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First-principles calculations of the energetics of stoichiometric TiO_2 surfaces

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We present self-consistent *ab initio* total-energy calculations of the equilibrium relaxed structures and surface energies of the stoichiometric (1×1) (110), (100), (001), and (011) surfaces of TiO_2. The relaxations of atoms on these surfaces are found to be substantial, and are responsible for a large reduction of the calculated surface energies. A Wulff construction is used to display the relative energetics of these surfaces. The (100) surface is found to be stable with respect to forming macroscopic (110) facets, while the (001) surface is nearly unstable with respect to forming macroscopic (1×1) (011) facets. These results shed light on published experimental results on the structures of these surfaces.

I. INTRODUCTION

The surfaces of TiO_2 have been the subject of a large number of investigations motivated largely by the interest in understanding their catalytic properties.[1,2] The (110), (100), and (001) surfaces have been the subject of numerous experimental investigations over a wide range of temperatures and with a variety of surface treatments, employing a number of surface-sensitive techniques.[3] Structural information on these surfaces has been obtained using low energy electron diffraction, electron stimulated desorption, scanning tunneling microscopy, and grazing incidence x-ray diffraction. The (110) and (100) surfaces were found to be stable with respect to faceting on thermal annealing at elevated temperatures.[4] The (110) surface formed a (1×2) reconstruction on annealing at 600 °C,[5–7] while the (100) surface exhibited a series of (1×3), (1×5), and (1×7) reconstructions upon annealing at 600 °C, 800 °C, and 1200 °C, respectively.[4,8–11] The (001) surface was found to be unstable above 475 °C, exhibiting macroscopic (2×1) reconstructed facets of the (011) orientation.[12–15] At temperatures above 950 °C this surface undergoes a structural transition to a phase which is yet to be characterized precisely.

The experimental investigations of the structural properties of these surfaces, cited above, address a number of issues. One is the thermodynamic stability of a given stoichiometric TiO_2 surface, with respect to reconstruction or faceting at zero temperature. Another is the stability of a surface with respect to reconstruction or structural phase transition at an elevated temperature, possibly under conditions of nonstoichiometry. The evidence to date indicates that the (110) and (100) surfaces are stable with respect to faceting, but form nonstoichiometric reconstructed structures at elevated temperatures. The (001) surface appears to be unstable with respect to faceting (presumably only kinetic limitations prevent faceting below 475 °C). Also at elevated temperatures, it undergoes a structural phase transition.

In this investigation, we address the issue of stability of the stoichiometric surfaces with respect to faceting through first-principles total-energy calculations. The results of our calculations are strictly valid only at zero temperature. We calculate the surface energies of the stoichiometric (1×1) (110), (100), (011), and (001) surfaces of TiO_2, including the relaxations of the surface atoms from the positions indicated by the truncation of the bulk crystal along these orientations. We then construct the equilibrium shape of a macroscopic crystal of TiO_2 from this information, and discuss the implications of this work for understanding the experimental investigations cited above. These surfaces present a range of bonding configurations and degree of corrugation. We found it to be of interest to investigate the effect of these factors in determining the stability of each stoichiometric surface at zero temperature. The influence of finite temperature and nonstoichiometry would be subjects for future investigations. To our knowledge, this is the first investigation of the relative energetics of several low-index surfaces of a transition metal oxide using total-energy calculations, with all the structures considered being relaxed to equilibrium.

II. CALCULATION METHOD AND TESTS

The calculations were performed using *ab initio* Vanderbilt ultrasoft pseudopotentials[16] expanded in a plane-wave basis. A cutoff of 25 Ry was used for the valence electron wave functions, which included the Ti 3*s*, 3*p*, 3*d*, and 4*s* states and the O 2*s* and 2*p* states. The inclusion of shallow core states on the Ti atom leads to an exceptionally transferable Ti pseudopotential. The core radii for Ti and O were taken to be 1.8 a.u. and 1.3

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a.u., respectively. Two reference energies were taken for each angular momentum channel on each atom to bring the logarithmic derivatives of the pseudo wave functions close to those of the all-electron wave functions over a wide range of energies.

The total energies of periodic slabs of TiO_2 were calculated using the local-density approximation (LDA) for the exchange and correlation energy, with the Ceperley and Alder form of the exchange-correlation potential.[17] The valence electron wave functions were obtained by minimizing the Kohn-Sham energy functional using a preconditioned conjugate-gradient method,[18] which is similar in many respects to that pioneered by Teter, Payne, and Allan.[19] The different feature of the present approach is the use of a generalized Kohn-Sham energy functional, in a space of nonorthogonal orbitals,[20] with all bands at all k points being updated simultaneously. This makes it feasible to study supercells with as many as 144 bands and four special k points in the surface Brillouin zone with a reasonable computational effort. The forces on all the ions were calculated, and used to relax the ions to equilibrium using a modified Broyden scheme.[21] In the relaxed structures, the forces on the atoms were smaller in magnitude than 0.05 eV/a.u. Tests of the pseudopotentials on bulk rutile gave the lattice parameters within 1% and several zone center phonon frequencies within 4% of experimental values,[22,23] as reported earlier.[24]

The surfaces were simulated by supercells repeated periodically along the surface normal, separated by vacuum layers. The vacuum layer thickness, the number of layers in the supercell, and the k-point sampling were all varied to obtain a converged value of the surface energy for a given orientation. A vacuum layer thickness of 10.5 a.u. was found to be adequate to give surface energies convergent to within 2%. The supercells contained up to 36 atoms. The number of layers needed to converge the surface energies varied with the orientation. The (100) and (001) surfaces have one unit of TiO_2 per layer; six layers of the former and ten layers of the latter were found to be enough to converge the surface energies of these surfaces to within 1.5%. The (110) and (011) surfaces have two TiO_2 units per layer, and the thickest slabs simulated had six layers, respectively.

The special k-point set used for the (110), (100), and (001) surfaces unfolded into 16 points in the surface Brillouin zone. The (011) surface unit cell has especially low symmetry and a k-point sampling of this density proved to be problematic. The results for the surface energy of this surface, for the six-layer slab, is based on the average of two calculations, with two special k points along one axis of the surface Brillouin zone and one k point along the other. As these two surface energies agree within 2.6%, we do not believe this to be a significant source of error.

III. STRUCTURE

Bulk TiO_2 has a tetragonal unit cell with two TiO_2 units per cell,[25] as shown in Fig. 1. The Ti atoms occupy the corners and body-center positions in each unit cell. Each Ti atom is coordinated to six neighboring O atoms situated at the vertices of a distorted octahedron, with two apical Ti-O bonds about 2% longer than the four equatorial Ti-O bonds. Each O atom is coordinated to three Ti atoms, with all three O-Ti bonds lying in one plane. The structure may best be pictured as chains of TiO_6 octahedra, lying parallel to the [001] direction, with adjacent octahedra along a chain sharing an edge. In adjacent chains the octahedra share vertices, and are rotated by 90° about the [001] axis. The apical Ti-O bonds lie along the [110] or [$1\bar{1}0$] directions.

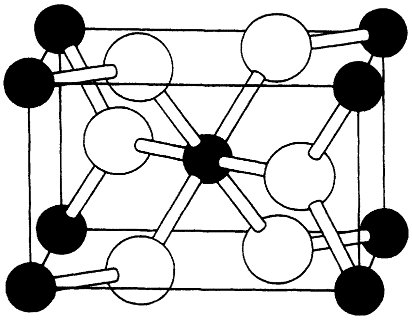

FIG. 1. The structure of bulk TiO_2.

On the surfaces of TiO_2 these octahedra are truncated in various ways, giving rise to patterns of atomic coordinations at the surface differing from the bulk. The low-index surfaces which were studied span a wide range of surface atomic coordination numbers. The (110) surface has only one-half of the surface Ti atoms fivefold coordinated, with the remaining one-half being sixfold coordinated, as in the bulk. The (100) and (011) surfaces have only fivefold coordinated surface Ti atoms, while the (001) surface has all its surface Ti atoms only fourfold coordinated. On all these surfaces, the most exposed O atoms on the surface are twofold coordinated. On the (110) and (011) surfaces there are both twofold and threefold coordinated O atoms, while on the (100) and (001) there are only twofold coordinated ones.

A. The (110) surface

The (110) surface, shown in Fig. 2, is rather flat and among all the low-index surfaces of TiO_2 has the least density of dangling bonds on the surface. The surface unit cell has Ti atoms lying in a centered rectangular arrangement, with the atoms at the cell corners being sixfold coordinated, while the atom in the center is fivefold coordinated. The shorter surface unit cell vector is along the bulk [001] direction and the longer one along the bulk [$1\bar{1}0$]. The equatorial planes of the octahedra of O atoms around the sixfold coordinated Ti atoms are perpendicular to the surface. This gives rise to chains of twofold coordinated O atoms, parallel to the bulk [001] direction, raised above the plane of the surface Ti atoms by about 2.36 a.u. These O atoms are called "bridging O atoms." The distance between two adjacent chains is about 12.21 a.u., which is rather large. Rows of three-

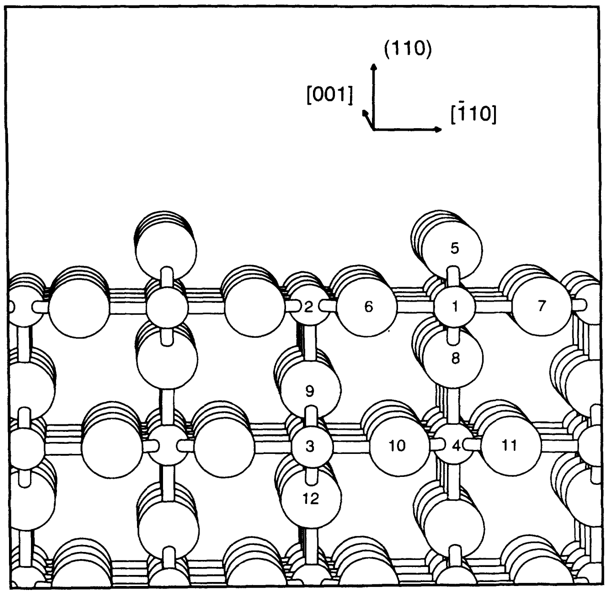

FIG. 2. The structure of the unrelaxed stoichiometric (110) surface.

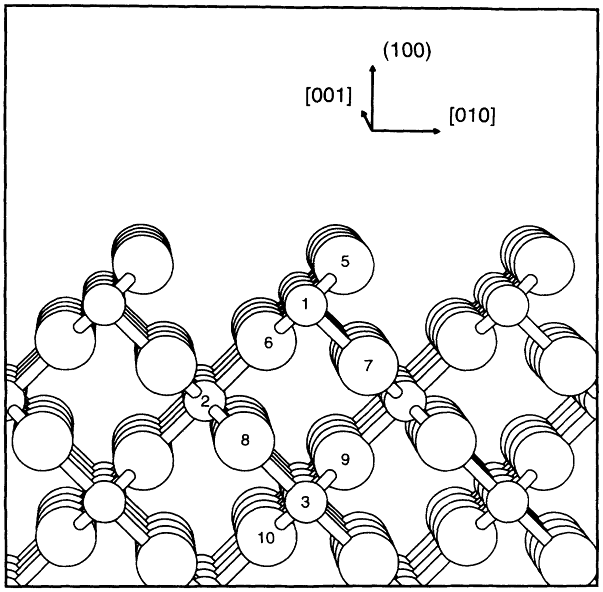

FIG. 3. The structure of the unrelaxed stoichiometric (100) surface.

fold coordinated O atoms lie in the plane of the Ti atoms, connecting the chains of sixfold and fivefold coordinated Ti atoms.

The relaxations of the surface atoms on the (110) surface are given in Table I. The dominant relaxations are along the surface normal. The undercoordinated Ti and O atoms are drawn inward, by 0.32 and 0.15 a.u., respectively, reducing the lengths of their bonds with subsurface atoms. The sixfold coordinated Ti atoms and the threefold coordinated O atoms move outward by about 0.25 a.u. Thus the relaxed surface has a puckered appearance.

B. The (100) surface

The (100) surface, shown in Fig. 3, is more corrugated than the (110) surface. The surface unit cell is rectangular, with axes along the bulk [010] and [001] directions. There is one TiO_2 unit per surface unit cell. All the Ti atoms on this surface have their oxygen octahedra truncated and are fivefold coordinated. On the unrelaxed surface, the equatorial planes of the octahedra are inclined at 45° with respect to the surface normal. As in the case of the (110) surface, this gives rise to chains of twofold coordinated O atoms (bridging O atoms) lying at the highest level on this surface. The chains of TiO_2 units in the second layer are rotated by 90°. This makes the surface look like a periodic array of ridges and troughs parallel to the [001] direction.

The relaxations of this surface are specified in Table II. The dominant relaxations are along the [010] axis, the surface Ti and O atoms moving in opposite directions by about 0.32 a.u. The inward relaxation, along the di-

TABLE I. Unrelaxed coordinates (u, v, w) and relaxations $(\Delta u, \Delta v, \Delta w)$ of surface and near-surface atoms on the (110) surface. The u, v, and w axes lie along the $[\bar{1}10]$, [001], and [110] directions, respectively. Atom labels refer to Fig. 2. Units are a.u.

Label	u	v	w	Δu	Δv	Δw
1	0.0000	0.0000	0.0000	0.00	0.00	0.25
2	-6.1049	2.7716	0.0000	0.00	0.00	-0.32
3	-6.1049	0.0000	-6.1049	0.00	0.00	-0.15
4	0.0000	2.7716	-6.1049	0.00	0.00	0.12
5	0.0000	2.7716	-2.3565	0.00	0.00	-0.12
6	-3.7484	0.0000	0.0000	-0.07	0.00	0.24
7	3.7484	0.0000	0.0000	0.07	0.00	0.24
8	0.0000	2.7716	2.3565	0.00	0.00	-0.14
9	-6.1049	2.7716	-3.7484	0.00	0.00	0.03
10	-2.3565	0.0000	-6.1049	0.09	0.00	-0.05
11	2.3565	0.0000	-6.1049	-0.09	0.00	-0.05
12	-6.1049	2.7716	-8.4614	0.00	0.00	-0.02

TABLE II. Unrelaxed coordinates (u, v, w) and relaxations $(\Delta u, \Delta v, \Delta w)$ of surface and near-surface atoms on the (100) surface. The u, v, and w axes lie along the [010], [001], and [100] directions, respectively. Atom labels refer to Fig. 3. Units are a.u.

Label	u	v	w	Δu	Δv	Δw
1	4.3168	2.7714	4.3168	0.32	0.00	-0.14
2	0.0000	0.0000	0.0000	0.20	0.00	-0.01
3	4.3168	2.7714	-4.3168	0.13	0.00	0.03
4	0.0000	0.0000	-8.6336	0.13	0.00	0.03
5	5.9831	0.0000	5.9831	-0.34	0.00	0.01
6	2.6505	0.0000	2.6505	-0.23	0.00	0.03
7	6.9673	2.7714	1.6663	-0.06	0.00	0.04
8	1.6663	2.7714	-1.6663	0.01	0.00	0.05
9	5.9831	0.0000	-2.6505	-0.01	0.00	0.02
10	2.6505	0.0000	-5.9831	-0.04	0.00	0.03
11	6.9673	2.7714	-6.9673	-0.04	0.00	0.03
12	1.6663	2.7714	-10.2999	-0.01	0.00	0.02

rection of the surface normal, is about 0.14 a.u. for the surface Ti atoms and negligibly small for the O atoms. The relaxations of these surface atoms enable the surface Ti atoms to sink below the level of the equatorial plane of the truncated oxygen octahedra and shorten their bonds with the apical O atoms lying below the surface. The inclination of these latter planes with the surface normal on the (100) surface changes from being 45° on the unrelaxed surface to a value close to 30° when relaxations are included.

C. The (011) surface

The (011) surface is shown in Fig. 4. Like the (110) surface, it has two TiO_2 units per layer. However, it is much more corrugated than the (110) surface. The Ti atoms on the surface are all fivefold coordinated. On the unrelaxed surface they lie in a centered rectangular lattice with one basis vector along the [100] direction and the other along the $[0\bar{1}1]$. The octahedra of O atoms around the surface Ti atoms are all truncated and lack an equatorial O atom. The inclination of their equatorial planes is different for the Ti atoms at the center of the unit as compared to the atoms at the cell corners. The bond lengths between the surface O atoms and the surface Ti atoms fall into two symmetrical pairs of slightly different lengths, giving rise to zig-zag chains of twofold coordinated O atoms at the highest level on the surface, and threefold coordinated surface O atoms at a level below that of the surface Ti atoms. This arrangement makes the O atoms on the surface lie in chains, alternately along crests and troughs.

As shown in Table III, the dominant relaxations of the surface Ti atoms are in the plane of the surface, along the [100] direction, by about 0.4 a.u., and along the surface normal inward by about 0.17 a.u. This relaxation has a similar effect to those of the fivefold coordinated surface Ti atoms on the (100) and (110) surfaces, moving these undercoordinated surface Ti atoms into the truncated oxygen octahedra. The relaxations of the surface O atoms are equally distributed along the [100] and along the surface normal, and are of the order of 0.14 a.u. On the relaxed surface, the truncated oxygen octahedra around the surface Ti atoms are rotated from those in the bulk.

TABLE III. Unrelaxed coordinates (u, v, w) and relaxations $(\Delta u, \Delta v, \Delta w)$ of surface and near-surface atoms on the (011) surface. The u and v axes lie along the [100] and $[01\bar{1}]$ directions, respectively. The w axis lies along the normal to the (011) plane. Atom labels refer to Fig. 4. Units are a.u.

Label	u	v	w	Δu	Δv	Δw
1	0.0000	0.0000	0.0000	-0.40	-0.13	-0.17
2	-4.3168	-5.1298	0.0000	0.40	-0.13	-0.17
3	0.0000	-7.2651	-4.6643	0.22	0.07	0.07
4	-4.3168	-2.1354	-4.6643	-0.22	0.07	0.07
5	-2.6505	2.2304	1.4319	0.15	0.03	-0.14
6	2.6505	-2.2304	-1.4319	-0.02	0.07	0.05
7	-1.6663	-2.8994	1.4319	-0.15	0.03	-0.14
8	1.6663	-7.3602	-1.4319	0.02	0.07	0.05
9	-2.6505	-5.0347	-3.2323	0.05	-0.03	-0.10
10	2.6505	-9.4956	-6.0962	-0.04	0.03	0.00
11	-1.6663	0.0950	-3.2323	-0.05	-0.03	-0.10
12	1.6663	-4.3657	-6.0962	0.04	0.03	0.00

D. The (001) surface

As shown in Fig. 5, the (001) surface has all its surface Ti atoms fourfold coordinated and all surface O atoms twofold coordinated. The unrelaxed surface is rather flat.

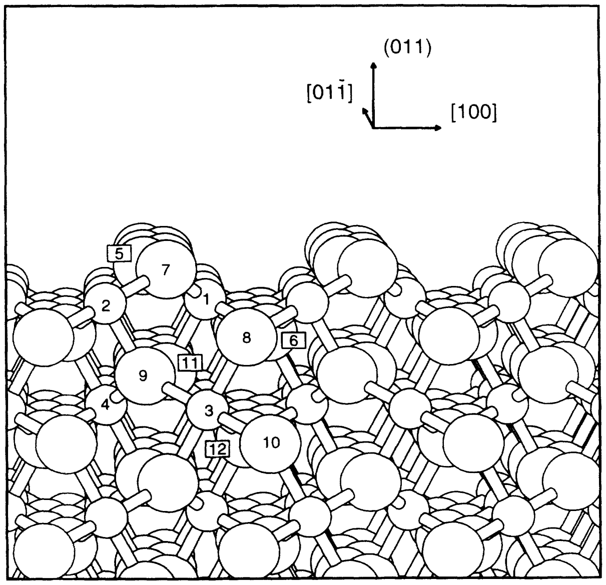

FIG. 4. The structure of the unrelaxed stoichiometric (011) surface.

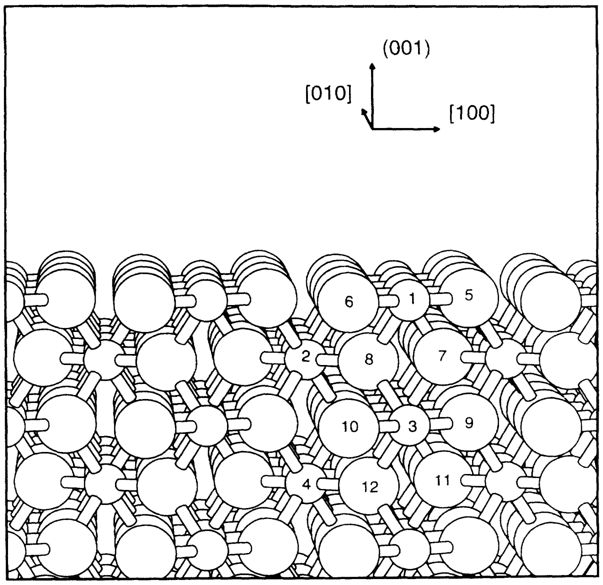

FIG. 5. The structure of the unrelaxed stoichiometric (001) surface.

TABLE IV. Unrelaxed coordinates (u, v, w) and relaxations $(\Delta u, \Delta v, \Delta w)$ of surface and near-surface atoms on the (001) surface. The u, v, and w axes lie along the [100], [010], and [001] directions, respectively. Atom labels refer to Fig. 5. Units are a.u.

Label	u	v	w	Δu	Δv	Δw
1	0.0000	0.0000	0.0000	0.00	0.00	-0.60
2	-4.3168	4.3168	-2.7714	0.00	0.00	0.60
3	0.0000	0.0000	-5.5428	0.00	0.00	-0.40
4	-4.3168	4.3168	-8.3142	0.00	0.00	0.40
5	2.6505	2.6505	0.0000	-0.19	-0.19	0.06
6	-2.6505	-2.6505	0.0000	0.19	0.19	0.06
7	1.6663	-1.6663	-2.7714	0.07	-0.07	-0.08
8	-1.6663	1.6663	-2.7714	-0.07	0.07	-0.08
9	2.6505	2.6505	-5.5428	-0.05	-0.05	0.05
10	-2.6505	-2.6505	-5.5428	0.05	0.05	0.05
11	1.6663	-1.6663	-8.3142	-0.05	0.00	-0.06
12	-1.6663	1.6663	-8.3142	0.05	0.00	0.06

The oxygen octahedra around the surface Ti atoms all have their equatorial planes perpendicular to the surface and are truncated. This deprives the surface Ti atoms of two nearest-neighbor O atoms as compared to the bulk. On the unrelaxed surface, each Ti atom is bonded to two O atoms in its plane and two O atoms in the layer below the surface, with two former bonds 2% longer than the latter.

The relaxed coordinates are given in Table IV. The surface Ti atoms move dramatically inward by 0.60 a.u., while those in the layer below move towards the surface by about the same extent. These relaxations of the surface and subsurface Ti atoms are a very significant fraction of the interlayer spacing on the unrelaxed surface, which is 2.7714 a.u., and decay rather slowly with the distance below the surface. The relaxations of the O atoms are rather small in comparison. The relaxed surface is now rather puckered, and like the other orientations has surface O atoms at the topmost level on the surface.

IV. ENERGETICS

The surface energy of each surface is calculated from the total energy of a supercell of that surface orientation as follows :

$$2E_{\text{surf}} = E_{\text{tot}}(\text{supercell}) - n\, E_{\text{tot}}(\text{bulk}) \ . \qquad (1)$$

Here, $E_{\text{tot}}(\text{bulk})$ is the total energy of bulk TiO_2, per TiO_2 unit, and $E_{\text{tot}}(\text{supercell})$ the total energy of the given supercell, containing n TiO_2 units. The overall factor of two comes from the fact that each supercell has two surfaces.

The calculation of the surface energy of the (110) orientation presented the unusual feature that the odd-layer and even-layer supercells were inequivalent. In the odd-layer supercells there was present an extra symmetry of reflection about the plane of the central layer. This constrained the relaxations of these supercells in comparison to the even-layer supercells, which did not possess this symmetry. Thus the estimated surface energies of the four- and six-layer slabs were lower than those of the three- and five-layer slabs. The surface energies of the odd-layer slabs appear to converge from above and those of the even-layer slabs from below to the surface energy of a slab of infinite layers. We have indicated the calculated surface energies of unrelaxed and relaxed (110) supercells, with a various number of layers in the supercells, in Table V. The final values of surface energy adopted for this orientation were obtained by taking the average of the five- and six-layer results.

TABLE V. The surface energies of relaxed and unrelaxed supercells of the (110) orientation, indicating the oscillatory convergence of the surface energy with slab thickness. The surface energies are in units of meV/(a.u.^{2}).

Number of layers	Surface energy (unrelaxed)	Surface energy (relaxed)
3	31.2	19.2
4	30.1	13.3
5	31.2	16.7
6	29.9	14.5

The surface energies of the various orientations are tabulated in Table VI. As expected from conditions of coordination, the (110) surface has the lowest surface energy and the (001) the highest, among the surfaces considered here. The possibility of the (100) surface undergoing faceting to give macroscopic facets of (110) orientation was considered, as was the possibility of the (001) surface forming macroscopic facets of the (011) orientation. The thermodynamic stability of a surface of orientation $(h_1k_1l_1)$ with respect to forming macroscopic facets of orientation $(h_2k_2l_2)$ depends on the sign of the formation energy:

$$\Delta G = \frac{E_{\text{surf}}(h_2k_2l_2)}{\cos(\theta)} - E_{\text{surf}}(h_1k_1l_1) \ . \qquad (2)$$

Here θ is the angle between the planes, and the factor of $\cos(\theta)$ takes into account the increase in surface area if facets were formed. The contribution of edges and vertices has been neglected. If the above expression is negative, then the free energy change on the formation of facets is negative and the surface $(h_1k_1l_1)$ is not thermodynamically stable. Whereas if it is positive, then the surface $(h_1k_1l_1)$ is stable against the formation of facets of orientation $(h_2k_2l_2)$.

For the consideration of the stability of the (100) sur-

TABLE VI. Surface atomic coordination and surface energy for several 1×1 surfaces of different orientations. The surface energies are in units of meV/(a.u.^{2}).

Surface	Surface Ti coordination	Surface O coordination	Surface energy (unrelaxed)	Surface energy (relaxed)
(110)	5,6	2,3	30.7	15.6
(100)	5	2	33.8	19.6
(011)	5	2,3	36.9	24.4
(001)	4	2	51.4	28.9

face, forming facets of the (110) orientation, which make an angle of 45° with the (100) plane, the above expression becomes

$$\Delta G = \frac{15.6}{\cos(45^\circ)} - 19.6 = 2.46\ \mathrm{meV/(a.u.^2)}. \quad (3)$$

Thus the (100) surface is stable with respect to forming (110) facets. In the case of the stability of the (001) with respect to forming (011) facets, the appropriate expression is

$$\Delta G = \frac{24.4}{\cos(32.7^\circ)} - 28.9 = 0.1\ \mathrm{meV/(a.u.^2)}\ . \quad (4)$$

Though the above number is positive, it is within a percent of the surface energy of each surface. This is within the error bars of our calculation, with regard to slab thickness and k-point sampling. We conclude that within these errors, the (001) surface appears to be almost unstable with respect to the formation of macroscopic (1×1) (011) facets. The importance of including relaxations in the calculation of the surface energies is brought out in the consideration of the stability of the (001) surface. If the surface energies of the unrelaxed (001) and (011) surfaces were used, the formation energy per unit area, for macroscopic (1×1) (011) facets on the (001) surface, would be large and negative. This would be in complete contradiction to the result obtained on including relaxations.

The standard method of quantifying the above information concerning the surface energies of different surfaces, and their thermodynamic stability, is through the Wulff construction.[26] A three-dimensional plot of the surface free energy of orientation $\hat{n}$ as a function of $\hat{n}$ is made as follows. Along each unit vector $\hat{n}$, a radius is drawn of magnitude $E_{\mathrm{surf}}(\hat{n}.)$ A plane perpendicular to each such radius vector is drawn passing through its tip. The inner envelope of all these planes is the Wulff construction. Only planes that are part of the Wulff construction are thermodynamically stable. Our construction for $\mathrm{TiO_2}$ with the data we have is shown in Fig. 6. A more complete construction would require knowledge of the energetics of other low-index surfaces, the (111) for instance.

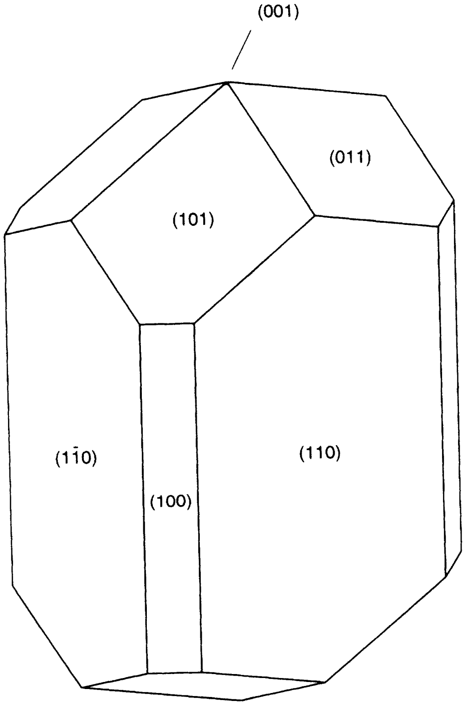

FIG. 6. The equilibrium shape of a macroscopic crystal of $\mathrm{TiO_2}$ using the Wulff construction and the surface energies of Table VI.

The facet that contributes the largest area to the crystal is the (110) surface, which our calculations indicate to be the surface of lowest energy. The remaining area within the four surfaces we have studied is almost entirely composed of the (100) and (011) orientations. The very high surface energy of the (001) surface, and its near instability with respect to forming macroscopic (011) facets, makes it contribute rather miniscule facets to the equilibrium crystal. (Such a facet is present but barely visible in Fig. 6.)

V. DISCUSSION

Our calculations have indicated that the (110) surface is the surface of lowest energy, as the low density of dangling bonds on this surface would lead one to expect. The stability of the (100) surface with respect to forming macroscopic (110) facets is in agreement with the early experiments of Chung, Lo, and Somorjai.[4] The (001) surface has the highest surface energy of the four surfaces considered here, again bearing up the expectation based on a naive consideration of the density of surface dangling bonds. Its marginal stability with respect to forming macroscopic (011) facets, even without consideration of possible reconstruction, is an interesting result in its own right. It indicates that, under stoichiometric conditions, the (001) surface would not form (1×1) (011) facets. However, the formation energy per unit area of such facets is small enough to be easily outweighed by entropic effects at finite temperature.

The experimental investigations of thermally annealed surfaces of $\mathrm{TiO_2}$ detect various reconstructions on these surfaces. The (110) surfaces were found[5,6] to undergo a (1×2) reconstruction on annealing at 600 °C, and the (100) exhibited[4] a series of reconstructions, the (1×3), the (1×5), and (1×7). These reconstructed surfaces have been shown to be nonstoichiometric.[4,7,10,11] The (2×1) reconstruction observed on the (011) planes bounding the observed pyramidal facets on thermally annealed (001) surfaces may likewise indicate nonstoichiometry. Conceivably, nonstoichiometry may assist in driving the surface free energy of the (2×1) (011) surface significantly below that of the (001) surface, to give rise to the large-scale faceting seen in annealing experiments at elevated temperatures.

Our total-energy calculations are strictly valid only at zero temperature. Only stoichiometric, unreconstructed surfaces were considered. The results bring out the influence of varying surface bonding configuration and corrugation on the energetics of several surfaces of TiO_2, and give insight into some qualitative features of published experiments. A more detailed comparison with experiments would require further calculations on nonstoichiometric surfaces, including the effects of finite temperature.

VI. CONCLUSIONS

We have studied the energetics of several low-index surfaces of TiO_2, using first-principles total-energy calculations. Our calculations indicate that the (110) surface has a much lower surface energy than the (001) surface, as expected on the basis of counting dangling bonds. The (100) and (011) surfaces have surface energies lying in between these extremes. The (100) surface is clearly stable with respect to forming facets of the (110) orientation, while the (001) surface apppears to be marginally stable with respect to forming macroscopic (011) facets. The relaxations of atoms on the surfaces are large and make a significant contribution to the calculated surface energies, to the extent of making conclusions based on the unrelaxed surface energies misleading. Qualitative insight into some aspects of published experimental results on these surfaces was obtained.

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