

Stress-Driven Reconstruction of an Oxide Surface: The Anatase $\text{TiO}_2(001)-(1 \times 4)$ Surface

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The recently discovered (1×4) reconstruction of the stoichiometric anatase $\text{TiO}_2(001)$ surface is studied via first principles density functional calculations. We propose a new structural model for this reconstruction, which is energetically much more favorable than all the other available models, including the unreconstructed (1×1) surface. In this model, rows of TiO_3 species periodically replace rows of surface bridging oxygens of the (1×1) surface, thus leading to a relief of the large surface tensile stress present on that surface. The corresponding empty-state charge density distribution correctly describes the experimental scanning tunneling microscopy images.

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The structure and stability of metal oxide surfaces are usually analyzed using simple electrostatic criteria [1] and electron counting rules [2], combined with an evaluation of the number of oxygen-cation bonds that have been broken during the surface formation [3]. These criteria predict that nonpolar and autocompensated oxide surfaces should be stable with only limited relaxations of the ions in the surface region and no reconstruction. This should be particularly true when no strongly undercoordinated cations and oxygen atoms are present on the surface. While these predictions appear to be qualitatively correct for a large variety of oxide surfaces [3], some cases are known for which the surface structure cannot be explained by the usual rules. In this paper we examine one of these cases, namely the (1×4) reconstruction that has been recently discovered on the nonpolar and autocompensated (001) surface of anatase [4–6]. This is a TiO_2 polymorph, slightly less stable than rutile, on which much attention has been recently focused because of its wide use in catalysis [7], photocatalysis [8], and charge-separating devices [9]. The (1×4) reconstruction of the anatase (001) surface has been found to be stable in a wide temperature range (up to $\sim 850^\circ\text{C}$) and under a variety of experimental conditions [4–6]. In addition, x-ray photoelectron spectroscopy (XPS) experiments indicate that only Ti^{4+} atoms are present on the anatase $\text{TiO}_2(001)-(1 \times 4)$ surface [4,6]. This means that the surface is perfectly stoichiometric, so that structural models involving surface oxygen vacancies, as suggested in Ref. [5], must be excluded. By contrast, most reconstructions of oxide surfaces, including rutile [10,11], are associated with deviations from the “perfect” bulk stoichiometry and frequently imply an ordering of surface oxygen vacancies [3].

Based on low-energy electron diffraction (LEED), XPS, and angle-resolved mass spectroscopy of recoiled ions, Herman *et al.* [4] suggested a surface model for $\text{TiO}_2(001)-(1 \times 4)$, characterized by (103) and $(\bar{1}03)$ microfacets (MF). More recently, however, Liang *et al.* [6] found that the MF model is inconsistent with their empty state scanning tunneling microscope (STM) images. Thus they proposed an “added-and-missing row” (AMR) model,

which should explain these images on the basis of the geometrical arrangement of the surface Ti atoms [12].

In this work we study the (1×4) reconstruction of anatase $\text{TiO}_2(001)$ by means of first principles density functional (DFT) calculations. We propose a new structural “ad-molecule” (ADM) model for this reconstruction, which is energetically much more stable than the unreconstructed surface, and can be easily adapted to describe other $(1 \times n)$ periodicities that have been occasionally observed on the (001) surface [6]. Using the ADM model, we show that the occurrence of the reconstruction can be rationalized in terms of the relief of the large surface stress present on the unreconstructed surface. Finally, we make a comparison with available STM measurements.

While in bulk TiO_2 anatase each Ti (O) is coordinated to six (three) neighboring O (Ti) atoms, on the unreconstructed $(001)-(1 \times 1)$ surface (see Fig. 1a) fivefold coordinated Ti atoms [Ti(5)] are bonded to twofold coordinated bridging oxygens [O(2)] along the $[100]$ (\hat{x}) direction. The two bonds formed by each O(2) with its neighboring Ti(5) atoms, which are equivalent and have a length of 1.94 \AA on the bulk-truncated surface, have been found to become strongly inequivalent, with lengths of 2.20 and 1.76 \AA , upon relaxation [14]. This symmetry breaking, as well as the fact that the calculated surface energy, $\gamma_{1 \times 1}^{(001)} = 0.90 \text{ J/m}^2$, is more than twice the value for the most stable (101) surface [$\gamma^{(101)} = 0.44 \text{ J/m}^2$ [15]], suggests that the $\text{TiO}_2(001)-(1 \times 1)$ surface is actually rather unstable, consistent with the experimental observation that the surface is reconstructed.

As a first step in our study of the (1×4) reconstruction, we calculated the surface energies of several stoichiometric and autocompensated models, including the MF [4], the AMR [6], and the ADM (see Figs. 1b–1c) models. The ADM model is obtained by periodically adding rows of TiO_2 molecules to the flat unreconstructed surface or, better, by replacing rows of bridging oxygen atoms (along the \hat{y} direction in Fig. 1) with rows of TiO_3 species forming a chain. Calculations were performed using a plane-wave pseudopotential [16] approach and the gradient-corrected PBE [17] exchange-correlation functional. Other

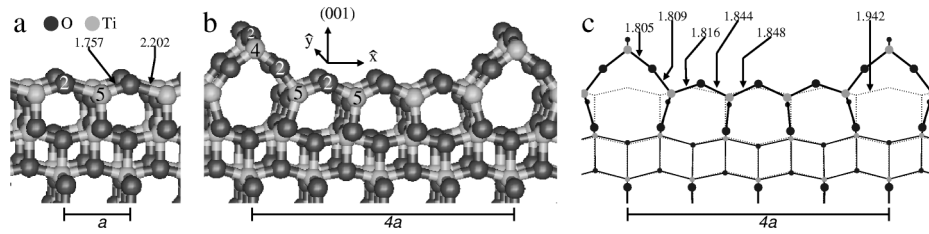


FIG. 1. (a) Relaxed (001)-(1 \times 1) surface of TiO₂ anatase. (b) Relaxed structure of the ADM (1 \times 4) reconstruction. (c) Projection of the atomic positions of the ADM model on the plane perpendicular to the \hat{y} direction. Dots with different size represent atoms belonging to different planes parallel to the figure. Dotted lines represent bonds in the ideally bulk-truncated surface. The length in Å of some surface bond is indicated. a is the theoretical bulk in-plane lattice spacing ($a = 3.786$ Å). \hat{x} and \hat{y} correspond to [100] and [010] directions [13]. The coordination of some surface atom is shown.

computational details (cutoff energy, k -point sampling, etc.) are as in Ref. [14]. The systems were described by a (1 \times 4) supercell geometry with a slab thickness of four TiO₂ layers, and the lower surface always had a bulk-truncated structure. All the atomic positions of the three uppermost TiO₂ layers were relaxed by energy minimization while the lower surface atoms were kept fixed [18].

The calculated surface energies of the MF, AMR, and ADM models are 1.25, 1.35, and 0.51 J/m², respectively, and are to be compared to $\gamma_{1 \times 1}^{(001)} = 0.90$ J/m², for the (001)-(1 \times 1) surface. In a previous study [14] we showed that the surface energy of various anatase surfaces is roughly proportional to the density of undercoordinated titanium atoms on the surface. As both the MF and AMR models have one fivefold, and two fourfold coordinated Ti atoms [Ti(4)] per (1 \times 4) cell, it is not surprising that both surfaces have larger energy than the unreconstructed one. On the basis of this argument one should expect the ADM model [which has four Ti(5) and one Ti(4)] to have a larger surface energy than the (1 \times 1) surface. Instead, we find a much smaller one, that is of the same order as $\gamma^{(101)}$. Thus, other mechanisms must be present to stabilize the ADM-reconstructed surface.

On this surface, the fourfold coordinated Ti atoms, belonging to the rows of bridging TiO₃ species, are bonded to twofold coordinated O atoms only, in a distorted tetrahedral environment (see Figs. 1b–1c). The stability of this kind of configuration is suggested by the fact that it occurs in a variety of systems, ranging from the Ti(OH)₄ species [19], to Ti-substituted zeolites [20], to the metastable “rosette” structure which is observed on the rutile TiO₂(110) surface after various sputtering and annealing treatments [21]. In this configuration, electron counting rules can be satisfied locally, with nominal charge transfers of one electron between a Ti(4) and neighboring O(2) [22]. This is not the case in the MF and AMR models, where charge transfers between cations and anions at larger distance must be invoked to satisfy the charge neutrality.

This argument does not explain why the reconstructed ADM-(1 \times 4) structure is so much favored with respect to the (1 \times 1) surface. Also, we have to determine whether

the (1 \times 4) periodicity is indeed the most stable among the various (1 \times n) periodicities that can be obtained by varying the spacing between the rows of bridging TiO₃. Therefore, we optimized the structure and determined the surface energy of various ADM-(1 \times n) reconstructions ($n = 3$ -6), and also computed the corresponding surface stress [23]. Results are shown in Table I. It appears that the (1 \times 4) periodicity is indeed the most favorable, but the predicted surface energy differences are very small, consistent with the experimental observation by STM of small regions with periodicities of $n = 3$ and 6 [6]. From Table I, it is also clear that the surface stress plays a major role in the reconstruction of the TiO₂(001) surface.

The occurrence of inequivalent surface Ti(5)-O(2) bonds on the relaxed (1 \times 1) surface [14], as well as the presence of a huge tensile stress in the direction parallel to these bonds (see Table I), suggest that the “natural” Ti(5)-O(2) bond length is shorter than the one that is allowed on the unreconstructed surface. On the ADM-(1 \times 4) surface the Ti(5)-O(2) bonds have a length ranging from ~ 1.82 to ~ 1.85 Å, that is $\sim 6\%$ smaller than in the bulk, and the stress along \hat{x} is much smaller than on the (1 \times 1) surface (see Table I). The occurrence of the reconstruction can be thus related to the fact that the added “defects” (the rows of TiO₃ molecules) lead to a compression of the Ti(5)-O(2) bonds, so that these can acquire a bond length closer to their “natural” value. In this way the system can reach an energetically more favorable configuration. The average Ti(5)-O(2) bond length on the ADM-(1 \times n) reconstructed surfaces (1.81, 1.84, 1.85, and 1.87 Å for $n = 3$,

TABLE I. TiO₂ anatase (001) surface: surface energy (γ) and diagonal elements of the surface stress (g) calculated for the unreconstructed (1 \times 1) and for the ADM-(1 \times n) reconstructed surfaces ($n = 3$ -6). All values are in J/m². $g > 0$ ($g < 0$) is tensile (compressive) stress, i.e., the surface would prefer to contract (expand).

	(1 \times 1)	(1 \times 6)	(1 \times 5)	(1 \times 4)	(1 \times 3)
γ	0.90	0.58	0.53	0.51	0.58
$g_{\hat{x}\hat{x}}$	6.1	4.1	3.1	0.9	-0.9
$g_{\hat{y}\hat{y}}$	-1.2	0.3	0.9	1.1	2.4

4, 5, and 6, respectively) increases monotonically with n , a small (large) value of n implying a high (low) density of added “defects,” i.e., a greater (reduced) compression of the Ti(5)-O(2) bonds. These trends are reflected in the behavior of the stress along \hat{x} , which is large and positive (tensile) for $n = 6$ and $n = 5$, also positive but much smaller for $n = 4$, finally becoming negative (compressive) for $n = 3$. The surface stress along the \hat{y} direction seems to play a less important role.

It is interesting to notice that the z position of the O(2) atoms in the trenches of the reconstructed surface is higher than on the (1×1) surface, consistent with the fact that one of the driving forces of surface relaxation is the repulsion between oxygens [14]. Also, in analogy to the outward relaxation of surface anions on the nonpolar surfaces of compound semiconductors, the increased height of the undercoordinated O atoms on an oxide surface can be associated to an orbital rehybridization which stabilizes the electron charge in the “dangling bonds,” as suggested in Ref. [2].

The real-space structure of the (001) - (1×4) reconstruction has been recently studied by STM under positive sample bias conditions [6]. In this configuration, the local structure of the empty electronic state density near the conduction band edge is probed. The STM images of Ref. [6] consist of bright atomic rows at a distance of $\sim 16 \text{ \AA} \sim 4a$ [where a is the (1×1) spacing] one from the other, with two additional faint rows in between each pair of adjacent bright rows. The distance between a faint row and the adjacent brighter row is $\sim 6.2 \text{ \AA} \sim 1.5a$. To explain these images, the authors of Ref. [6] proposed the AMR model. Our “theoretical STM images” of the ADM and AMR models calculated within Tersoff-Hamann’s approach [24] are shown in Fig. 2. The agreement between

the calculated image of the ADM model and the experimental one is remarkable, e.g., the two faint rows observed in Ref. [6] are also visible in our simulation. As in the case of the rutile (110) surface [12], empty states near the conduction band edge are Ti derived, and from Fig. 2a one can see that the bright and faint rows correspond to Ti(4) and Ti(5) surface atoms, respectively. However, only the two central Ti(5) atoms give rise to visible features in the image, while those adjacent to the added TiO_3 rows are “hidden” by the brighter Ti(4) atoms. The charge density corrugation (in the direction perpendicular to the rows) extracted from Fig. 2c is of $\sim 3 \text{ \AA}$ at a distance of $\sim 2\text{--}3 \text{ \AA}$ above the topmost Ti atoms. Experimentally the corrugation of the bright rows was found to depend on voltage, being typically in the range of from 0.8 to 1.7 \AA . Taking into account that the experimental image includes some tip effects that tend to smooth out the intrinsic corrugation of the surface, we conclude that also the calculated corrugation is in reasonable agreement with the experiment.

On the basis of the geometrical arrangement of the surface Ti atoms [6], one should expect that also the AMR model yields the features observed by STM. Instead, the agreement of the calculated image for this model with the experiment is rather poor (Fig. 2), confirming the well-known importance of an accurate description of the electronic structure for the interpretation of STM results. Bright rows associated to the topmost Ti(5) atoms are split in two as the nodal plane for the d states on these atoms is a plane perpendicular to the surface. A single, wide faint row is present, reflecting a weak bond formed by the two Ti(4) atoms adjacent to the missing row. In addition there is not much contrast between bright and faint rows, as the charge corrugation is quite small, and does not exceed

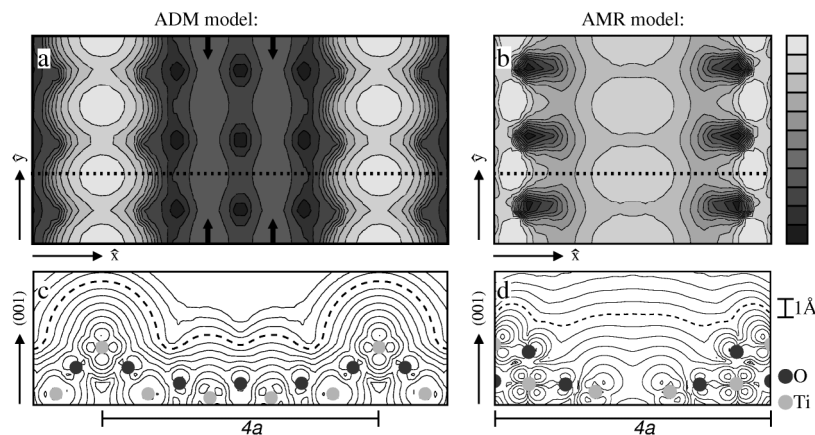


FIG. 2. Upper panels [(a) and (b)]: simulated STM images (under positive sample bias conditions) of two different models of the anatase $\text{TiO}_2(001)$ - (1×4) surface (see text). Lower panels [(c) and (d)]: local density of states integrated in a 2-eV energy window near the conduction band; contour lines (in geometric progression) of a plane perpendicular to the surface which passes through the surface Ti atoms, corresponding to the dotted line in the upper panels. The two upper panels show the contour lines of points equally distant from the surface on the isodensity surface corresponding to the dashed line in the lower panel (the relative heights of the different contours is 0.4 and 0.3 \AA for the ADM and AMR panels, respectively). Lighter shading corresponds to regions of larger distance from the surface, and the arrows inside “a” panel highlight the two faint rows described in the text.

~ 1 Å at distance of $\sim 2-3$ Å above the topmost Ti atoms, which is smaller than the experimental value.

In conclusion, on the basis of DFT total energy calculations we have proposed a new model of the recently discovered (1×4) reconstruction of the anatase $\text{TiO}_2(001)$ surface. Besides being energetically favored, our model provides a satisfactory description of recent STM results, including the observation of less frequent (1×3) and (1×6) periodicities. We have shown that the primary mechanism of this reconstruction is the relief of the surface stress. The importance of this mechanism is well known in the context of metal and semiconductor surface reconstructions [25], but its relevance for oxide surfaces has not been established yet.

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