemically edged W-tip sharpened from time to time in situ by applying 5–10 V pulses between the tip and the sample. A bias of $+1.5$ V and current of 0.2 nA were typically used for the imaging. The STM pictures, consisting of 256×256 points, were collected within 1–3 min depending on the corrugation of the surface. The characteristic pictures shown in this work were chosen from numerous records obtained on different regions of the sample.

3. Results and discussion

3.1. The effect of duration and energy of the Ar^+ bombardment on $TiO_2(1\,1\,0)$–(1×2)

The preparation method of the clean and ordered $TiO_2(1\,1\,0)$–(1×2) surface was described earlier in detail [6]. The duration of the annealing at 1200 K needed to transform the (1×1) phase into the more stable (1×2) arrangement depended sensitively on the prehistory of the sample [6–10]. This behaviour is probably connected to the gradual reduction of the sample (bulk) during the experiments. The well-ordered (1×2) surface can be seen in Figs. 1A and B. Before the bombardment, the clean surface imaged on a scale of 50 nm × 50 nm exhibits monoatomic steps running mainly in the [0 0 1] orientation (Fig. 1B). The terraces are decorated by periodic rows separated by 1.35 nm parallel to the steps, as can be seen in Fig. 1A registered on a 20 nm × 20 nm area.

The STM images in Fig. 1 depict the characteristic changes of the surface morphology detected after Ar^+ bombardments at energies of 0.5 and 1.5 keV (B, C and D, E respectively). The duration of the treatments were 6 min in both cases. The dependence on the duration of the bombardment was also studied (not presented here) and it was found that 6 min is sufficient to achieve a final stage of the modified morphology. The larger scale image shows that the terraces are visible after the treatment with 0.5 keV Ar ions, although

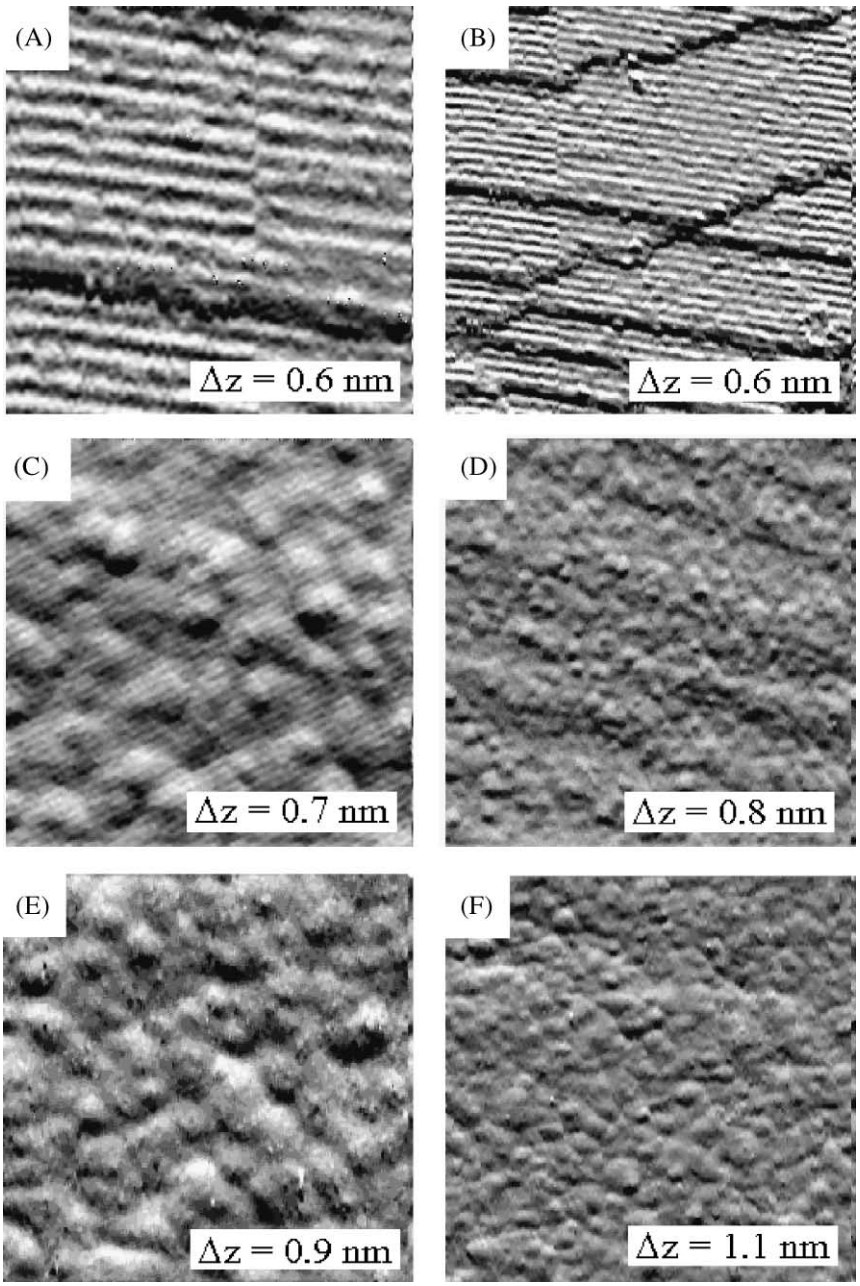

Fig. 1. Effect of the Ar^+ bombardment on (A, B) clean $TiO_2(1\,1\,0)$–(1×2) surface for 6 min at two different energies: (C, D) 0.5 keV and (E, F) 1.5 keV. The ion flux of 3×10^{13} ion $cm^{-2}\,s^{-1}$ was applied in both cases. The size of the images: (A, C, E) 20 nm × 20 nm; (B, D, F) 50 nm × 50 nm.

protrusions of 2–3 nm appear everywhere (Fig. 1D). These out-rising features can be seen in higher resolution in Fig. 1C. In the case of 1.5 keV ion energy the size of the out-rising dots formed is nearly the same as for lower energy (Figs. 1E and F), at the same time the terrace structure is completely destroyed and undetectable on the STM images of 50 nm × 50 nm size (Fig. 1F).

It is well known that the morphology imaged by STM in atomic resolution is strongly affected by the electronic structure of the surface. In this way, it can be supposed that the out-rising features detected by STM may be assigned to vacancies generated by the preferential removing of the surface oxygen atoms, as the tunnelling probability is higher above these sites. Otherwise, however, the clear separation and the more or less well-defined size of these features may refer to the formation of real nano-objects. This latter conclusion will be supported in the next paragraph dealing with the thermal behaviour of these nanostructures.

3.2. Thermally activated rearrangement of the nanostructures formed by Ar^+ bombardment

The surface bombarded for 6 min at 300 K with Ar^+ beam of 0.5 keV energy (2×10^{-6} A cm^{-2}) (Figs. 1C and D) was annealed at different temperatures (Figs. 2A–C). In each case the size of the STM image was 50 nm × 50 nm. Fig. 2A shows the surface morphology after 10 min annealing in UHV at 500 K. This image exhibits only a slight alteration relative to the original morphology: the out-rising features became more separated, although their distribution remained more or less homogeneous. The annealing at 700 K in UHV for 10 min results in a substantially changed structure: the out-rising nanodots constitute one dimensional (1D) strings consisting of several dots and aligned in the [0 0 1] orientation parallel to the rows of the terraces (Fig. 2B). Some of the dots stay individually separated and exhibit characteristic geometric properties: height of 0.18 nm, and diameter of 1.40 nm. It may be noted that these values are practically the same as those of the out-rising features detected after annealing at lower temperatures. The periodic inner structure of the 1D chains may suggest that they comprise the same nanodots connected to each other. This behaviour may also mean that the dots diffuse anisotropically

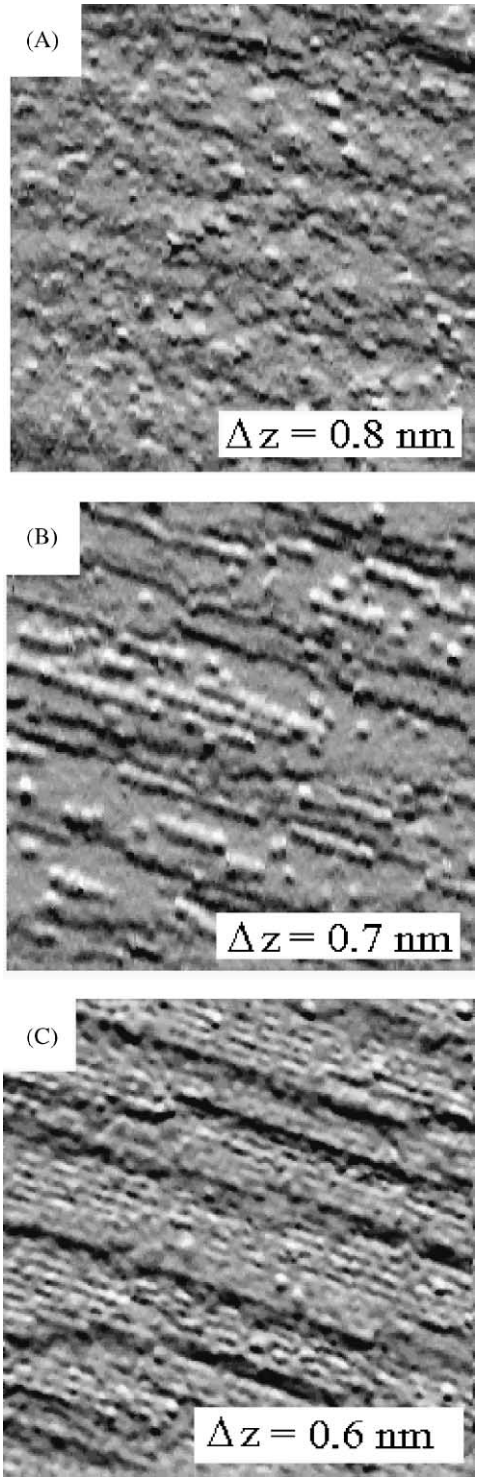

Fig. 2. Effect of the annealing of an Ar^+ bombarded (0.5 keV, 3×10^{13} ion cm^{-2} s^{-1}, 6 min) surface at different temperatures (A) 500 K, (B) 700 K, (C) 900 K. The image size: 50 nm × 50 nm.

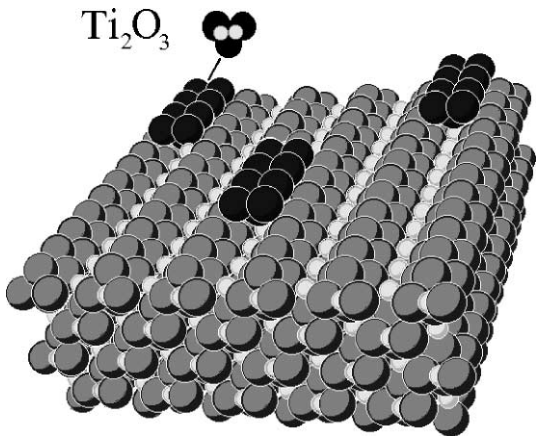

Fig. 3. Ball-model of the characteristic 0D nanodots with a stoichiometry of $(Ti_2O_3)_4$ supported on a (1×1) terrace of the $TiO_2(1\,1\,0)$ surface.

on the surface as compact units. The two-dimensional Fourier analysis of the latter STM image has shown that the terraces supporting the out-rising 0D and 1D nanostructures possess a (1×1) arrangement. On the effect of further annealing at 900 K, the surface converts into a complete (1×2) reconstruction (Fig. 2C).

By accepting the conclusion suggested above that the characteristic nanodots can be identified with a real phase (they are not simply the result of the imaging of oxygen vacancies), it may be concluded that the chemical composition of these dots is probably $(Ti_2O_3)_n$, where n can be varied between 4 and 6. These 0D units seemingly show a high stability and they can play a substantial role in the phase transition of $(1 \times 1) \rightarrow (1 \times 2)$ arrangements. Fig. 3 depicts the suggested 0D objects on a ball model. According to the STM pictures registered in Fig. 2B, the oxide nanodots are located on a $TiO_2(1\,1\,0)$-(1×1) surface.

Looking over the different characteristic nanostructures of reduced dimensionality reported on $TiO_2(1\,1\,0)$ surfaces it can be deduced that the appearance of 0D nanodots and 1D strings on the effect of high temperature annealing or oxidation is a quite general feature [6–10]. Moreover, Biener et al. have demonstrated in a recent paper that the evaporation of vanadium onto a $TiO_2(1\,1\,0)$ surface results in the formation of nanodots of approximately 2 nm [11]. They explained this process by the evolution of isolated nanoclusters of vanadium oxide which can align themselves along the [0 0 1] direction of the underlying titania surface. It was also supposed that the nanodots possess V_2O_3 stoichiometry consisting of 10–20 atoms. This conclusion closely resembles that of the present work, and it suggests that the nanodot with the size of 2 nm is a very stable nano-unit form of these oxides. Moreover, taking into account the experimental results of the present paper, one may come to the conclusion that the low energy ion bombardment results also in the formation of nanodots with a reduced stoichiometry rather than in the generation of simple oxygen vacancy sites.

4. Conclusions

(i) The Ar^+ bombardment with low ion energy of 0.5 and 1.5 keV results in the formation of 0D oxide nanodots of approximately 2 nm on the $TiO_2(1\,1\,0)$–(1×2) surface.
(ii) The annealing of the bombarded surface activates the alignment of the isolated 0D nanodots along the [0 0 1] orientation. The composition of the 0D units is probably $(Ti_2O_3)_n$, where n varies between 4 and 6.

Acknowledgements

This work was supported by the Hungarian Scientific Research Foundation Grant OTKA 29952, 32040.

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