

# Surface evolution of rutile $\text{TiO}_2$ (100) in an oxidizing environment

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## Abstract

Transmission electron microscopy (TEM) has been used to study the rutile  $\text{TiO}_2$  (100) surface in an oxidizing environment. By changing annealing conditions,  $\text{TiO}_2$  surfaces with different morphologies are obtained. We report a new centered ( $2 \times 2$ ) surface reconstruction on this surface. Our experimental data indicates that this is a meta-stable, oxygen deficient structure formed as the disordered surface regains its stoichiometry in an oxidizing annealing environment.

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## 1. Introduction

As a commonly used catalyst support and substrate for studies of thin films, rutile  $\text{TiO}_2$  has been the subject of active investigation for decades. Various methods have been employed in order to gain information about its surface properties, and to understand and improve the performance of  $\text{TiO}_2$ -related materials and devices. The local surface environment, especially oxygen vacancies near to the surface, is very important due to the role they play in water dissociation [1–3], the interactions between metal particles and rutile in supported metal catalysis [4–6] and in gas sensing for oxygen [7]. Since rutile can be reduced [8], different reduction and oxidation treatments yield significantly different surfaces [9]. A large amount of work has focused on the (110) surface [10–14]. Using scanning tunneling microscopy (STM), a number of reconstructions and surface features have been identified [10], including, under certain conditions, ad-atom rows of  $\text{Ti}_2\text{O}_3$  [11], shear-planes [12,13] and so-called “rosettes”: sub-stoichiometric, quasi-hexagonal overlayer islands [14]. Principal

variables in the formation of these structures appear to be the oxygen partial pressure and temperature during annealing. Experimental studies of the rutile (100) surface thus far have been primarily carried out under ultra high vacuum (UHV) using STM [15,16], low energy electron diffraction (LEED) [17], surface X-ray diffraction (SXRD) [18], and grazing incidence X-ray diffraction (GIXD) combined with direct methods (DM) [19]. Under these strongly reducing conditions the dominant surface structure is a ( $1 \times 3$ ) reconstruction for which various models have been proposed. In this paper, we present the first study of rutile (100) surface annealed under oxidizing conditions.

## 2. Experiment

Transmission electron microscopy (TEM) was the primary experimental tool employed in this study. TEM samples were made from commercially available rutile single crystals (MTI Corp, (100) rutile, purity 99.98%, miscut  $<0.5^\circ$  using conventional sample preparation techniques. Bulk crystals were cut into 3 mm discs and were mechanically thinned and dimpled from one side. The dimpled discs were subsequently sputtered to electron transparency using a 5 keV  $\text{Ar}^+$  ion beam. Samples were then subjected to

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Table 1  
Parameters used in annealing experiments

Sample	Temperature (°C)	Time (h)	Gas (1 atm)	Notes
1	750	1	O <sub>2</sub>	No c(2×2)
2	800	1	O <sub>2</sub>	c(2×2)
3	900	1	O <sub>2</sub>	No c(2×2)
4	750	2	O <sub>2</sub>	c(2×2)
5	800	1	Ar	c(2×2)
6	830	6	O <sub>2</sub>	No c(2×2)

various annealing treatments in a tube furnace as listed in Table 1. The alumina boat and tube used for the anneals were thoroughly cleaned in nitric acid prior to every annealing experiment. X-ray photoelectron spectroscopy (XPS) was used to check the cleanliness (other than a trace amount of carbon, no impurities were detected) of the sample surface before and after annealing. The structure and morphology of the surface were studied using bright/dark field imaging and diffraction techniques in Hitachi UHV-H9000 (300 kV) and Hitachi 8100 (200 kV) electron microscopes. Although TiO<sub>2</sub> can damage in an electron microscope [20,21] the rate is generally quite slow and primarily occurs at the high fluxes used for high-resolution electron microscopy. In this analysis more conventional microscopy with much lower fluxes were used, and damage caused by electron irradiation was not observed.

### 3. Results

#### 3.1. Rutile TiO<sub>2</sub> (100) surface evolution with temperature

To ensure a common reference point, all samples were ion milled to disorder the surface prior to annealing. Due to the differences in the relative sputtering rates of titanium and oxygen, as well as electron stimulated desorption [22–24], ion milling produces samples that are oxygen deficient. This is manifested as a bluish tint for thin TEM samples and has been widely reported in literature [25,26]. In bright field TEM images from this sample (Fig. 1a), thickness fringes and bend contours are the two dominant features. The former is a direct result of the sample preparation technique employed, which produces a wedge-shaped region around the hole (with thickness increasing into the sample), and the latter is from the strain resulting from ion bombardment since this both changes the stoichiometry near the surface as well as implants argon atoms. The diffraction pattern (DP) (Fig. 1a) shows only the bulk (100) diffraction spots and diffuse diffraction (indicated by arrows) from ordered defects near the surface.

Images and diffraction patterns from samples after various treatments are shown in Fig. 1b–d. Annealing resulted in the formation of extended faceting with flat (100) terraces separated by step bunches. Step edges composed of (010) and (001) planes readily formed even for samples annealed at 750 °C for only 1 h (Fig. 1b). The width of the terraces along the [010] direction is much smaller com-

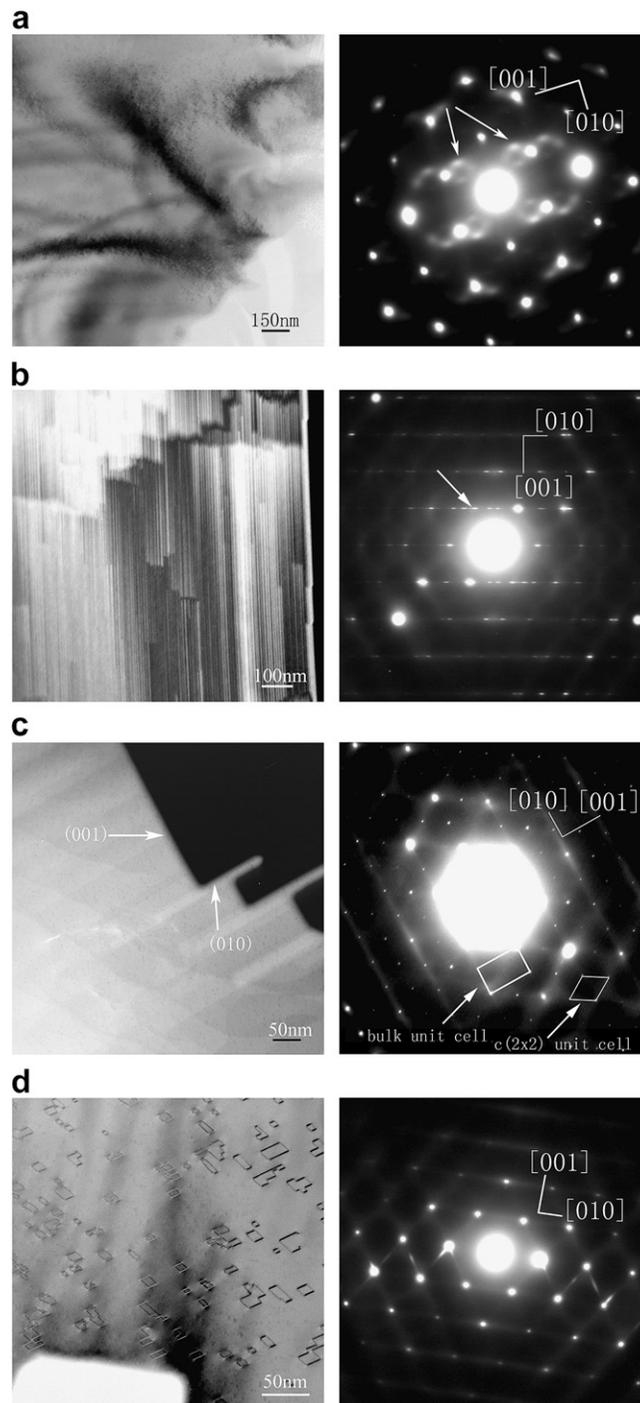


Fig. 1. Rutile TiO<sub>2</sub> (100) surface evolution with temperature: (a) after ion milling sample, bright field image with DP; (b) 750 °C 1 h in O<sub>2</sub>, dark field image with DP; (c) 800 °C 1 h in O<sub>2</sub>, dark field image with DP; (d) 900 °C 1 h in O<sub>2</sub>, bright field image with DP.

pared to that along the [001] direction, which results in streaks along the [010] direction in the DP. Rutile TiO<sub>2</sub> has a tetragonal structure so the [010] and [001] directions are very different and this anisotropy is clearly demonstrated in the images and DPs of annealed samples.

For samples annealed at 800 °C, the width of surface terraces became noticeably larger, which led to the disappearance of streaks along the [010] direction in the DP

(Fig. 1c). At the same time, low index faces, (001) and (010), formed at the edge of the sample, which are indicated in the dark field image. The faceting of the sample edge was observed in all the annealed samples and can be used as a measure to judge the amount of surface diffusion. In all the samples studied thus far, there is a positive correlation between faceting of the edge and degree of surface ordering. The most important observation for samples annealed at 800 °C is the presence of a  $c(2 \times 2)$  surface reconstruction. This was the first observation of this reconstruction on the rutile (100) surface, and the unit cell for the surface reconstruction and bulk  $\text{TiO}_2$  are outlined in Fig. 1c. The formation and structure of this surface reconstruction will be discussed elsewhere [27].

After annealing at 900 °C for an hour, the surface became flat and the  $c(2 \times 2)$  diffraction spots were not present over most of the sample. In parts of the sample where ion-milling damage was severe, straight defects were observed (Fig. 1d) parallel to the (011) plane. These defects were formed by in-plane pure shear, which is common in the rutile-type structure. In this case annealing did not fully restore the surface stoichiometry but instead made oxygen vacancies coalesce to form (011) type shear structures. The corresponding DP (Fig. 1d) shows two sets of diffuse streaks confirming the presence of ordered defects.

### 3.2. Rutile $\text{TiO}_2$ (100) surface evolution with annealing time and annealing environment

Longer annealing time did not affect the general morphology of the surface after annealing. Flat and well oriented terraces and low index faces at the edge were still the main features observed. However the surface structures were completely different from those observed after shorter annealing time. Fig. 2a shows the sample after 2 h of  $\text{O}_2$  annealing at 750 °C. Not only have the streaks along the [010] direction disappeared (compared to Fig. 1b), but also the  $c(2 \times 2)$  spots were clearly visible. After annealing at 830 °C for 6 h, the DP (Fig. 2b) shows only clear  $\text{TiO}_2$  bulk spots, no  $c(2 \times 2)$ . It seems that the  $c(2 \times 2)$  surface reconstruction only develops in a small temperature and time window. The implications of this will be discussed later.

The effect of annealing environment was further studied by changing the annealing gas from  $\text{O}_2$  to Ar (Boc Gases, Ar 99.999%,  $\text{O}_2 < 1$  ppm). This annealing experiment was done within the “window” for the  $c(2 \times 2)$  formation. After annealing, the sample (Fig. 2c) showed the same morphology as samples annealed in  $\text{O}_2$ , and additionally the  $c(2 \times 2)$  was observed. At first, this result seems to contradict a model of the  $c(2 \times 2)$  being a structure which occurs during reoxidation. However, it needs to be recognized that one only needs very low concentrations of oxygen for reoxidation to occur. For instance, the equilibrium pressure of oxygen for phase equilibrium between  $\text{Ti}_{20}\text{O}_{39}$  and  $\text{TiO}_{2-x}$  at 1100 K is about  $10^{-23}$  atmospheres [28], and depending upon impurities in the feed gas as well as leaks we can easily have more than this. The  $c(2 \times 2)$  was

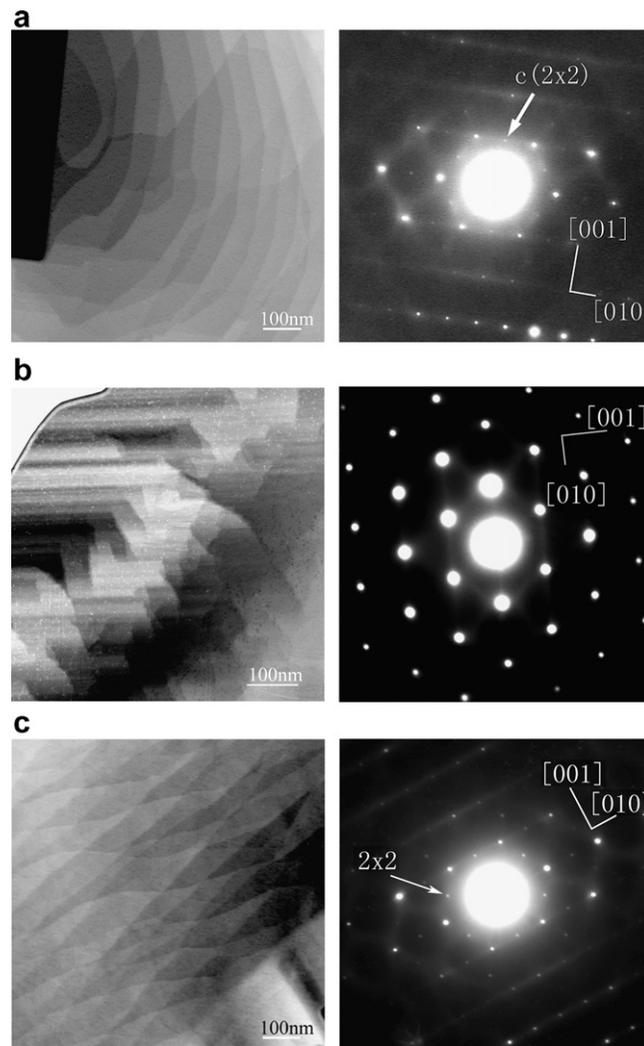


Fig. 2. Effects of time and annealing environment on rutile  $\text{TiO}_2$  (100) surface: (a) 750 °C 2 h in  $\text{O}_2$ , dark field image with DP; (b) 830 °C 6 h in  $\text{O}_2$ , bright field image with DP; (c) 800 °C 1 h in Ar, dark field image with DP.

only observed after annealing in  $\text{O}_2$  environments, and not in UHV, indicating that the presence of some  $\text{O}_2$  in the gas phase is necessary for its formation from the initial, damaged and reduced surface. (It should be noted that depending upon whether a UHV system is dominated by air-leaks or by reducing gases such as CO and  $\text{H}_2$ , the effective oxygen pressure can vary by many orders of magnitude from  $10^{-13}$  to  $10^{-30}$  atmospheres particularly if atomic hydrogen is present due to cracking by an ion gauge.)

### 3.3. “Healing effects” of $\text{O}_2$ on rutile $\text{TiO}_2$ surface

For samples which had been ion-milled for a long period of time, annealing at 800 °C in  $\text{O}_2$  for 1 h did not completely recover the damaged surface. Fig. 3a shows a large number of small grains on the surface, which were found to be the  $\text{Ti}_2\text{O}_3$  phase as demonstrated by the diffraction pattern in

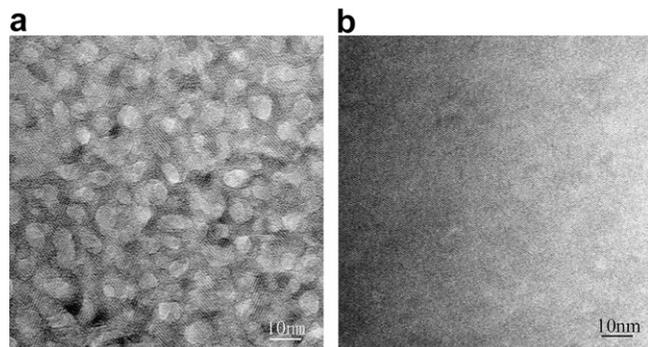


Fig. 3. “Healing effects” of O<sub>2</sub> on rutile TiO<sub>2</sub> (100) surface: (a) 800 °C 1 h in O<sub>2</sub>; (b) 830 °C 6 h in O<sub>2</sub> image.

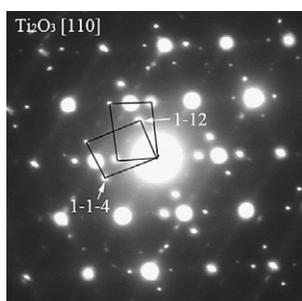


Fig. 4. Diffraction pattern of a heavily reduced sample showing evidence for Ti<sub>2</sub>O<sub>3</sub> at the surface.

Fig. 4. Considering the phase diagram of the Ti–O system [29], it is understandable that on annealing a deeply reduced surface would form Magnelli phases during re-oxidation. Annealing at 830 °C for 6 h in O<sub>2</sub> entirely healed the reduced surface (Fig. 3b). Therefore, Figs. 3 and 4 provides direct proof of a surface re-oxidation process during annealing.

## 4. Discussion

### 4.1. The process of surface recovery

In this study, the process of surface recovery from ion-mill damage was a process of surface re-oxidation and recrystallization. Although the same process happens when reduced TiO<sub>2</sub> is annealed in vacuum, it seems to have a different mechanism due to a different annealing environment, which can be straightforwardly demonstrated by the color change of annealed samples. It is well established that the blue color in TiO<sub>2</sub> single crystals is associated with bulk defects which are formed upon reduction of the bulk [8]. In previous studies, vacuum-annealing samples showed a (1 × 1) surface with the color of the bulk changing to various shade of blue, implying that the bulk TiO<sub>2</sub> was reduced. In this study, all samples were transparent after annealing, including the one treated in Ar, suggesting a decrease in the number of oxygen vacancies and Ti interstitials in the bulk. This difference in bulk structures is

caused by different oxygen partial pressures used during annealing and is strongly related to the formation of c(2 × 2) surface reconstruction, as discussed later.

Figs. 1 and 2 show the effect of temperature and time on surface morphology during O<sub>2</sub> annealing. Before annealing, the sample is damaged and full of defects near the surface. Annealing treatments at 750 °C and above always resulted in the reduction of surface disorder and recovery of the surface crystallinity. Even after a short time of annealing, the disordered layer at the surface (Fig. 1a) was no longer present and the surface exhibited signs of flattening, terraces began to form and low index surfaces appeared at the profile edge of the sample. Higher annealing temperatures and longer annealing times generally correlated with larger terrace widths and fewer step bunches, characteristic of the synergistic role of temperature and time in diffusion controlled processes.

In all samples, the steps were entirely composed only of the (010) and (001) facets; (110) facets were not observed. The (100) terraces appeared in the form of long strips along [001] direction. Such anisotropic faceting behavior offers an insight into mechanism of formation and the atomic structure of the c(2 × 2) reconstruction, since the c(2 × 2) might form right at the moment when small (100) terraces expand along [010] direction and atomic height steps disappear (Figs. 1b,c and 2a).

### 4.2. Formation and structure of c(2 × 2) surface reconstruction

The c(2 × 2) reconstruction is obtained over a certain range of annealing temperatures and time and is typical of the surface recovery process. This study suggests that the small “window” condition for formation of c(2 × 2) is around 800 °C for about 1 h in an environment where O<sub>2</sub> partial pressure is not very low (compared to UHV). Since it has never been observed in UHV surface re-oxidation studies, it is believed that the c(2 × 2) is introduced and stabilized by the presence of O<sub>2</sub> in the gas phase. The O<sub>2</sub> partial pressure plays a crucial role in this process, although the c(2 × 2) itself is a structure with oxygen vacancies at the surface, which is supported by the fact that extended annealing in O<sub>2</sub>, at higher temperatures or for longer times, results in the annihilation of the c(2 × 2) domains.

Previous studies on the rutile (100) surface have underscored the active role of oxygen vacancies in the surface reconstruction process. It was widely believed that oxygen vacancies obtained under reducing conditions would be inherently unstable when exposed to oxygen [10,11]. In this study, we found that the slightly reduced surface (even after annealing in O<sub>2</sub>) is quite stable in air. Moreover the reconstruction can be reproducibly obtained by annealing under conditions usually considered reducing, i.e. annealing under flowing Ar at 800 °C. The oxygen vacancies that stabilize the surface reconstruction are introduced in the ion milling stage of sample preparation, and annealing primarily serves to provide the energy for ordering of these point defects. It

seems that ion milling provides an alternative route to selectively reduce the surface, and the degree of reduction can be controlled by varying the time of sputtering.

The atomic structure and thermodynamics of a  $c(2 \times 2)$  structure on the  $\text{TiO}_2$  (rutile) (100) surface were studied using a combination of direct methods with transmission electron diffraction data and density functional calculations which are described elsewhere [27]. However, we would like to point out that both experimental and theoretical work on this surface suggests that the surface is oxygen-deficient. This is a rather interesting observation, since the reconstruction was obtained by annealing in  $\text{O}_2$  and is stable in air.

It is natural to compare the  $c(2 \times 2)$  reconstructed surface with other surface reconstruction on the same surface. The rutile (100) –  $1 \times 3$  surface is reported to form after annealing at temperatures between 600 and 1000 °C in a UHV environment [30–32]. Although the structure of this surface has not been determined conclusively, there is a general consensus that this surface is deeply oxygen deficient. The  $(1 \times 3)$  surface was never observed in this study and we believe that this is due to the high partial pressures of  $\text{O}_2$  employed during annealing. Most of our annealing experiments were carried out under an oxidizing environment. Even in the case of annealing in Ar, the oxygen partial pressure is probably much higher than the pressure in a UHV experiment which, as mentioned previously, can vary by many orders of magnitude depending upon whether the UHV system is air-leak dominated or dominated by reducing gases such as CO and  $\text{H}_2$ . The experimental evidence points to the conclusion that the  $(1 \times 3)$  surface is much more strongly reduced than the  $c(2 \times 2)$  surface. The  $c(2 \times 2)$  forms when the oxygen deficient (100) surface is close to regaining its stoichiometry and this regime was not explored in previous studies.

## 5. Conclusions

The structure and morphology of rutile (100) surface under oxidizing conditions was studied and a new  $c(2 \times 2)$  reconstruction is reported. The role of this reconstruction on the various properties of the rutile surface is currently under investigation.

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