# Interrelationship of Structural Elements on $TiO_2(100)$-$(1\times3)$

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Scanning tunneling microscopy (STM) has been used to investigate the interaction of nanoscale structural elements associated with rutile $TiO_2(100)$-$(1\times3)$. These are the $1\times3$ reconstruction, vicinal off-cut steps in the [001] direction, and up-down steps in the [010] direction. The STM data image the microfacet morphology of the $1\times3$ reconstruction suggested by diffraction measurements. They also provide an explanation for the stabilization of the up-down steps by the vicinal off-cut, which involves maximizing the area of the (110) microfacets at the expense of high-energy (001) step edges.

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We describe in this Letter a study of the interrelationship of nanoscale structural elements on a metal oxide surface, a field as yet unexplored. Specifically, we have used scanning tunneling microscopy (STM) to investigate the origin of up-down steps created on a $TiO_2(100)$-$(1\times3)$ surface by the introduction of staircase steps in the perpendicular direction. This turns out to be associated with the massive $1\times3$ surface reconstruction.

The surfaces of rutile $TiO_2$ are important model systems with which to explore the surface physics and chemistry of metal oxides. A relatively large database exists [1], which owes much to the technological applications of $TiO_2$ in areas as diverse as photovoltaics and environmental control. Their surface morphologies, which are crucial to these applications, have previously been the subject of diffraction and STM studies [1–8]. Diffraction studies of $TiO_2(100)$-$(1\times3)$ have suggested the microfacet structure depicted in Fig. 1(a) [6,7] and evidenced the formation of up-down steps on a vicinal substrate [8].

These diffraction results identify the key elements in the structure but do not describe their interaction. Here we present STM results which provide an explanation for the stabilization of up-down steps while also imaging the complete reconstruction. We believe this work provides a timely illustration of the rapid progress being made in understanding the surface structures of metal oxides.

Measurements employed an Omicron STM operating in ultrahigh vacuum (UHV) at a pressure of $\leq 10^{-10}$ mbar. The tungsten tip, which is held at ground potential while the sample is biased, was $Ar^+$ sputtered prior to use. All of the images obtained were recorded at positive sample bias, i.e., tunneling into unoccupied Ti $3d$ states [5]. As in earlier work, we were unable to reproducibly obtain images at negative bias [2–5]. The sample (Commercial Crystals Inc.) was cut and polished (0.25 $\mu$m) $(2.6\pm0.1)^\circ$ off the (100) plane towards [001] as determined by Laue diffraction. It was vacuum reduced to introduce $n$-type conductivity (ca. $10^{18}$ cm$^{-3}$) and cleaned *in situ* by cycles of $Ar^+$ bombardment and annealing to about 870 K. This was sufficient to produce a clean, well-ordered $1\times3$ surface, as judged by low-energy electron diffraction (LEED) and Auger spectroscopy.

Large-area, constant current images of the surface contain Ti rows parallel to [001] which run along broad (ca. 500 Å) terraces to terminate in ragged step edges [5]. These are the steps directly produced by the vicinal off-cut. In addition, more regular, up-down steps are observed in the perpendicular, [010] direction. The separation of the rows is about 14 Å, consistent with the larger side of the $1\times3$ unit cell ($3a=13.77$ Å). In general, only by using the faster, constant height scan mode have we been able to obtain atomic resolution along the [001]-direction Ti rows and pinpoint the $1\times3$ unit cell [5].

Images obtained by the use of one particular tip provide confirmation of the microfacet morphology. An example of the constant current images obtained using this tip is shown in Fig. 1(b). We tentatively ascribe the enhanced contrast obtained with this special tip to the adsorption of an atom or a molecule close to its apex. Such an enhancement would arise from an increase in the overlap of tip and substrate orbitals, an explanation proposed to explain the observation of a similar effect in STM measurements of Pt/Ni alloy surfaces [10].

The first point to note about the image in Fig. 1(b) is that the overall morphology is that expected on the basis of the microfacet model [Fig. 1(a)]. This type of reconstruction, which involves large mass transport, appears to be a feature shared by a number of materials. For instance, Au(110) [11] and TaC(110) [12] reconstructions contain microfacets. In Fig. 2, we compare the enhanced-contrast image with the surface projection of Ti atom positions from the microfacet model. In doing so we have reduced the size of the image by 16% to match the model, representing a correction for calibration error. All the values of STM-derived horizontal distance referred to below have been corrected by this factor.

Although the images in Figs. 1(b) and 2 contain a number of topographic details, only two types of atomically resolved features are present, being annotated as $A$ and $B$ in Fig. 2. Those labeled $A$ correspond to the Ti atoms which are observed in the previously reported constant height image [5]. With the reasonable assumption that the $B$ features correspond to Ti atoms [5,13], they

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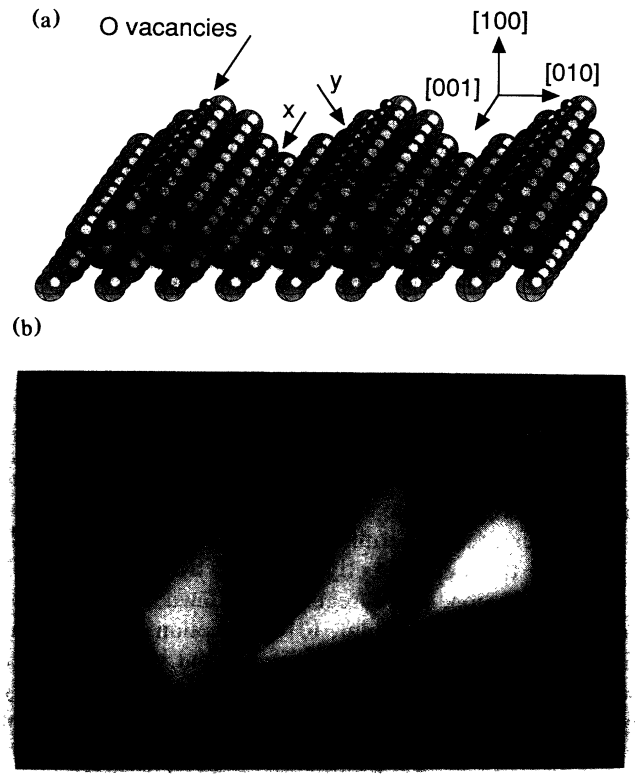


FIG. 1. (a) Model of the $TiO_2(100)$-$(1\times3)$ reconstruction derived from diffraction data [6,7]. Small (large) spheres represent Ti (O) atoms, scaled to the appropriate ionic radii [9]. The $1\times3$ unit cell (2.96 Å$\times$13.77 Å) is indicated, as well as the positions of exposed Ti atoms. The amplitude of the corrugation is about 5 Å. (b) A constant current image of the vicinal $TiO_2(100)$-$(1\times3)$ surface (+2 V, 0.3 nA) recorded with the special tip. The image, in which the rows lie parallel to the [001] direction, is displayed as a tilted, three-dimensional figure for ease of viewing. The length scales have not been corrected.

are in the position expected for one type of fivefold coordinated Ti atom.

There are three types of fivefold coordinated Ti atoms in the originally proposed microfacet reconstruction [6]; other Ti atoms in the structure are sixfold coordinated. Only two of these remain in the model modified to include O vacancies in the top layer [7]. The third type, which would lie at the top of the microfacet structure, is transformed into a threefold coordinated site [7]. The O vacancy and fivefold coordinated Ti sites are indicated on the microfacet model in Fig. 1(a). These are the only Ti atoms on the exposed surfaces of the microfacet unit cell.

The model in Fig. 1(a) illustrates the point that the O sublattice does not contain a center of inversion. Hence, the [010] and [0$\bar{1}$0] directions are not equivalent and the fivefold coordinated Ti atoms are not symmetrically disposed in the surface unit cell. The asymmetry in the images of Figs. 1(b) and 2 is consistent with this morphology. Features *A* and *B* are offset relative to one another by a translation of one unit cell along [010]. The

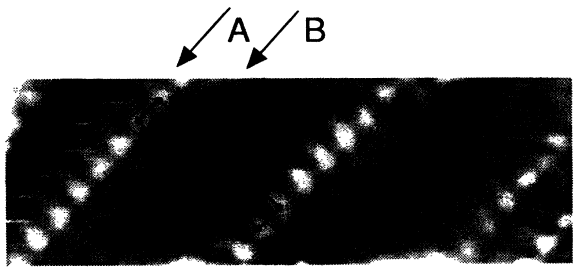


FIG. 2. The two-dimensional display of the image in Fig. 1(b). Superimposed on this image are the positions of "surface-layer" Ti atoms in the microfacet model of the $1\times3$ unit cell [6]. The positions of atomically resolved features are indicated. The size of the image has been reduced by 16% to match the model.

only means of reconciling the relative positions of these Ti atoms with the microfacet model is to associate *A* and *B* with, respectively, the O-vacancy and *x* sites indicated on the model in Fig. 1(a). This being the case, the model is oriented to approximately represent the viewing angle chosen to display the STM image in Fig. 1(b). We suggest that *y* sites [see Fig. 1(a)] are not imaged as individual species because of their proximity to the O-vacancy sites, which would give rise to a loss of contrast. However, they may give rise to the apparent [010]-direction elongation of the bright areas corresponding to O vacancies, which is observed in Fig. 2.

We now turn our attention to the step structure. In doing so, we refer to the image in Fig. 3, which contains an

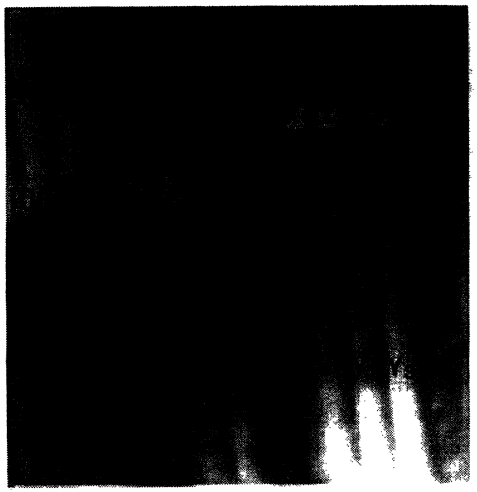

FIG. 3. A 150 Å$\times$150 Å$^2$ constant current image of vicinal $TiO_2(100)$-$(1\times3)$ (+2 V, 0.3 nA), which contains the point of intersection of [001]- and [010]-direction steps. Height profiles were measured along *X* and *Y*. The rows labeled $X_n$ and $Y_n$ are referred to in the text. In this image impurity atoms decorate the bottom of [010]-direction up-down combined steps. One row of impurity atoms can be observed to the right of row $X_3/Y_3$.

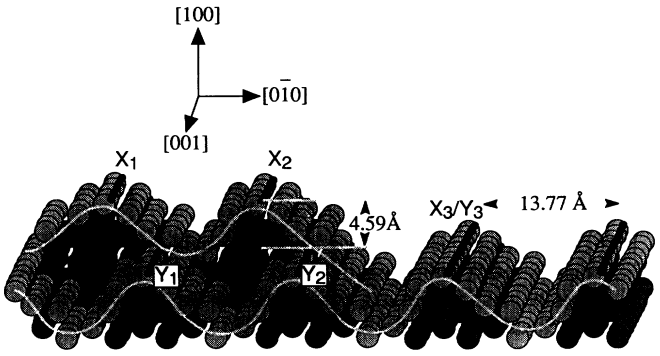


FIG. 4. A structural model of the intersection of [010]- and [001]-direction steps on vicinal $TiO_2(100)$-$(1\times3)$ derived from the STM data. The relationship of the rows marked $X_n$ and $Y_n$ to the model are indicated. Small (large) spheres represent Ti (O) atoms, scaled to the appropriate ionic radii [9].

intersection of the two types of step present on the vicinal $TiO_2(100)$-$(1\times3)$ surface. In this image the rows represent the Ti atoms which lie at the top of the microfacet reconstruction [5]. A rough step edge nominally parallel to [010] bisects the image. Figure 3 also contains a number of [010]-direction up-down steps, for instance, between rows $X_2$ and $X_3$.

We first focus on the [001]-direction steps, using the difference in the height profiles along the lines at $X$ and $Y$ in Fig. 3 to determine the step height. This method has an advantage over the alternative approach of using a line profile directly over the step, in that it eliminates problems associated with structure at the step edge. Using the latter method would introduce an artifact in this case, since the Ti rows appear brighter where they terminate at the step edge. A comparison of the heights of rows $X_1$ and $X_2$ with $Y_1$ and $Y_2$ in Fig. 3 indicates that the steps in the [001] direction have a height of 4.3 Å, close to that expected for a unit cell step along the surface normal, 4.59 Å. We also note that the Ti rows on the upper $(X_1,X_2)$ and lower $(Y_1,Y_2)$ terraces are offset by one unit cell (4.59 Å) along [010].

We now consider the [010]-direction up-down steps. That $Y_1$, $Y_2$, and $Y_3$ lie on the same terrace and $X_3$ and $Y_3$ are the same row indicates that the step between $X_2$ and $X_3$ is also one unit cell along the surface normal. This is consistent with a recent LEED spot profile analysis of the vicinal surface [14]. It follows from the discussion above that the Ti row on the lower terrace is separated along [010] by 18.4 Å from the Ti row on the upper terrace. This corresponds to a separation of $4a$, compared with the $3a$ separation between rows on the terrace. These parameters for the step structure are consistent with its being a continuation of a (110) facet.

With three rows of the microfacet reconstruction contained within the [010]-direction terraces (e.g., $Y_1,Y_2,Y_3$ in Fig. 3) a terrace width of 41.3 Å is given, consistent with that derived from LEED [8,14]. A survey of the number of ridges between steps on our sample indicates that three rows are often found, although two (e.g., $X_1,X_2$ in Fig. 3) is the preferred value, which corresponds to a terrace width of 27.5 Å, and larger values are observed. In some areas Ti rows are separated by a down step followed immediately by an up step, which results in a separation of about 23 Å between rows which are at the same height. These can clearly be observed in Fig. 3, since we have deliberately chosen an image in which atomically resolved impurity atoms decorate the bottom of the corresponding valleys. Areas of the surface have also been imaged in which these valleys do not contain impurity atoms.

We are now able to propose a model linking the steps in the [001] and [010] directions, which is shown in Fig. 4. This model provides an explanation for the stabilization of [010] up-down steps by the vicinal off-cut steps in the [001] direction. The latter have as step edges the (001) plane, the highest-energy low-Miller-index surface [1]. By introducing the up-down steps, which involve an extension of the $1\times3$ microfacets containing the lowest-energy, (110) face [1], the adopted morphology replaces areas of (001) by (110), hence lowering the surface energy. That the up-down step edges provide the thermodynamic driving force explains the presence of down steps immediately followed by up steps with no terrace in between.

In conclusion, we have investigated the relationship between the $1\times3$ reconstruction and steps on vicinal $TiO_2(100)$-$(1\times3)$ using STM. The results indicate that the [010]-direction up-down steps are a continuation of (110) plane microfacets which form the basis of the $1\times3$ reconstruction. The driving force for up-down step formation is the surface energy of exposed crystal planes. By creating up-down steps, the surface maximizes the area of the (110) face while minimizing the area of the (001) step edges created by the vicinal off-cut.

This work indicates that it should be possible to engineer the morphology of $TiO_2$ and related surfaces to suit particular applications. For instance, the impurity structure observed in Fig. 3 suggests an application in the formation of one-dimensional arrays.

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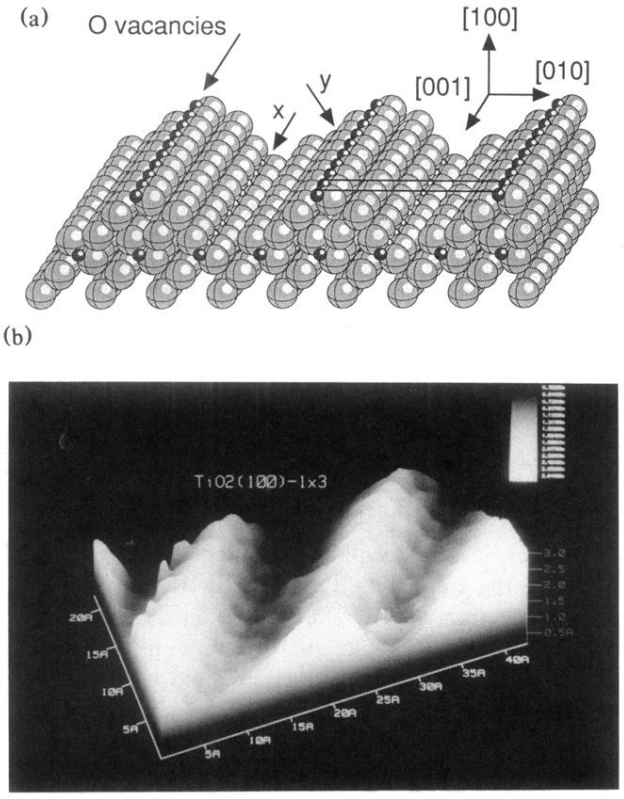


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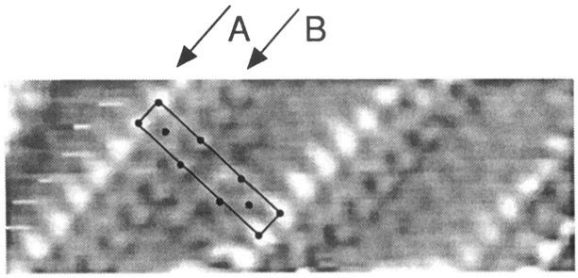


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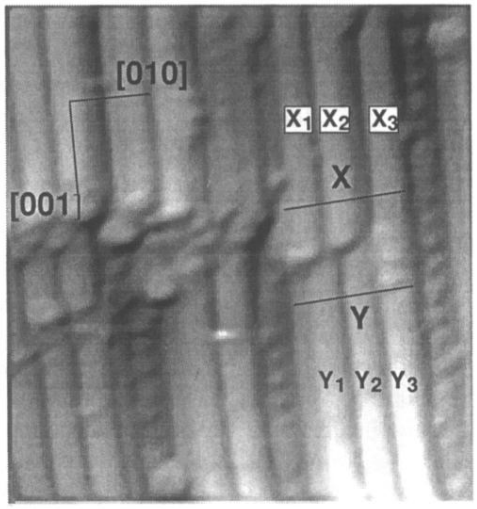


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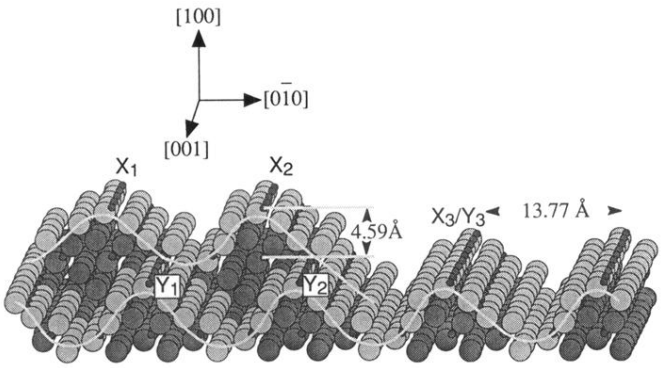


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