Two (1×2) Reconstructions of $TiO_2(110)$: Surface Rearrangement and Reactivity Studied Using Elevated Temperature Scanning Tunneling Microscopy

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We have employed elevated temperature scanning tunneling microscopy to elucidate the reactivity and surface structure of the (1×2) reconstructed $TiO_2(110)$ surface. We find two distinctly different ordered surface reconstructions depending upon the level of bulk reduction of the crystal (degree of nonstoichiometry). On the near stoichiometric surface reactivity to oxygen is low and attributed to the formation of the stable Ti_2O_3 type termination. For heavily reduced crystals a cross-linked (1×2) reconstruction forms with high activity to oxygen resulting in a well-defined cyclic reaction (TiO_2 growth). [S0031-9007(99)09062-6]

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The ability to prepare conducting TiO_2 samples in UHV has lead to a wealth of studies on its surface structure and chemistry [1–13]. However, there has been relatively little work exploiting the effect of varying the bulk stoichiometry on surface structure and reactivity [8]. The link between surface structure and bulk defect formation is strong in reducible d^0 metal oxides (TiO_2, V_2O_5, MoO_3, and WO_3) where defects can cluster and form crystallographic shear planes (CS) within a crystal [1,14,15]. These have recently been shown to terminate at the surface in a well-ordered array of half-height steps [16–19] on $TiO_2(110)$.

There are at present two structural models considered to be in broad agreement with the wide range of techniques that have been used to probe the $TiO_2(110)$-(1×2) reconstruction. The first, proposed by Onishi *et al.*, is for an added row of stoichiometry Ti_2O_3 which grows upon the (1×1) terrace in an oxygen ambient as a result of transport of Ti^{n+} interstitials to the surface [2,3,20]. More recently, a second added row model has been proposed by Pang *et al.* on the basis of atomic resolution STM data and theoretical calculations in which the added rows consist of strings of the fully reduced bulk termination (Ti_3O_5) [9]. However, there are a number of reports in the literature of (1×2) rows that have been stabilized by cross-linking every few tens of Å [5,6,8]. Most notably these cross-links are reported to be more prevalent after annealing a reduced surface in oxygen. Structural models proposed to explain the cross-links were based on a missing row reconstruction that has largely been rejected because of conflicting evidence by other techniques.

In this Letter we propose that both models are, in essence, correct as we show that there are indeed two forms of the (1×2) reconstruction on the surface, the straight (1×2), and the cross-linked (1×2). With the aid of time resolved reoxidation scanning tunneling microscopy (STM) experiments on lightly and heavily reduced $TiO_2(110)$ crystals we show that the surface termination is dictated by bulk nonstoichiometry. These observations are also compatible with, and contribute to, recent reports of the reoxidation behavior of $TiO_2(110)$ [5,6,13]. The ability to image the reoxidation process *in situ* is essential to the creation of reliable models of the reactivity of titania. Room temperature imaging after reaction will undoubtedly scramble information on the surface structural phase diagram as functions of temperature and oxygen overpressure.

The experiments were performed using an Oxford Instruments variable temperature STM described in detail elsewhere [21]. Two $TiO_2(110)$ single crystals (PI KEM, UK) were employed during this study. The first was subjected to repeated sputter (600 eV, 1000 K) and anneal (1200 K) cycles to produce a dark blue/black crystal. This crystal was just starting to show ordering of surface defects which we take to be a precursor to CS plane formation, thus giving an assessment of the bulk stoichiometry of close to $TiO_{2-x}, x \approx 10^{-3}$ [22,23]. The second crystal employed was treated to fewer sputter/anneal cycles, at lower temperature, to produce a medium blue crystal. Tip induced artifacts, such as selective growth under the tip and the movement of adsorbed species, were not seen.

Figure 1 shows STM images of the (1×2) reconstructions, with 1(a)–1(f) showing the nonstoichiometric crystal reacting at 833 K in 5.5×10^{-7} mbar O_2 at 1 min intervals. These images were taken from an extended sequence in which the reoxidation of the (1×2) reconstructed surface was followed. Figures 1(g) and 1(h) show the reaction for the near stoichiometric crystal at 673 K taken 38 min apart during which time the exposure to the surface was 1200 L oxygen (where $1 \text{ L} = 10^{-6}$ torr sec). Fig. 1(a), taken half way to formation of a complete (1×1) layer, serves to illustrate all the surface features observed; a large island of (1×1) surface (top of image) upon which are growing bright and dark strings (marked BS and DS, respectively) along with an array of bright points (BP). Also apparent is a large area of cross-linked (1×2) close to the step edge within which smaller islands of (1×1) have nucleated, these islands preferentially

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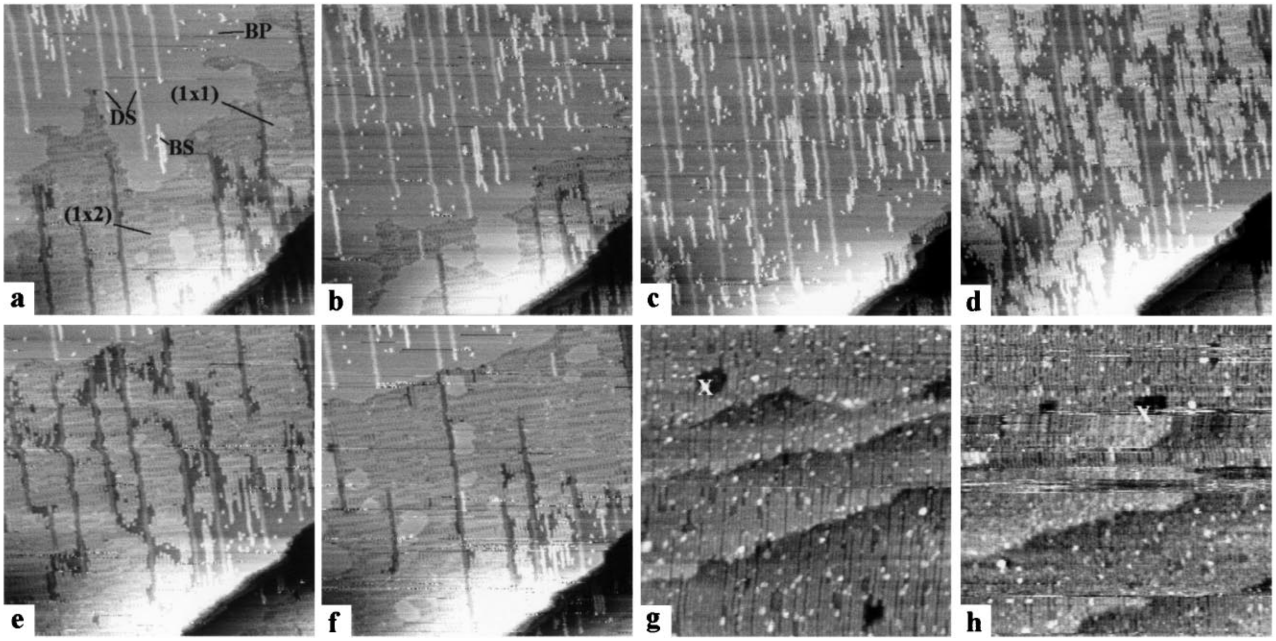

FIG. 1. The reaction of $TiO_2(110)$ with oxygen at elevated temperatures for two (1×2) surface reconstructions. (a)–(f) show the reaction of a nonstoichiometric crystal at 833 K to 5.5×10^{-7} mbar O_2 with each image taken 1 min apart. The main features apparent are labeled in (a) as the dark string DS, bright string BS, bright points BP, and the (1×1) and cross linked (1×2) terminations. (g) and (h) show the unreactivity of the (1×2) reconstruction on the near-stoichiometric crystal at 673 K. The image shown in (h) has 1200 L exposure of oxygen and is taken 38 min later than (g). "X" marks the same point in both images. All images are 1000 Å square and were taken with 1 nA tunnel current and 1 V sample bias.

formed at the cross-linked sites. The smaller islands are not adorned with bright points or strings. The (1×1) terraces grow by converting the (1×2) terrace at the interface of the two regions and appear to be coplanar, Fig. 1(b). Eventually, Fig. 1(c), the terrace becomes completely converted to (1×1), removing the initial (1×2) reconstruction. However, the bright and dark strings continually grow on the (1×1) terrace, the dark strings stretching across the length of the (1×1) island while the bright strings form shorter sections. By Fig. 1(d) the bright strings have begun to aggregate to form a new overlayer of cross-linked (1×2). However, the dark strings on the terrace appear unreactive and constrain the growth of the (1×2) regions, Fig. 1(e), until surrounded by the (1×2) at which point they convert into the brighter strings and cross-links. In Fig. 1(f) the surface has returned to a similar state as Fig. 1(a). The growth process is repetitive, with alternate terminations of (1×1) and (1×2), and can be followed until completion of several monolayers of growth.

Key observations that can be drawn from these images, and others not shown in this sequence, are that the (1×1) surface grows into the (1×2) overlayer whereas the (1×2) nucleates on top of the (1×1), which dictates that the (1×2) is an added layer structure. The bright strands nucleate and grow from bright points on the surface, although the bright points do not seem to be particularly mobile between images, i.e., on time scales of minutes. Furthermore, the images are not highly streaked as would be expected for surface species diffusing on time scales comparable to the imaging time (~25 s). The dark strands grow in one dimension traversing the entire terrace and do not convert directly to the (1×1). However, they do eventually convert to bright strands if surrounded and then to (1×1). Both the bright and dark strands terminate in a bright point.

Fig. 1(g) shows the near stoichiometric crystal prepared by vacuum annealing and imaged at 673 K displaying (1×2) rows which are not cross-linked. Figure 1(h) shows the surface after exposure to ~1200 L of oxygen with the reconstruction little changed. In comparison to the cross-linked surface this (1×2) reconstruction shows little reactivity.

In order to investigate the structure of the reactive features of the nonstoichiometric crystal indicated above it is necessary to take high resolution images of all the structures simultaneously to avoid extraneous tip changes. Such an image is shown in Fig. 2 in which the reaction has been stopped by removal of the oxygen overpressure but maintained at 833 K. Line profile *A-B* is taken across both bright and dark strings and indicates that the darker string has an apparent height of ~1.3 Å and the brighter features ~2.8 Å above the (1×1) terrace (for comparison the measured step height is 2.8 Å under these conditions). The brightest features in the image are bright points and rows (BR) with an apparent height of ~4 Å. Both string structures have a double row internal structure and like the bright rows and points

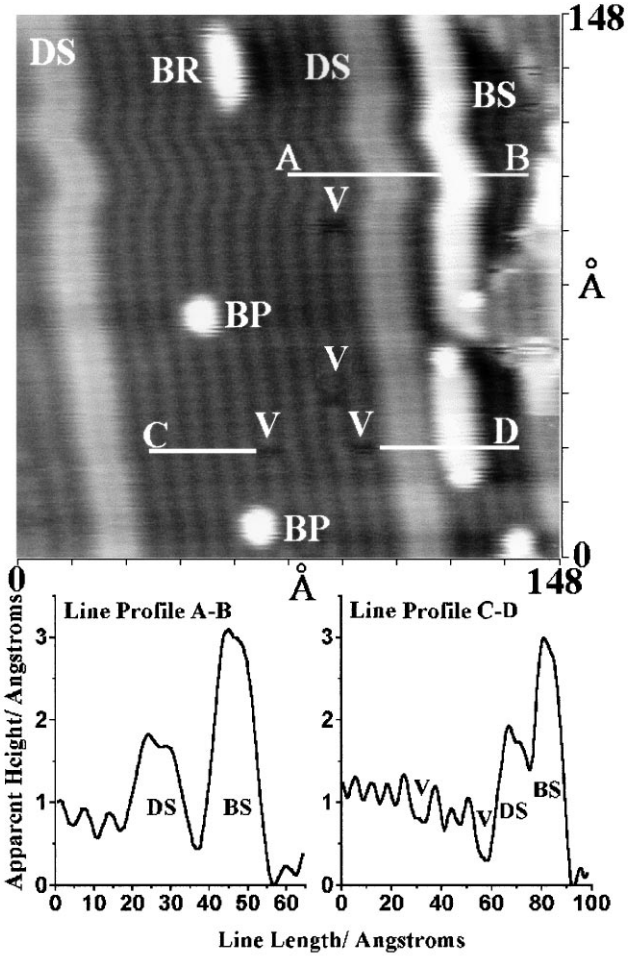

FIG. 2. The nonstoichiometric surface stopped midreaction and imaged at 833 K showing detailed line profiles of the structures apparent in Fig. 1(a)–(f) (using the same naming convention). Additionally, bright rows and vacancies are visible on the (1×1) surface (marked BR and V, respectively). Line profiles are taken in the fast scan direction to minimize thermal drift and tip change problems.

are centered on the bright rows of the (1×1). Also shown in the image, and line profile C-D, are point defects (V) which appear to be vacancies in the (1×1) surface. Interestingly, the rows neighboring the defects appear with slightly higher corrugation. Accepting the established assignment for normal tunneling conditions [7,24], where the fivefold coordinated Ti in the (1×1) surface are imaged bright, all the added points, rows, and strings are centered over the fivefold coordinated Ti.

The detailed analysis of the growth mechanism is outside the scope of this Letter, but we believe interstitial Ti^{n+} ions present in the bulk and near surface region are captured by the oxygen ambient at the surface [25]. The growth of the overlayer is limited by supply of Ti and oxygen to the surface. However, this surface termination can also be generated by vacuum annealing a well-sputtered surface to 1200 K. The formation of the cross-linked (1×2) reconstruction in both oxidizing and reducing environments suggests that it is the kinetically favored structure, possibly with a stoichiometry very close to TiO_2.

Figure 3(a) shows a high resolution STM image of the cross-linked (1×2) structure taken at room temperature. The strings contain two rows of atoms and the cross links are clearly seen to be composed of four bright points with a slightly elongated central feature. Additionally, some strings are joined by single links composed of a bright point in each string and a bright feature ($\frac{1}{2}$ unit cell displaced in the $\langle 001 \rangle$ direction) centered in the trough. Figure 3(b) shows a model for the strings and cross-links. The formation of the rows is based upon the added Ti_3O_5 model proposed by Pang *et al.* [9] slightly modified by the inclusion of bridging oxygen atoms on their fourfold coordinated Ti. In our model the added rows are therefore composed of stoichiometric TiO_2 with the ions in essentially their bulk positions. This model agrees very well with the observation of strings with the apparent height of ~ 2.8 Å (the same as a step edge) with a double row internal structure. The cross-linking sites form as a result of terminating the fivefold coordinated Ti in the troughs between strings with oxygen and allowing Ti to move from the strings to bridge this oxygen. Neighboring Ti and oxygen atoms relax around this site reducing the coordination of the Ti which then appears bright in the image. The entire structure is best described as a (12×2) reconstruction and is based upon the bulk structure of TiO_2 with an ordered array of missing atom defects. The origin of the cross-links may be due to strain relief along the rows. The cross-links generally form cross shapes but many images show chains of single links, Fig. 3(a). These may simply be constructed from one-half of the cross. Interestingly, the cross-links are structurally similar to the "rosette" structures proposed to explain images obtained at 300 K upon the reoxidation of the (1×1) TiO_2 surface at 570 K [13].

The cross-linked rows form an ordered structure on the well-annealed surface with a spacing of ~ 12 units in the $\langle 001 \rangle$ direction [5,6,8,25]. This is reflected in the LEED pattern from this surface, Fig. 3(c), which shows 12th order spots (see inset) with some streaking in the $\langle 001 \rangle$ direction.

Returning briefly to the stoichiometric crystal, the apparent corrugation of these rows is low, ~ 1.8 Å above small regions of (1×1) on the surface. The low corrugation, low reactivity, and their formation on both near and nonstoichiometric crystals suggests to us that this most closely resembles the Ti_2O_3 added row model of Onishi and Iwasawa [2]. The Ti_2O_3 added row model predicts the corrugation across the structure to be ~ 1.5–2 Å [24] above the fivefold Ti on the (1×1) which is as measured here and by others [4].

The STM and LEED results presented here show that there are two stable reconstructions of the $TiO_2(110)$ surface which generate (1×2) rows and cross-linked (1×2) rows in STM. Differences in apparent height of

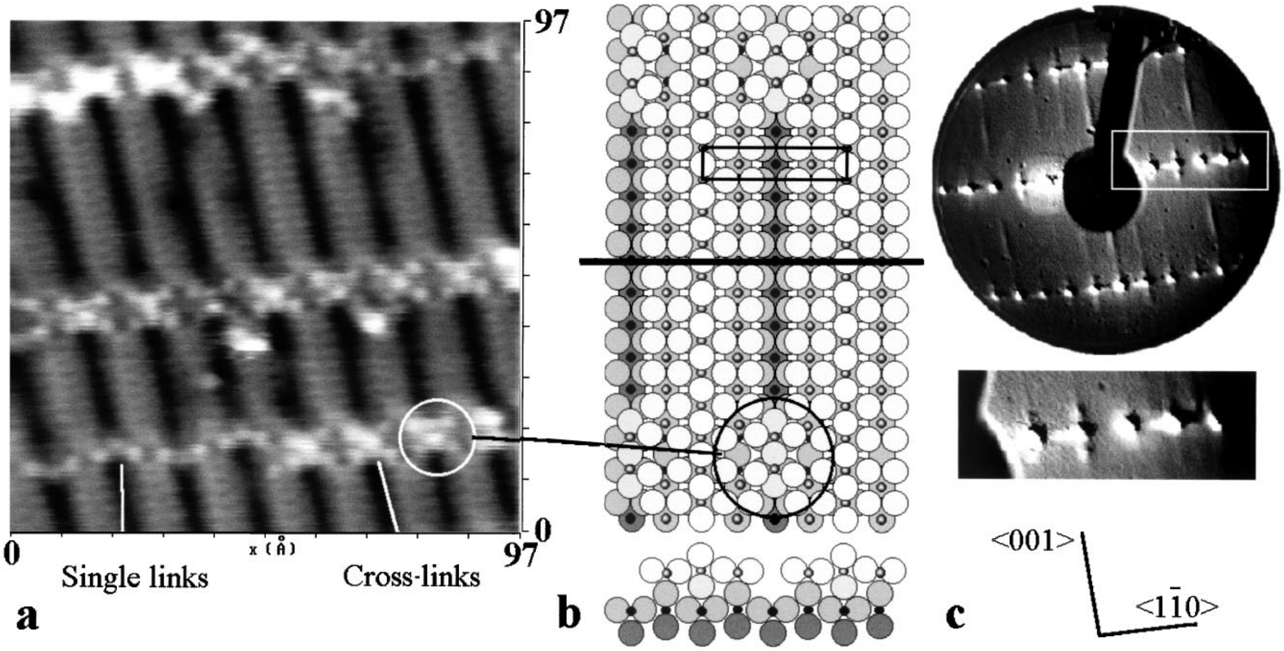

FIG. 3. The surface structure of the cross-linked (1 × 2) reconstruction. (a) shows a high-resolution STM image taken at 310 K of the reconstructed surface. The cross shapes form a local $c(2 \times 2)$ surface which is composed of two bright points per bright string and a slightly elongated feature centered in the trough between strings. The bright strings themselves appear with two rows of atoms within the string. In (b) we show a schematic model, in plan and side view, for the reconstruction in which the rows are composed of added TiO_2 strings with the troughs formed by TiO_2 vacancies. The cross-links are proposed to form when the troughs start to be filled by oxygen with Ti ions moving out of the strings to bridge the oxygen. Single links may be considered to be one-half of a fully developed cross. (c) shows the LEED pattern for the fully developed reconstruction generated by annealing, which is well ordered with cross-links every 12 lattice spacings in the ⟨001⟩ direction (STM image not shown, see Refs. [5,6,8,25]).

the row structures show that the lower corrugation rows are identical to the added Ti_2O_3 row model of Onishi and Iwasawa while the higher (cross-linked) rows appear similar to the added Ti_3O_5 model of Pang *et al.* However, in the latter model we have proposed additional oxygen to create added TiO_2 rows with ordered defects constituting the cross-shaped links which are composed of atoms in their bulk positions. The reactivity of the (1 × 2) surface based upon the Ti_2O_3 model when exposed to oxygen is low, whereas the added TiO_2 row is highly active.

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