Added row model of $TiO_2(110)1\times2$

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Scanning tunneling microscopy and first-principles atomic orbital based calculations have been used to study $TiO_2(110)1\times2$. A structure is proposed that resolves the controversy surrounding the surface morphology. Our model is simple, in that it consists only of atoms in their bulk-terminated positions. Theoretical modeling of the images shows an agreement with the experimental data that cannot be achieved even qualitatively for the previously proposed models. Furthermore, a previously unobserved 1×3 phase has been imaged that can be simply explained in terms of the model. [S0163-1829(98)02327-3]

In recent years the surfaces of transition-metal oxides have received considerable attention due to their importance in a number of technological areas. These include, for instance, catalysis and gas sensing.[1] The surfaces of TiO_2 in particular have been studied in detail as they represent model systems with which to explore the physics and chemistry of oxide surfaces.[2–11] $TiO_2(110)$ is the lowest energy face; it forms two long-range-ordered phases, having 1×1 and 1×2 symmetry. The structure of the 1×1 phase is well established from surface x-ray diffraction (SXRD) (Ref. 9) and *ab initio* calculations of the energy minimized surface,[7] which point to a bulk termination modified to include relaxations. However, the structure of the defected 1×2 phase remains a matter of debate and has been the subject of a number of recent studies.[4–6,11]

An early study suggested the simple missing-row model for the 1×2 phase[2] depicted in Fig. 1(a), in which alternate bridging oxygen rows are removed. This model is consistent with the presence of oxygen vacancies, which are evidenced by photoemission.[2] Such defects are believed to play a key role in determining the properties of oxide surfaces. The model was later refined by scanning tunneling microscopy (STM) studies to include lateral and in-plane relaxations.[5] More recently, a model based on variable temperature STM data has been proposed by Onishi *et al.*[4,6] This consists of added Ti_2O_3 structures as depicted in Fig. 1(b). Interpreting STM data from TiO_2 surfaces is made difficult by the question of the Ti and O contribution to the tunneling current. The two experimental studies above, as well as a simulation,[10,19] have concluded that the tunneling at positive sample bias is predominantly due to Ti species.

On the theory front, the added Ti_2O_3 row type reconstruction is favored by recent *ab initio* total energy calculations[12] of the 1×2 structure. Very recent spin-polarized density-functional theory (DFT) calculations by Lindan *et al.*[13] concentrate on oxygen vacancy models, concluding that the missing-row model is no more stable than a 2×1 model in which every other bridging O along each row is removed.

In this paper we present a model for the 1×2 phase based on high-resolution STM images, which have also been simulated using first-principles atomic orbital calculations. On the basis that electrons are tunneling into Ti-dominated states, atomically resolved STM images show features that are inconsistent with the added Ti_2O_3 structures. We propose a structure that consists of added rows of the 1×1 surface with all bridging oxygens removed. All atoms in our model are in their bulk-terminated positions. This structure is also consistent with recent electron stimulated desorption ion angular distribution (ESDIAD) data in which O^+ ion emission consists of two off-normal lobes.[11] Furthermore, we have also imaged a previously unobserved 1×3 phase, which can-

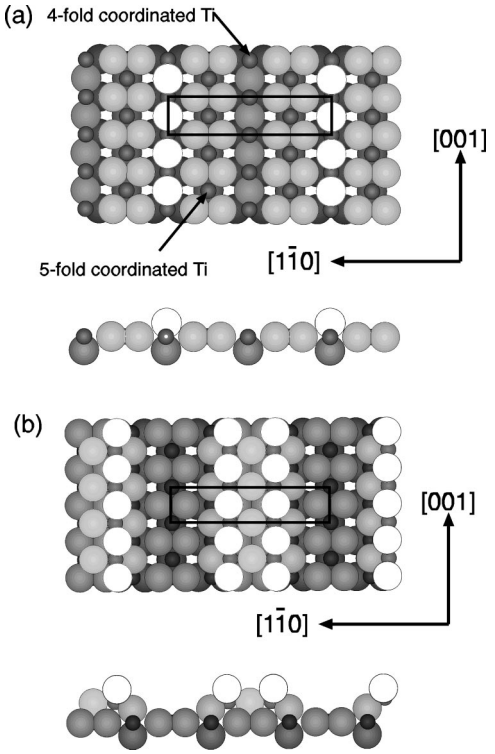

FIG. 1. Previously proposed models for the $TiO_2(110)1\times2$ surface. Large circles represent O atoms, with Ti atoms represented by small filled circles. Both top and side views are shown. (a) The missing O-row model in which alternate bridging-O rows are removed from the stoichiometric 1×1 termination. (b) The added Ti_2O_3 structure proposed by Onishi *et al.* Unit cells are outlined in both models.

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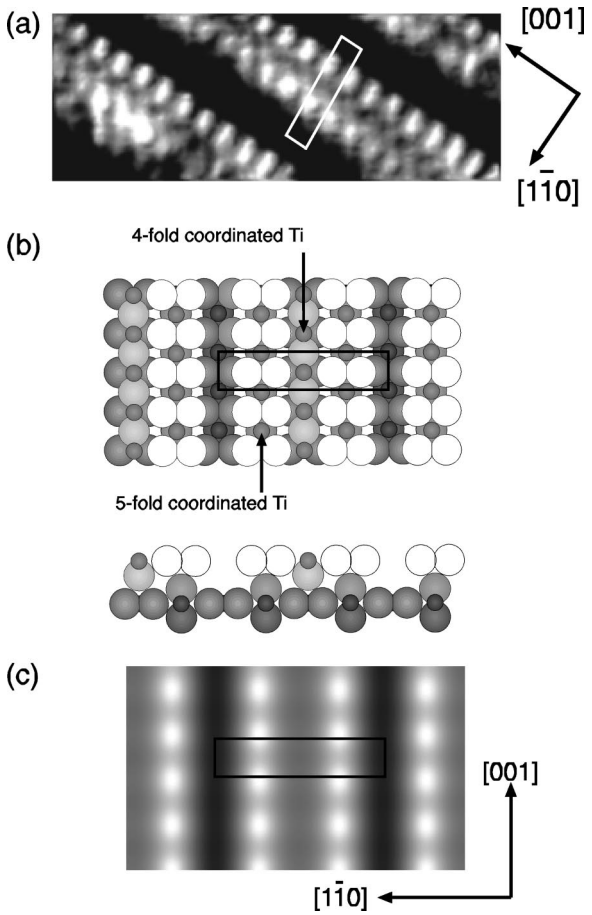

FIG. 2. (a) Atomically resolved image (20 Å$\times$ 50 Å) of the 1 $\times$2 phase. Two bright rows parallel to [001] are observed with a separation of 5.5 Å. In between and out of phase with this pair is observed a fainter row, the features of which are out of phase. The periodicity of the features along [001] for both types of row is about 3 Å. (b) Proposed model for the 1×2 phase, which consists of added rows of a fully reduced 1×1 termination. (c) Computed surface charge density within 1.5 eV of the conduction-band edge for the proposed model, at a constant height of 4 Å above the surface. (b) and (c) are scaled and aligned to one another.

not be explained in terms of added Ti_2O_3 layers, but which is completely consistent with the model proposed.

The experiments were performed using a commercial Omicron STM operating at room temperature (RT), housed in an ultrahigh-vacuum chamber (base pressure $\leqslant 10^{-10}$ mbar). Sample preparation was carried out by repeated cycles of Ar ion bombardment (1 keV) and annealing to 1150 K in vacuum until the surface was judged clean and ordered by Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and STM. All images were recorded in the constant current mode using a W tip, which was held at ground with the sample biased. Positive tunneling bias was always used, as in previous studies, with typical parameters of +1 V and 0.5 to 1 nA.

An atomically resolved image of $TiO_2(110)1\times2$ is shown in Fig. 2(a), in which paired rows can be seen running along [001]. These rows lie 2.5 Å above the surrounding 1×1 structure.[5] The separation of these features along [001] is approximately 3 Å, consistent with the unit-cell dimension (2.96 Å) in this direction. The distance between the atomic features in the perpendicular direction is 5.5 ± 0.1 Å. There are weaker features between the bright rows with the same periodicity along [001], but half a unit cell out of phase. Given the tunneling parameters used, simple electronic structure arguments indicate that tunneling would be into Ti states, a proposition supported by recent first-principles pseudopotential calculations.[10] On this basis, the added Ti_2O_3 model is ruled out by the presence of the central row. Although the simple missing-row structure is consistent with the STM data, it is ruled out by the ESDIAD data.[11] Finally, the corrugations of 2.5 Å above corresponding areas of 1×1 support an added type row model.

Taking these factors into account, we suggest a model for the 1×2 structure, which is shown in Fig. 2(b). The model consists of added rows along the [001] direction, in which the termination is of a completely reduced 1×1 surface. This accommodates the reduced Ti species observed in photoemission. The edges of the added rows are terminated by O atoms, which achieves the photoemission-derived stoichiometry[2] as well as a geometry consistent with the O^+ ion angular distribution observed in ESDIAD.

To test our model further, we have carried out first-principles atomic orbital based calculations.[14] The basis set comprised the valence orbitals for Ti ($4s$, $4p$, and $3d$) and O ($2s$ and $2p$). The numerical atomic orbitals were generated using a standard local-density approximation for exchange and correlation, and the potential in the solid was calculated by superposing neutral-atom charge densities. The Schrödinger equation was then solved for the electronic structure of 13.2 Å thick TiO_2 slabs. Self-consistency was included only to the extent that the occupancy of the Ti $3d$ state in the slab was made consistent with that in the neutral atom; this leads to an occupancy of 1.85 d electrons per Ti atom in bulk TiO_2, with small variations from this value at the surface. The method has previously been used to study the electronic structure of various TiO_2 surfaces.[15,16] Although this approach is less rigorous than fully self-consistent *ab initio* calculations (see Refs. 7, 8, 10, 12, 13, and 17 for examples that involve low-index TiO_2 surfaces), it is much cheaper computationally, and produces surface charge densities that compare well with those from more sophisticated calculations.[12]

We make the simplistic assumption that the STM images map the surface local density of states (LDOS) summed over an energy window corresponding to the bias voltage.[18] The lower bound of this window is taken as the bottom of the conduction band, since the experiments are at positive sample bias, and O vacancy states pin the Fermi level at or close to the conduction-band edge. In each of our calculations the surface Brillouin zone is sampled with a special k-point set corresponding to 49 points over the whole zone. The simulated LDOS shown in Fig. 2(c) is at a constant height above the proposed model of the 1×2 surface; since the surface is rather flat, we would expect a close correlation with constant current (or, in our simulations, constant LDOS) images.

Our model is the only one tested so far for which atomic resolution is simulated along both [1$\bar{1}$0] and [001] for charge densities taken out to 4 Å. This in itself is evidence in support of the model, since the surface LDOS should normally simulate the best-resolved image, corresponding to scanning with a perfect, δ-function tip.[18] Simulations of the

missing row and added Ti_2O_3-layer models at similar heights both fail to yield any features along or across the rows with atomic resolution.[19,20]

The correlation between Figs. 2(a) and 2(c) invites a clear interpretation of the STM image. The outer, dominant bright rows are associated with the two rows of fivefold-coordinated Ti atoms, and the central, weaker row with the fourfold-coordinated Ti atoms. In fact, the interplay between the $3d$ states largely responsible for these features is sufficient to cause some movement of the center-of-charge of the dominant fivefold Ti rows to be shifted along $[1\bar{1}0]$ towards the fourfold Ti. This shifting is an entirely electronic effect, as each atom in the simulation is in an ideal, bulk-terminated position. In addition, the central fourfold-coordinated atoms observed in the experimental image of Fig. 2(a) are not resolved here. However, contributions from such atoms are expected to be quite weak. This is supported by the fact that these features are indeed quite difficult to image experimentally.

It should be stated that there are limitations to the quantitative reliability of our calculations. They are unable to predict surface relaxations. Nor do they allow for electron spin polarization. Recent calculations of the missing-row model[13] suggest that the ground state is spin-polarized, with the excess spin charge highly localized on under-coordinated Ti sites. Each of these omissions will make a difference to the details of the position and relative strength of the Ti-derived features, but are unlikely to affect the high degree of correlation with experiment of our model compared with others.

Returning to experiment, we have also imaged a previously unobserved 1×3 phase. The images can be understood in the context of our proposed structure for the 1×2 surface. Figure 3(a) shows an image of the 1×3 phase, which is consistent with a thicker added row structure. Measurements of the periodicity of the structure along $[1\bar{1}0]$ give a value of 19.7 Å, consistent with a tripling of the bulk unit cell in this direction. The corrugation height across this structure is 1.5 Å. It can be seen from the image that the structure is made up of three rows parallel to [001]. The separation between each of these rows is approximately 6 Å, while the periodicity of the individual features along [001] is 3 Å. We attribute these features to three rows of fivefold-coordinated Ti atoms. On this basis the 1×3 structure appears to be simply an extension of the 1×2 phase along the $[1\bar{1}0]$ direction, as illustrated in Fig. 3(b). Extending the Ti_2O_3 added layer model to 1×3 periodicity would result in an image containing a quadruple rather than a triple row on the basis of the Ti atom periodicity. The calculated surface LDOS shown in Fig. 3(c) bears a close resemblance to the experimental image, even to the point of suggesting that the separation along $[1\bar{1}0]$ between fivefold Ti features is rather greater on this reconstruction than on the 1×2 surface. This provides convincing evidence that the 1×2 and 1×3 structures are closely related and arise from added rows of reduced $TiO_2(110)1\times1$.

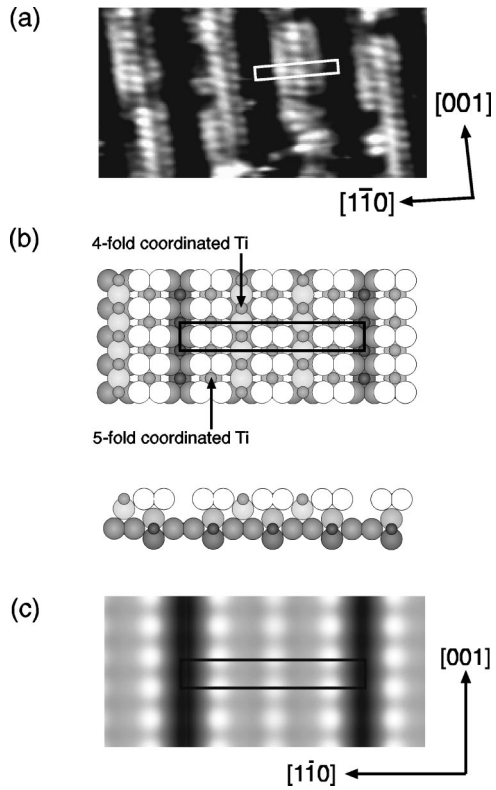

FIG. 3. (a) STM image of the 1×3 structure. The separation between the dark rows is 19.5 Å. Within the bright regions three rows parallel to [001] are observed, with the features in phase along $[1\bar{1}0]$. The separation between each row is 6.5 Å. Image size 100 Å$\times$ 50 Å. (b) Proposed model for the 1×3 phase, which is a simple extension of the 1×2 structure to incorporate a wider added row. (c) Computed surface charge density within 1.5 eV of the conduction-band edge for this model, at 4 Å above the surface. (b) and (c) are scaled and aligned to one another.

In summary, we have resolved a controversy regarding the structure of the reduced, 1×2 phase of the model oxide surface $TiO_2(110)$. Our model for this phase is based on added rows of reduced $TiO_2(110)1\times1$. This model is consistent with STM, ESDIAD, and photoemission data as well as with simulations of STM images. A 1×3 phase has also been observed with STM, having a morphology that is a simple extension of the 1×2 structure.

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