

## The energetics and structure of rutile TiO<sub>2</sub>(110)

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2006 J. Phys.: Condens. Matter 18 4207

(<http://iopscience.iop.org/0953-8984/18/17/009>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 28/05/2010 at 10:23

Please note that [terms and conditions apply](#).

# The energetics and structure of rutile TiO<sub>2</sub>(110)

A Kiejna<sup>1</sup>, T Pabisiak<sup>1</sup> and S W Gao<sup>2</sup>

<sup>1</sup> Institute of Experimental Physics, University of Wrocław, Plac M Borna 9, PL-50-204 Wrocław, Poland

<sup>2</sup> Department of Physics, Göteborg University, S-412 96 Gothenburg, Sweden

Received 24 January 2006

Published 13 April 2006

Online at [stacks.iop.org/JPhysCM/18/4207](http://stacks.iop.org/JPhysCM/18/4207)

## Abstract

Density functional theory and a pseudopotential plane wave method are applied to study electronic and structural properties of the defect-free TiO<sub>2</sub>(110) surface. The variations of the surface energy, work function, and atomic displacements are examined for partially and fully relaxed slabs modelling the rutile (110) surface, and consisting of up to 33 atomic layers. Relatively small relaxations of atomic positions in the outermost layers have a strong influence on the calculated surface energies and work functions. The effect of nonequivalence of the odd–even layer terminations is explored. A simple method is proposed which allows one to estimate accurate surface energies for relaxed systems from calculations for partially relaxed slabs.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Titanium dioxide surfaces have attracted considerable interest in recent years due to their fundamental properties and wide area of technological application [1, 2]. The stoichiometric O-bridge termination of TiO<sub>2</sub>(110), which arises when cutting the bulk crystal, is characterized by the lowest energy, and is the most stable among the rutile low index surfaces [1, 3]. In the past decade there have been several density functional theory (DFT) investigations of both the surface energy and the geometrical structure of clean TiO<sub>2</sub>(110) [3–11]. Earlier studies pointed out the important factors influencing the results. The plane wave pseudopotential calculations of Ramamoorthy *et al* [3] determined the relaxed equilibrium structures and surface energies of the low index atomic planes, and demonstrated the importance of surface relaxation. The oscillatory variation of surface energies with the number of layers in a slab has also been noticed. The atomic displacements were found to be substantial and responsible for a large reduction of surface energy for the (110) plane. Further calculations [4, 5] showed that the generalized gradient approximate (GGA) functional reduces surface energy by as much as 30%, compared to the local density approximation (LDA). It was also pointed out [6] that slabs of at least six layers are necessary to achieve convergence of the surface energy and the correct positions of surface atoms. The oscillating character of the TiO<sub>2</sub>(110) odd–even layer slab

properties as a function of the slab thickness has been recently discussed [10] and ascribed to surface-induced hybridization of Ti 3d and O 2p orbitals among the layers.

This oscillatory convergence with slab thickness, and the sensitivity to the exchange–correlation functional applied, are responsible for quite a scattered range in the calculated (from first principles) surface energies of TiO<sub>2</sub>(110) reported in the literature, which may differ even by 100%, depending on the relaxation effect, and the slab thickness. Quite surprisingly, despite its importance in experimental characterization of the state of an oxide surface [2], the variation of the work function versus the number of layers in the slab has not been examined so far. Besides this, only one group of the existing first principles calculations [12–14] addressed the absolute value of the work function of TiO<sub>2</sub>, which again may deviate from the experimental estimates even by 2 eV.

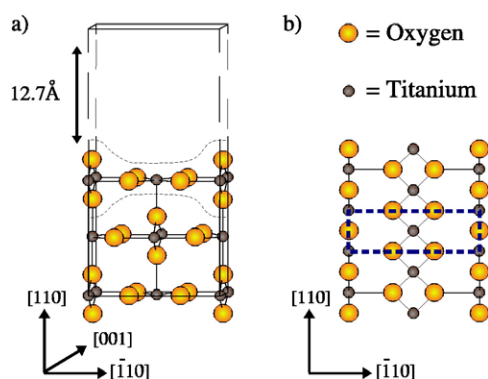
These large uncertainties in the surface quantities of TiO<sub>2</sub>(110) determined which are of major importance for various applications [1] of rutile TiO<sub>2</sub> single crystals warrant further theoretical investigations of the structure and energetics of the (110) surface. Reliable values of the clean surface characteristics are also necessary in order to build a solid basis for studies of adsorption systems. In this work we examine different modes of a slab relaxation and their influence on the surface energy, work function, and atomic displacement pattern, for a range of slab thicknesses wider than those studied previously. Such systematic study of work function variation for this system has not been presented before. We discuss the effect of nonequivalence of the odd and even layer slab terminations, and show that quite accurate estimates of surface properties can be obtained from a proposed extrapolation of results for thin slabs.

## 2. Methodology and details of the calculation

The DFT calculations were performed within the plane wave basis pseudopotential approach, as implemented in the Vienna *ab initio* simulation package (VASP) [15, 16]. The exchange–correlation energy is treated within the Perdew and Wang (PW91) version of the GGA [17]. The interaction of valence electrons with ionic cores was described using ultrasoft pseudopotentials [18, 19]. In some additional, comparative calculations we have applied the projector augmented wave (PAW) potentials [20] to represent the electron–ion interaction within the Perdew–Burke–Ernzerhof (PBE) version of the GGA [21]. In the Ti pseudopotential applied the 3d and 4s states were treated as valence states. The cut-off energy for the plane waves was set equal to 400 eV, throughout all computations.

The tetragonal unit cell of the rutile TiO<sub>2</sub> contains two Ti and four O atoms, and is characterized by the lattice parameters  $a$  and  $c$ , and the internal parameter  $u$ , describing a shift of the O<sup>2-</sup> anions about the Ti<sup>4+</sup> cation [22]. In the calculations of bulk properties a  $4 \times 4 \times 4$  mesh of Monkhorst–Pack special  $k$ -points was applied [23]. The dimensions of the unit cell determined:  $a = 4.639 \text{ \AA}$  (4.594  $\text{\AA}$ ),  $c = 2.976 \text{ \AA}$  (2.959  $\text{\AA}$ ), and  $u = 0.3048$  (0.306), agree well with the experimental data [22] given in parentheses.

The TiO<sub>2</sub>(110) surface is modelled by periodic slabs (figure 1) consisting of several (3–11) repeat units built of the O–Ti<sub>2</sub>O<sub>2</sub>–O trilayers, separated by a vacuum layer of  $\simeq 12.7 \text{ \AA}$  (10  $\text{\AA}$  with PAW potentials applied). Note that each repeat unit is charge neutral and has a zero dipole moment in the direction normal to the surface. A  $2 \times 4 \times 1$  mesh of  $k$ -points was used to sample the Brillouin zone of the  $1 \times 1$  surface unit cell of dimensions  $a\sqrt{2}$  and  $c$ , in the  $[\bar{1}10]$  and  $[001]$  directions, respectively. Gaussian smearing of 0.05 eV was applied to the Brillouin-zone integrations. During a structure optimization, the atoms were allowed to relax, either on one side of the slab or symmetrically on both sides, until the forces on unconstrained atoms were less than  $0.02 \text{ eV \AA}^{-1}$ . The electric field arising for asymmetric slab relaxations was compensated by a dipole correction [24].



**Figure 1.** (a) Side view of a three-trilayer slab representing the TiO<sub>2</sub>(110) surface. The dashed lines enclose a charge-neutral trilayer. (b) Top view showing the atoms of the two uppermost layers and a  $1 \times 1$  surface cell (dashed line).

In the calculations of surface energy for slabs, a standard method is to evaluate the slab formation energy by subtracting from the total energy of the slab the bulk energy per layer, that is obtained from a separate calculation. For an increased number of layers in the slab, the slab formation energy approaches surface energy  $\sigma$  (per unit cell). The latter is determined from the relationship

$$\sigma = \frac{1}{2}(E_n^{\text{slab}} - nE^{\text{bulk}}). \quad (1)$$

Here  $E_n^{\text{slab}}$  is the total energy of an  $n$ -layer slab and  $E^{\text{bulk}}$  is the bulk energy per layer of an infinite solid. The factor of one half takes into account the two surfaces of the slab. The surface energy calculated from (1) is very sensitive to the accuracy in determination of the bulk energy term [25, 26]. A small error in that term can make the calculated surface energies diverge linearly with increasing slab thickness. To avoid the divergence problem we have employed a method [27, 28] that makes use of equation (1) rewritten in the form

$$E_n^{\text{slab}} = 2\sigma + nE^{\text{bulk}}, \quad (2)$$

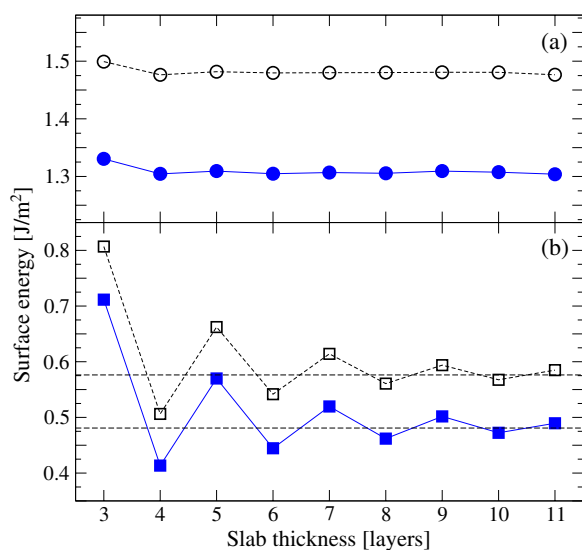
which implies that the bulk energy can be extracted from the slope of a linear fit of the slab's total energy plotted versus  $n$ . This value is subsequently used in equation (1).

### 3. Results

#### 3.1. Surface energy

The convergence of the surface energy of the unrelaxed slabs was checked for slabs built of three to eleven TiO<sub>2</sub> layers ( $L$ ). Using  $-53.6652$  eV for  $E^{\text{bulk}}$ , as determined from a linear fit (2) to the slab energies (by dropping the energy of a thinnest 3L slab), yields very well converged  $\sigma$ s (figure 2). Thus, the above value of  $E^{\text{bulk}}$  was adopted in all further calculations of  $\sigma$ .

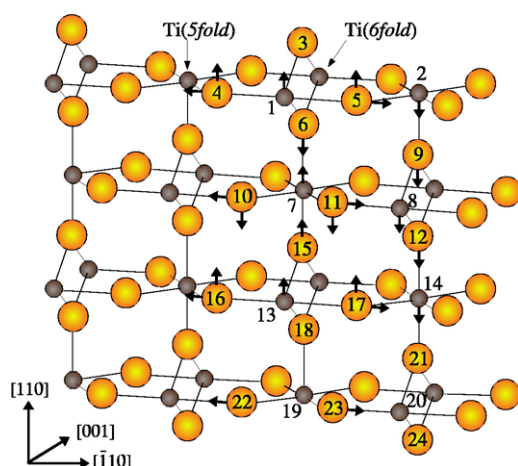
The surface energy of unrelaxed slabs calculated with GGA-PW91 (figure 2(a)) converges to  $1.48 \text{ J m}^{-2}$ , varying in the range  $1.477\text{--}1.482 \text{ J m}^{-2}$  (which gives the numerical uncertainty of  $\pm 0.3\%$ ). This is substantially less (13–17%) than the energy reported from previous plane wave pseudopotential calculations ( $1.71 \text{ J m}^{-2}$  [3], and  $1.78 \text{ J m}^{-2}$  [8]) for a 6L slab. This difference can be ascribed to different exchange–correlation functionals applied in this (GGA-PW91) and previous (LDA) works. This conjecture is supported by our calculations employing



**Figure 2.** Surface energy versus the number of layers in the slab calculated for unrelaxed (a) and fully relaxed slabs (b). The horizontal lines mark the converged surface energy. Open symbols, GGA-PW91; filled symbols, GGA-PBE.

PAW potentials and GGA-PBE, which again yield  $\sigma$  reduced by 12%, and equal to  $1.30 \text{ J m}^{-2}$  (figure 2(a)). It is also supported by the results of Lazzeri *et al* [8] who reported a much reduced  $\sigma$  ( $1.38 \text{ J m}^{-2}$ ) calculated for a 6L slab within GGA-PBE (see also [4]), and those of Lindan *et al* ( $1.43 \text{ J m}^{-2}$ , GGA-PW91, 3L slab [7]). Additionally, different pseudopotentials applied by those authors could also contribute to some part of the differences in  $\sigma$ , though, as demonstrated [31], the inclusion of the Ti semicore 3s and 3p states in the valence, does not change the total energies significantly. Therefore, any change in a quantity like the surface energy, which is determined by the total energy differences, is expected to be even smaller.

The surface energy of  $\text{TiO}_2(110)$  is very sensitive to the lattice relaxation. As one can see (figure 2), for the relaxed slabs the surface energy converges to  $0.57\text{--}0.58 \text{ J m}^{-2}$ , which means that it is greatly reduced (by 60%) compared to that for the unrelaxed case. These numbers are in line with the recent results obtained with the same code (GGA-PW91:  $0.56 \text{ J m}^{-2}$  [11]). Earlier calculations [3–9] gave substantially larger values of  $\sigma$ , falling in the ranges  $1.10 \text{ J m}^{-2}$  and  $0.83 \text{ J m}^{-2}$  (LDA, 3L and 6L slabs, respectively [3]),  $0.84 \text{ J m}^{-2}$  (LDA, 6L [8]),  $0.73 \text{ J m}^{-2}$  (GGA-PW91, 7L [6]),  $0.80 \text{ J m}^{-2}$  (GGA-PW91, 6L [9]),  $0.81 \text{ J m}^{-2}$  (GGA-PW91, 3L [7]);  $1.14 \text{ J m}^{-2}$ , and  $0.82\text{--}0.84 \text{ J m}^{-2}$  (3L, LDA, and GGA, respectively [4]),  $0.84 \text{ J m}^{-2}$  (GGA, 3L [5]), with the exception of a considerably lower value of  $0.31 \text{ J m}^{-2}$ , reported for a 6L slab calculation within GGA-PBE [8]. The empirical estimate of the surface energy is  $0.28\text{--}0.38 \text{ J m}^{-2}$  [29]. In most cases cited above the overestimation of the surface energy originates either from too thin slabs applied (compare figure 2(b)) or is due to a less adequate exchange–correlation energy functional applied. Our asymptotic surface energy ( $0.58 \text{ J m}^{-2}$ ), obtained from the well converged GGA-PW91 calculations, still almost doubles the experimental value. Comparative calculations performed by us, applying GGA-PBE for the exchange–correlation functional and PAW potentials [20], give surface energy values reduced by  $0.1 \text{ J m}^{-2}$ , and the asymptotic surface energy of  $0.47 \text{ J m}^{-2}$  (figure 2(b)). This, again, underlines a sensitivity of this system to the exchange–correlation functional applied, and shows that at least one half of the difference between calculated and measured surface energies



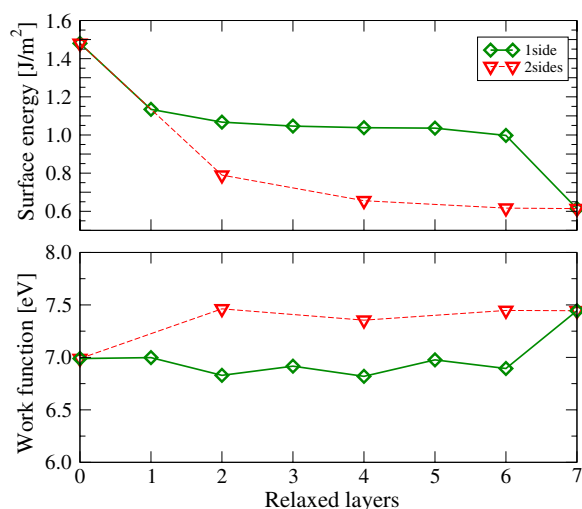
**Figure 3.** The directions of atomic displacements (calculated with respect to the average  $z$ -position of Ti atoms in a given layer) in upper layers of the seven-layer slab modelling the  $\text{TiO}_2(110)$ . An arrow is shown if the displacement is  $\geq 0.01$  Å. Small balls represent Ti and the large ones O atoms.

might be due to exchange–correlation effects. A verification of the experimental findings as regards the role of defects would be also desirable.

The results of figure 2(b) display the effect of nonequivalence of the relaxed odd and even layer slabs [3]. The surface energy exhibits damped oscillations versus number of layers, being larger for odd than for even layer slabs. Responsible for this are the displacements of titanium atoms together with the in-plane oxygens from the surface layers of a slab (figure 3) and the presence/absence of the mirror symmetry plane in the odd/even films. In the odd layer slabs the shifts of Ti atoms in the top and the bottom layers oppose each other. The atoms in the central layer remain almost in their bulk positions (only the in-plane O atoms move laterally by  $\pm 0.01$  Å). For even layer slabs the fivefold and sixfold coordinated Ti atoms (figure 3) from the top layer lie above the sixfold and fivefold titaniums from the bottom layer, respectively, so the displacements of atoms from the top and bottom layers do not balance each other. For an increased slab thickness, interactions between the atoms in the top and bottom layers become weaker which leads to a weaker buckling, and the oscillation in surface energy is reduced. As demonstrated in [10] this oscillatory convergence is connected with the change in the Ti 3d–O 2p interlayer hybridization along the direction normal to the surface.

Figure 2 shows that in order to get well converged surface energies, slabs of ten (or more) fully relaxed layers should be applied. Let us note that our data for surface energy follow the so-called 25% rule [11], which allows one to estimate the asymptotic surface energy from the average of the  $\sigma$  for the three- and four-layer slabs. Although this rule provides a reasonable guide to an asymptotic energetics of the clean  $\text{TiO}_2(110)$  surface its wider applicability should be treated with caution [30].

In order to examine in more detail the influence of relaxation on surface properties of the rutile (110) we performed a series of calculations for slabs consisting of differently relaxed layers. In the first case considered, only the layers on one side of the slab were relaxed (a dipole correction was used), while in the other, slabs were relaxed on both sides. In each case, the number of relaxed layers on the relaxed sides was increased by one. The results presented in figure 4 demonstrate that for the same number of relaxed layers, the two-sided relaxation significantly reduces (by  $0.27$ – $0.38$   $\text{J m}^{-2}$ ) the surface energy, compared to that



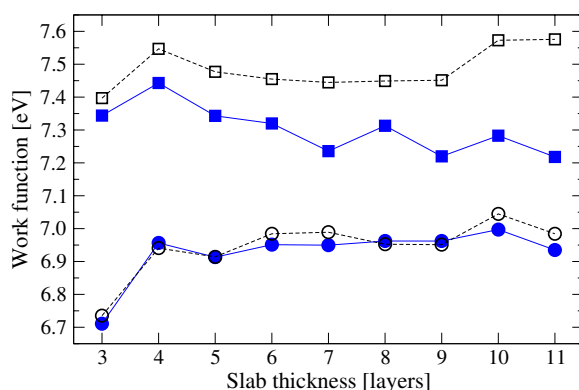
**Figure 4.** Calculated surface energy and work function versus the number of layers relaxed either on one side (diamonds) or on the two sides (triangles) of the seven-layer thick slab.

for the one-sided relaxed slab. The energy of the one-sided relaxed slabs changes very little ( $\simeq 0.06 \text{ J m}^{-2}$ ) if the number of relaxed layers is increased from two to six. The major part of the difference between the surface energies of the partially and completely relaxed slabs is compensated only by relaxing the positions of the atoms of the bottom layer (figure 4). It is clear that the largest effects on the surface energy are from the relaxations of the outermost layers on each side of the slab. Interestingly, for the one-sided relaxed slab, the surface energy plot (figure 4, diamonds) is inversely symmetric with respect to the slab centre. The same is observed also for thicker slabs of eight and eleven layers (and same relaxation mode). Thus, accurate determination of surface energy of the  $\text{TiO}_2(110)$  requires the slab to be fully relaxed. Consequently, calculations for the adsorption systems based on the results for partially (one-sided) relaxed slabs [32] may lead to an unrealistic energetics.

The surface energy formula (1) does not discriminate between relaxed and unrelaxed slabs, or between different modes of relaxation. The two-sided relaxation gives more reliable results, and already for four relaxed layers (two on each side), the surface energy differs by only  $\simeq 0.04 \text{ J m}^{-2}$  (7%) from that for an entirely relaxed slab (figure 4). In order to get the correct surface energies from the calculations for one-sided relaxed slabs, the relaxation energy has to be added to the  $\sigma$  for an unrelaxed surface. The latter is the total energy difference,  $\Delta E^{\text{rlx}} = E^{\text{rlx}} - E^0$ , of a slab with only a few outermost layers relaxed ( $E^{\text{rlx}}$ ) and an unrelaxed slab ( $E^0$ ). The energy difference is negative, and consequently, for a fully relaxed surface,  $\sigma$  can be calculated from the following formula:

$$\sigma = \sigma^0 + \Delta\sigma^{\text{rlx}}, \quad (3)$$

where  $\sigma^0$  is the converged surface energy for an unrelaxed slab, and  $\Delta\sigma^{\text{rlx}} = \Delta E^{\text{rlx}}/A$  ( $A$  being the area of surface unit cell). Using our results for a 7L slab (figure 4) one gets  $\Delta\sigma^{\text{rlx}} = -0.884 \text{ J m}^{-2}$  (when four layers are relaxed on one side). This gives the estimated surface energy equal to  $\simeq 0.60 \text{ J m}^{-2}$ , which agrees within 3.5% with the asymptotic result for a totally relaxed, the 11L slab (figure 2). A similar relation holds for the 8L and 11L slabs (again subtracting  $\Delta\sigma^{\text{rlx}}$  for the four relaxed layers). It means that equation (3) provides a simple way to estimate the surface energy of fully relaxed slabs from less computationally demanding



**Figure 5.** Work function variation with the thickness of unrelaxed (circles) and fully relaxed (squares) slabs. Open symbols, GGA-PW91; filled symbols, GGA-PBE.

results for the partially relaxed slabs. Such an estimation requires two calculations: one for an unrelaxed slab, yielding a converged value of  $\sigma^0$ , and another one with only four outer layers relaxed on one side.

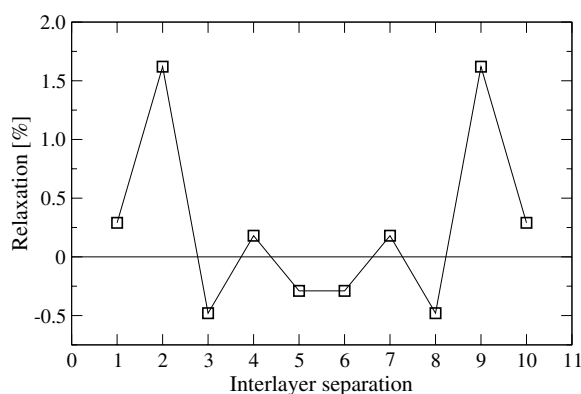
### 3.2. Work function

The work function is a very sensitive measure of the state of the oxide surface [2]. It can be defined as the difference between the electrostatic potential in a vacuum region and the Fermi energy of the slab. The calculated work functions for both frozen and relaxed slabs are presented in figure 5.

As can be seen, for the frozen slabs the work function converges to about 7.0 eV. For the entirely relaxed slabs a substantial (0.5–0.6 eV) increase of the work function is observed, to give 7.58 eV for the thickest slabs. The enhancement of the work function is due to the in-plane alignment of the negative O ions (see figure 3 and section 3.3), and a substantial increase in the dipole moment of the relaxed outer trilayer. Note that this increase is halved for the GGA-PBE, which again demonstrates a sensitivity of the relaxed system to the exchange–correlation effects. Interestingly, the difference between work function for the one- and two-sided relaxed slabs (figure 4) remains the same as that between the relaxed and unrelaxed slabs. However, relaxation of only one layer on each side sets the work function equal to the value corresponding to a completely relaxed slab. In contrast, the one-sided relaxation does not alter the work function until the last (second outer) layer is relaxed. Figure 4 illustrates this effect for a 7L slab, but a similar result is also observed for the thicker ones—both even and odd layer slabs. Thus, in order to determine the work function for the relaxed surface it is sufficient to relax only the outermost layers on two sides of the slab.

First principles calculations of the work function of TiO<sub>2</sub>(110) are rather rare. The full potential linearized augmented plane wave (FLAPW) calculations performed by Vogtenhuber *et al* for the relaxed 3L slabs (within the LDA) yielded 6.79 eV [12], 7.09 eV [13], and 7.16 eV [14]. The latter two numbers agree, within 0.30 eV, with the GGA-PW91 results of this work, and within 0.10 eV for GGA-PBE. A recent pseudopotential plane wave calculation [32], within the same (VASP) code, reported 6.90 eV, for a partially relaxed, 5L slab, in very good agreement with our results (figure 5). Much lower absolute values of 4.81 and 5.54 eV were reported for the relaxed and unrelaxed surface, respectively, from semiempirical tight binding calculations [33]. Note, however, that the difference between these two values is close to that





**Figure 6.** Relaxation of the interlayer spacing for the fully relaxed 11-layer slab, calculated with respect to the average  $z$ -position of all Ti atoms in a given layer.

resulting from figure 5. According to FLAPW calculations [12] the relaxation increased the work function by 0.13 eV only.

Most of the experimental estimates of the work function fall in the range 5.1–5.5 eV [2, 34, 35], i.e. they are approximately 2 eV lower than our results. The reason for this large difference is not quite clear. Following [14] we suspect that its main part originates from a significant concentration of oxygen vacancies at the surface of the sample. As reported in [14], changing the  $\text{Ti}_4\text{O}_8$  stoichiometry of the perfect surface layer to the  $\text{Ti}_4\text{O}_7$  results in the work function lowering of 2 eV. This view is supported by some other experimental STM data which report the work function of 6.83 eV (see a reference in [12]). Thus, our results for the unrelaxed  $\text{TiO}_2(110)$  slabs overestimate the experimental value by about 0.1 eV, and the relaxed ones by 0.4 eV. Speculating about the reasons for this remaining difference, which makes the results for the unrelaxed (or one-side relaxed)  $\text{TiO}_2(110)$  slabs closer to the experiment, one could imagine that for the macroscopic single crystals used in experiment, the other outer surface, on the opposite side of the slab, is not ‘felt’ by the surface investigated, and the sample could be considered as a supported, or fixed one. Thus, in view of our results for the one-sided relaxed slabs, the work function of such a supported sample will not alter upon relaxation.

### 3.3. Surface atomic structure

Figure 6 displays the relaxations,  $\Delta_{ij} = (d_{ij} - d)/d$ , of the distance  $d_{ij}$ , between the layers  $i$  and  $j = i + 1$  of the slab, calculated as a difference in the average  $z$ -position of all Ti atoms in subsequent layers ( $d$  is the bulk interplanar spacing). Relaxations vary in an oscillatory way, and the expansion of the second outer interlayer spacing is most significant. The relaxations are not particularly large but they have a meaningful effect on oscillations of the surface energy as a function of the slab thickness.

The displacements of individual atoms in a relaxed 7L slab, calculated with respect to the centre of gravity of the Ti atoms of each trilayer, are presented in table 1. They are compared to the two previous first principles calculations [6, 36], and the experimental data obtained with surface x-ray diffraction (SXR) [37], and quantitative low energy electron diffraction (LEED  $IV$ ) techniques [38].

The main displacements occur perpendicular to the surface. Only the in-plane oxygen atoms are subject to the lateral shifts (figure 3). For the odd layer slabs, the O(6) and fivefold Ti(2) relax inwards. The greatest relaxation is exhibited by the in-plane atoms: the sixfold Ti(1),

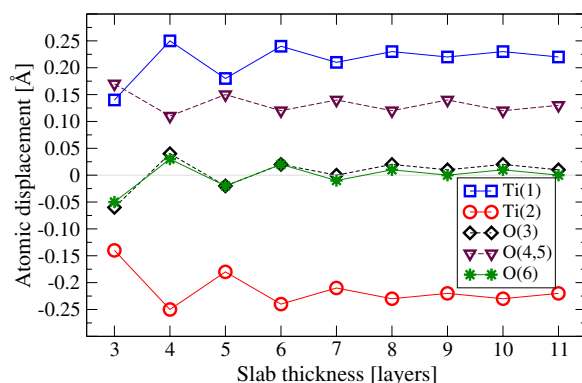
**Table 1.** Atomic displacements (in Å) along the [110] direction (and  $\bar{1}\bar{1}0$  where noted) calculated in this work for the relaxed seven-layer slab, and in selected first principles (plane wave pseudopotential (USPP) and full potential (FLAPW)) calculations, compared with the experimental data. The displacements are calculated with respect to the average  $z$ -position of all Ti atoms in a given layer. The wider line spacings separate atoms of different trilayers. The labels on atoms refer to those shown in figure 3.

Atom	Theory			Experiment	
	This work	USPP [6]	FLAPW [36]	SXRD [37]	LEED-IV [38]
Ti(1) (sixfold)	0.21	0.23	0.08	$0.12 \pm 0.05$	$0.25 \pm 0.03$
Ti(2) (fivefold)	-0.21	-0.11	-0.23	$-0.16 \pm 0.05$	$-0.19 \pm 0.03$
O(3) (bridging)	0.00	-0.02	-0.16	$-0.27 \pm 0.08$	$0.10 \pm 0.05$
O(4, 5)	0.14	0.18	0.09	$0.05 \pm 0.05$	$0.27 \pm 0.08$
O(4, 5) $\bar{1}\bar{1}0$	$\pm 0.05$	$\pm 0.05$	$\pm 0.06$	$\pm 0.16 \pm 0.08$	$\pm 0.17 \pm 0.15$
O(6)	-0.01	0.03	-0.09	$0.05 \pm 0.08$	$0.06 \pm 0.10$
Ti(7)	0.13	0.12	0.07	$0.07 \pm 0.04$	$0.14 \pm 0.05$
Ti(8)	-0.13	-0.06	-0.13	$-0.09 \pm 0.04$	$-0.09 \pm 0.07$
O(9)	-0.02	0.03	-0.05	$0.00 \pm 0.08$	$0.00 \pm 0.08$
O(10, 11)	-0.01	0.00	-0.04	$0.02 \pm 0.06$	$0.06 \pm 0.12$
O(10, 11) $\bar{1}\bar{1}0$	$\pm 0.02$	$\pm 0.02$	$\pm 0.03$	$\pm 0.07 \pm 0.06$	$\pm 0.07 \pm 0.18$
O(12)	-0.03	0.03	-0.04	$-0.09 \pm 0.08$	$0.00 \pm 0.17$
Ti(13)	0.06		0.02		
Ti(14)	-0.06		-0.08		
O(15)	0.02	0.00	-0.07	$-0.12 \pm 0.07$	$0.01 \pm 0.13$
O(16, 17)	0.01		-0.03		
O(16, 17) $\bar{1}\bar{1}0$	$\pm 0.01$		$\pm 0.02$		
O(18)	0.00		-0.02		

the fivefold Ti(2), and the O(4, 5). For titanium atoms our data are very close to the LEED measurements [38]. For O(4, 5) they are in between the SXRD [37] and LEED data [38]. A most controversial issue is the position of the bridging O(3). According to SXRD experiment [37] the O(3) should exhibit the largest (inward) shift of all atoms. In contrast, LEED measurements [38] predict an outward shift of medium size. Our calculations give zero shift for this atom, which is consistent with what was predicted by previous pseudopotential calculations [6]. The remaining atoms shift outwards with the largest displacement of sixfold Ti(1). The shifts of the topmost layer atoms versus the slab thickness of fully relaxed slabs are depicted in figure 7.

The displacements of atoms in deeper layers are still present, but their magnitude diminishes rapidly. Most of the atoms of every second layer shift in the same direction. In the slab centre, only the in-plane oxygens exhibit a small lateral shift (by up to  $\pm 0.01$  Å). With increasing number of optimized layers on two sides, the atomic displacements and the interlayer spacings converge rapidly to those for the entirely relaxed system. In the one-sided relaxation mode, starting from three relaxed layers, relaxation of an additional layer does not significantly change the atomic positions.

In general, the calculated atomic structure reproduces the experimental pattern [38] very well. It removes the discrepancy for the fivefold Ti(2), observed for previous pseudopotential calculations, compared both to SXRD and to LEED. A nearly zero, substantially weaker than experimentally measured [37] relaxation of the bridging oxygen is typical for all first principles calculations, and still remains under debate. It has been suggested that the discrepancy should be attributed to soft surface phonons [36]. This, however, has been questioned by the results



**Figure 7.** Displacements of the surface layer atoms along the [110] direction (calculated with respect to the average  $z$ -position of Ti atoms in a given layer) versus the thickness of relaxed slabs. The labelling of atoms refers to that adopted in figure 3.

of the molecular dynamics study [39], where it was shown that phonon contribution is very small, and in turn, the discrepancy was ascribed to asymmetric lateral relaxation of the bridging O(3). The latter effect was excluded from the experimental analysis [37] of the SXRD pattern. The most recent LEED  $IV$  experimental data [38] seem to clarify this point in favour of first principles calculations, providing a smaller and oppositely directed shift of the bridging O(3). It has been also shown that the soft surface phonons have no significant bearing on the LEED  $IV$  structure determination. These new data are found to be more consistent with some *ab initio* calculations [40]. On the other hand, though the new data are reducing the discrepancy for the positions of bridging O(3), they seem to produce another discrepancy (table 1), for the in-plane O(4, 5).

#### 4. Summary and conclusion

The geometric and electronic structure of stoichiometric rutile (110) have been re-examined. While we confirm that relaxation of atomic layers is a prerequisite for obtaining realistic surface energies we find that crucial for this is the relaxation of atoms in the two outermost surface layers. We find that the calculated surface energies and work functions are greatly affected by the surface relaxation mode and the exchange–correlation functional applied. This is of importance in accurate modelling of rutile  $\text{TiO}_2$  single crystal surfaces. We demonstrate that good estimates of asymptotic surface energies can be obtained from simpler calculations for the partially relaxed slabs. Our results show that in order to obtain reliable, well converged results for the energetic and structural properties of the clean rutile  $\text{TiO}_2(110)$ , fully relaxed slabs consisting of at least seven triple atomic layers are required.

#### Acknowledgments

This work was supported by the University of Wrocław, grant No 2016/IFD/04. Most of the calculations were performed on a computer cluster of the Institute of Experimental Physics, University of Wrocław. TP acknowledges with thanks support from the Foundation for Strategic Research of Sweden, through the Material Consortium—ATOMICS, during his two-month stay at the Chalmers University, Gothenburg, and allocation of computer time at the National Supercomputer Centre (Sweden) in an early stage of this project.

## References

- [1] Diebold U 2003 *Surf. Sci. Rep.* **48** 53
- [2] Henrich V E and Cox P A 1994 *The Surface Science of Metal Oxides* (Cambridge: Cambridge University Press)
- [3] Ramamoorthy M, Vanderbilt D and King-Smith R D 1994 *Phys. Rev. B* **49** 16721
- [4] Goniakowski J, Holender J M, Kantorovich L N, Gillan M J and White J A 1996 *Phys. Rev. B* **53** 957
- [5] Goniakowski J and Gillan M J 1996 *Surf. Sci.* **350** 145
- [6] Bates S P, Kresse G and Gillan M J 1997 *Surf. Sci.* **385** 386
- [7] Lindan P J D, Harrison N M, Gillan M J and White J A 1997 *Phys. Rev. B* **55** 15919
- [8] Lazzeri M, Vittadini A and Selloni A 2001 *Phys. Rev. B* **63** 155409
- Lazzeri M, Vittadini A and Selloni A 2002 *Phys. Rev. B* **65** 119901 (erratum)
- [9] Elliott S D and Bates S P 2003 *Phys. Rev. B* **67** 035421
- [10] Bredow T, Giordano L, Cinquini F and Pacchioni G 2004 *Phys. Rev. B* **70** 035419
- [11] Harris L A and Quong A A 2004 *Phys. Rev. Lett.* **93** 086105
- [12] Vogtenhuber D, Podloucky R, Neckel A, Steinemann S G and Freeman A J 1994 *Phys. Rev. B* **49** 2099
- [13] Vogtenhuber D, Podloucky R and Redinger J 2000 *Surf. Sci.* **454–456** 369
- [14] Vogtenhuber D, Podloucky R, Redinger J, Hebenstreit E L D, Hebenstreit W and Diebold U 2002 *Phys. Rev. B* **65** 125411
- [15] Kresse G and Hafner J 1993 *Phys. Rev. B* **47** 558
- Kresse G and Hafner J 1994 *Phys. Rev. B* **49** 14251
- [16] Kresse G and Furthmüller J 1996 *Phys. Rev. B* **54** 11169
- Kresse G and Furthmüller J 1996 *Comput. Mater. Sci.* **6** 15
- [17] Perdew J P, Chevary J A, Vosko S H, Jackson K A, Pederson M R, Singh D J and Fiolhais C 1992 *Phys. Rev. B* **46** 6671
- [18] Vanderbilt D 1990 *Phys. Rev. B* **41** 7892
- [19] Kresse G and Hafner J 1994 *J. Phys.: Condens. Matter* **6** 8245
- [20] Kresse G and Joubert D 1999 *Phys. Rev. B* **59** 1758
- [21] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
- [22] Grant F A 1959 *Rev. Mod. Phys.* **31** 646
- [23] Monkhorst H J and Pack J D 1976 *Phys. Rev. B* **13** 5188
- [24] Neugebauer J and Scheffler M 1992 *Phys. Rev. B* **46** 16067
- [25] Boettger J C 1994 *Phys. Rev. B* **49** 16798
- [26] Fiorentini V and Methfessel M 1996 *J. Phys.: Condens. Matter* **8** 6525
- [27] Boettger J C 1996 *Phys. Rev. B* **53** 13133
- [28] Gay J G, Smith J R, Richter R, Arlinghaus F J and Wagoner R H 1984 *J. Vac. Sci. Technol. A* **2** 931
- [29] Overbury S H, Bertrand P A and Somorjai G A 1975 *Chem. Rev.* **75** 547
- [30] Lindan P J D and Zhang C 2005 *Phys. Rev. Lett.* **95** 029601
- [31] Harris L A and Quong A A 2005 *Phys. Rev. Lett.* **95** 029602
- [32] Gomes J R B and Prates Ramalho J P 2005 *Phys. Rev. B* **71** 235421
- [33] Schelling P K, Yu N and Halley J W 1998 *Phys. Rev. B* **58** 1279
- [34] Schierbaum K D, Fisher S, Torquemada M C, de Segovia J L, Román E and Martin-Gago J A 1996 *Surf. Sci.* **345** 261
- [35] Ostermann D, Walther G and Schierbaum K D 2005 *Phys. Rev. B* **71** 235416
- [36] Harrison N M, Wang X G, Muscat J and Scheffler M 1994 *Faraday Discuss.* **114** 305
- [37] Charlton G, Hoowes P B, Nicklin C L, Steadman P, Taylor J S G, Muryn C A, Harte S P, Mercer J, McGrath R, Norman D, Turner T S and Thornton G 1997 *Phys. Rev. Lett.* **78** 495
- [38] Lindsay R, Wander A, Ernst A, Montanari B, Thornton G and Harrison N M 2005 *Phys. Rev. Lett.* **94** 246102
- [39] Langel W 2002 *Surf. Sci.* **496** 41
- [40] Swamy V, Muscat J, Gale J D and Harrison N M 2002 *Surf. Sci.* **504** 115