The Journal of Chemical Physics

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Cite as: J. Chem. Phys. **121**, 7427 (2004); https://doi.org/10.1063/1.1796253
Submitted: 09 June 2004 . Accepted: 29 July 2004 . Published Online: 01 October 2004

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AIP Publishing

J. Chem. Phys. **121**, 7427 (2004); https://doi.org/10.1063/1.1796253 **121**, 7427

JOURNAL OF CHEMICAL PHYSICS VOLUME 121, NUMBER 15 15 OCTOBER 2004

Oxygen vacancies on TiO_2 (110) from first principles calculations

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(Received 9 June 2004; accepted 29 July 2004)

We have carried out a systematic study of oxygen vacancy formation on the TiO_2 (110) surface by means of plane-wave pseudopotential density-functional theory calculations. We have used models with the mean number of vacancies per surface unit cell being $\theta=0.25$ and $\theta=0.5$. The study comprises several kind of vacancies within the outermost layers of the surface. The use of a suitable set of technical parameter is often essential in order to get accurate results. We find that the presence of bridging vacancies is energetically favored in accordance to experimental data, although the formation of sub-bridging vacancies might be possible at moderate temperatures. Surprisingly, the spin state of the vacancy has little influence on the results. Atomic displacements are also analyzed and found to be strongly dependent on the particular arrangement of vacancies. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1796253]

I. INTRODUCTION

There has been an increasing effort in studying transition metal oxides during the last decade because of their broad technological applicability.[1] Among these systems, titanium dioxide has been one of the most investigated compounds. There are two important structures of TiO_2, anatase and rutile.[2]

Rutile has been extensively characterized both experimentally[1–4] and theoretically.[1,5–19] Among the different low index surfaces, the (110) is the most stable and also the most studied.[2] This surface is readily and reproducibly prepared so it has been considered a prototype of an oxide surface.[1] Its structure can be described as formed by neutral layers. Each layer is made of three planes of composition O-Ti_2O_2-O. For instance, in Fig. 1 a three-layer TiO_2 (110) slab is shown. In the surface, there are two kinds of titanium atoms, fivefold and sixfold coordinated, forming alternating rows. All oxygen atoms are threefold coordinated as in the bulk except those ones in the outermost plane called bridging atoms, which lose one bond when the upper layer is removed.

The bridging oxygen atoms have attracted an enormous interest because they can be easily removed by thermal annealing leading to point defects that alterate the chemical properties of the surface.[1,2] Scanning tunneling microscopy (STM) measurements quantify as 7%–10% the ratio vacancies/oxygen atoms when annealing at 900 K.[20–22]

The vast amount of experimental data has become a challenge to theorists who have extensively studied the surface. However, the results are often in discrepancy, and are difficult to compare because of the variety of methods and technical conditions. The periodic density functional theory (DFT) method with pseudopotentials and plane waves have been used successfully to model oxide surfaces in recent years.[5–10,12–15,17,18,23] We have made use of it throughout this study.

One of the main aims of the present work is to get a deeper insight into the energetics of oxygen vacancy formation and also into the structure of the relaxed defective surfaces. In addition, we have tested the influence of some important technical parameters on the results. We shall show that the set of conditions used in a calculation may be crucial in order to get meaningful results. Despite the fact that creation of bridging vacancies has already been studied with different methods and models,[6–14] there is little information about other type of vacancies. In order to investigate several kind of vacancies we have removed diverse oxygen atoms, which are named in Fig. 1. As a consequence of this systematic study we shall establish some rules that could assist in the process of choosing models to represent defective surfaces.

The rest of the paper is organized as follows. In the second section we describe some technical details about the methodology applied. In the third section we discuss our results. We start with some preliminary calculations on the bulk and the stoichiometric surface and follow with an analysis of how the choice of a surface model and a set of parameters affect the energetics of formation of defective surfaces. Finally, we discuss the structure of relaxed surfaces. In the fourth section we establish the conclusions from our work.

II. TECHNICAL METHODS

In the present work we use the implementation of DFT with pseudopotentials and plane waves.[24] We use the generalized gradient approximation (GGA) for the exchange-correlation energy, which seems to describe better the formation and creation of bonds on surfaces.[25] We use the GGA due to Perdew *et al.*[26,27]

The calculations were performed with the VASP (Vienna *ab initio* simulation package) code.[28–31] This is a particularly efficient and stable code, which searches for the self-consistent ground state using residual minimization and charge mixing. As in all pseudopotential plane-wave codes, the forces on the atoms are automatically calculated, and

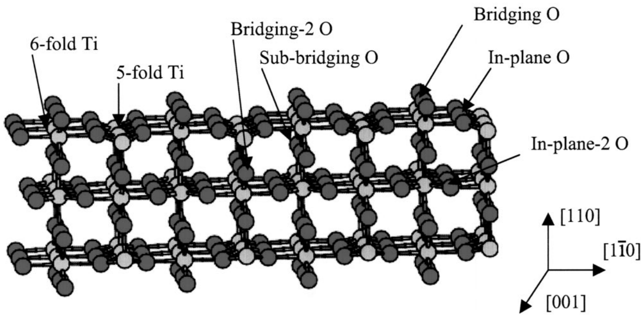


FIG. 1. Three layer slab to model a stoichiometric TiO_2 (110) surface. Several kind of vacancies discussed in the text are labeled.

relaxation of all atoms in the system to their equilibrium position is also automatic.

In pseudopotential calculations, we must decide which states are treated as core states and which as valence states. For oxygen, the core consists only of $1s$ states whereas for Ti, up to and including the $3p$ shells are frozen and the reference state for pseudopotential generation is s^1d^3. We used the standard ultrasoft pseudopotentials included in the VASP package.[32]

III. RESULTS

A. Preliminary tests: bulk and stoichiometric surfaces

In order to analyze some technical details, a set of preliminary calculations have been performed. First, we made energy convergence tests for the TiO_2 bulk with energy cutoffs up to 495 eV. For k-point sampling, we used the Monkhorst-Pack scheme[33] with sets of several sizes. We concluded that an energy cutoff of 396 eV and a 4×4×4 k point set including the Γ point are enough to get energy convergence within 0.002 eV/atom. The optimized lattice parameters are $a=4.616$ Å, $c=2.974$ Å, and $u=0.304$, which compares well with the experimental ones [$a=4.594$ Å, $c=2.959$ Å, and $u=0.305$ (Ref. 34)] and previous theoretical work.[5] The calculated a and c values have been used for the (110) surface throughout the present work.

In order to do calculations on the rutile surface we use the traditional approach, that is, to employ a cell that includes a portion of vacuum, and replicate it in the three directions of space, so an array of slabs separated by vacuum is created. We must ensure that the slab thickness and the vacuum width are wide enough to obtain meaningful results. We have checked that using a vacuum width of 5 Å absolute energy values are converged within 0.001 eV/atom that is precise enough for the present work. The influence of slab thickness on the results is more critical.

The surface energy [defined in the usual way (Refs. 5 and 23)] versus the number of layers is plotted in Fig. 2 for a (1×1) model in the singlet state. The converged surface energy is about 0.5 J/m^2 that is in agreement with previous reported values for calculations using GGA.[5,14] We can see that the surface energy does not converge until a considerable number of layers is used. There is also an oscillating odd-even behavior that has been noted previously.[5,15] The surface energy for slabs with an odd number of layers is higher because they have an additional symmetry plane at the slab center (i.e., in Fig. 1) so the atomic displacements on both sides of the slab are mirrored and tend to reinforce each other. As a consequence, the energy for the slab increases and the relaxation energy decreases. As we increase the number of layers, the interaction between both sides of the slab become weaker and the surface energy converge to a limit value, although the convergence rate is faster for slabs with an even number of layers. For comparison purposes we have included in Fig. 2 average values between odd and even number of layers (i.e., 3.5 layers is a mean value between 3 and 4 layer surface energies). It is quite evident from these numbers that the average values converge much faster and all the values from 4.5 layers are converged within 0.05 J/m^2. We will show that the same behavior is observed for the vacancy energy formation.

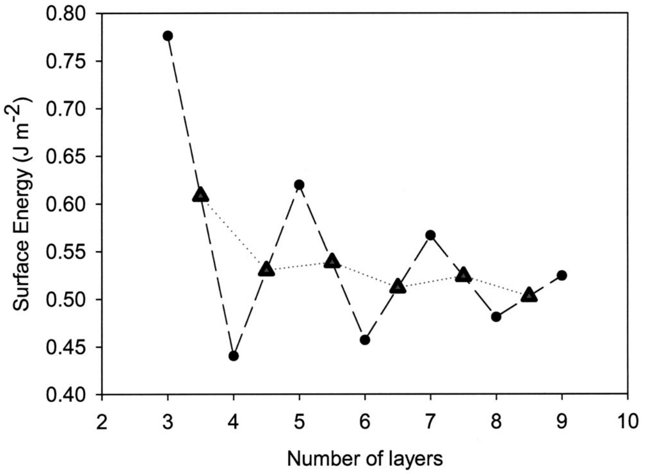
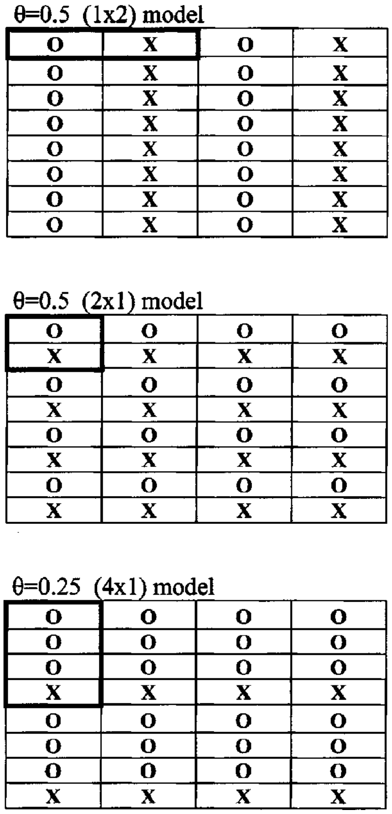


FIG. 2. Surface energy vs number of layers in the slab for a (1×1) model in the singlet state. Energies from direct calculations are shown with circles and the average energy between slabs with odd and even number of layers are shown with triangles.

B. Energetics of vacancy formation

The main aim of this work is to study vacancy formation energies for rutile surfaces. When we create a vacancy on a surface we break the surface symmetry and, depending on the vacancy coverage, different arrangements of vacancies are possible. It is expected that the interactions among vacancies will be stronger when the vacancy density is high. We have made calculations for several vacancy concentrations and different arrangements of vacancies (see Fig. 3). We should keep in mind that in experimental conditions the vacancy concentration is usually low [less than 10% (Ref. 20)]. Therefore, in order to do suitable comparisons we should use prohibitive large unit cells. In our work we have considered two different vacancy concentrations $\theta=0.5$ and $\theta=0.25$, where θ is the mean number of vacancies per surface unit cell. For $\theta=0.5$ we have used two arrangements, named (1×2) and (2×1) models. The unit cell we use in the calculations is made of several primitive surface unit cells: the first digit (i.e., 1×2) represents the number of primitive surface unit cells, of size $c\times\sqrt{2}a$, in the (001) direction and the second digit represents the number of primitive unit cells



θ=0.5 (1x2) model

O	X	O	X
O	X	O	X
O	X	O	X
O	X	O	X
O	X	O	X
O	X	O	X
O	X	O	X
O	X	O	X

θ=0.5 (2x1) model

O	O	O	O
X	X	X	X
O	O	O	O
X	X	X	X
O	O	O	O
X	X	X	X
O	O	O	O
X	X	X	X

θ=0.25 (4x1) model

O	O	O	O
O	O	O	O
O	O	O	O
X	X	X	X
O	O	O	O
O	O	O	O
O	O	O	O
X	X	X	X

FIG. 3. Schematic chart that shows the models we use in the present work, with the nomenclature used in the text. The unit cell, that is made of two or more primitive surface unit cells, is remarked in bold lines. Primitive surface unit cells that contain defects are represented by crosses and stoichiometric ones by circles.

in the $(1\bar{1}0)$ direction. The largest unit cell used in this study is a (4×1) model that corresponds to $\theta=0.25$ and contains vacancies separated by ~6 Å. The energy from this calculation constitutes our best approximation to the formation energy of an isolated vacancy.

It has been established experimentally[1,20–22] that bridging vacancies (i.e., removing bridging oxygen atoms) are the most stable. However, comparisons among earlier theoretical reports, even using the same periodic DFT schemes, are difficult because there are a considerable number of technical parameters to set up such as *k*-point sampling, energy cutoff, vacuum width, slab thickness, cell shape, vacancy concentration, vacancy arrangement, spin polarization, etc. We can easily cope with the first three, however, the influence of the rest of the parameters is more subtle and has been analyzed in detail in this work.

An additional choice to set up when creating vacancies is to remove the atom from only one of the slab sides or from both of them. Although both alternative ways should converge to the same result at an infinite slab thickness, due to the limited slab size of our models some discrepancies may occur. We have chosen the first option because the creation of a couple of vacancies may introduce some difficulties in the electronic convergence to triplet states. We have made some tests and checked that this particular choice leads to small differences in vacancy formation energies that become smaller than 0.1 eV for slabs thicker than four layers.

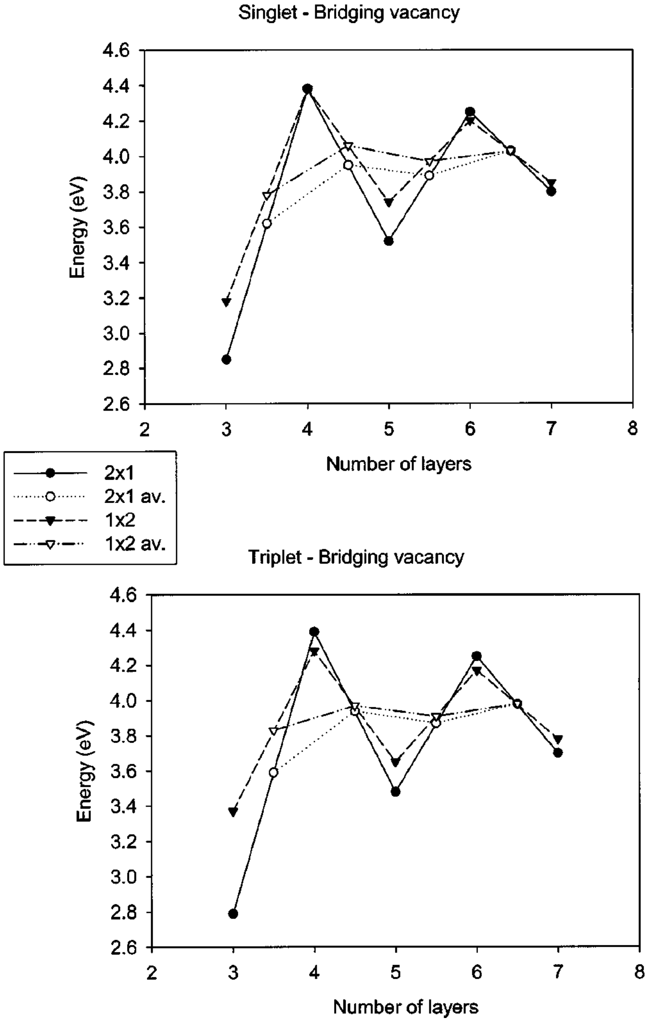


FIG. 4. Vacancy formation energy for bridging vacancies versus the number of layers. Results for the (1×2) and (2×1) models in their singlet and triplet states are included.

The vacancy formation energy is defined as the energy required to remove an oxygen atom from the surface and to create molecular oxygen in the gas phase,

$$E_{vac}=E_{\mathrm{Ti}_n\mathrm{O}_{2n-1}}+\tfrac{1}{2}E_{\mathrm{O}_2}-E_{\mathrm{Ti}_n\mathrm{O}_{2n}},$$

where $E_{\mathrm{Ti}_n\mathrm{O}_{2n-1}}$ and $E_{\mathrm{Ti}_n\mathrm{O}_{2n}}$ are the total energies of the defective and stoichiometric slabs, respectively, and E_{O_2} is the total energy of an isolated O_2 molecule in its ground triplet state. We should emphasize that in order to get meaningful results we have made calculations of $E_{\mathrm{Ti}_n\mathrm{O}_{2n-1}}$ and $E_{\mathrm{Ti}_n\mathrm{O}_{2n}}$ in exactly the same technical conditions in order to get an effective cancellation of errors.

In Fig. 4 we have plotted the vacancy formation energy for bridging vacancies in their spin polarized singlet and triplet states for $\theta=0.50$. From the figure we can draw some conclusions. First of all, the energy shows an oscillating behavior with the number of layers as we have noticed earlier. This effect could originate an important disagreement, even higher than 1 eV, between energies taken from calculations made with thin slabs (i.e., three or less layers) and those with slabs that are thick enough. The vacancy formation energy increases (decreases) for slabs with an odd (even) number of

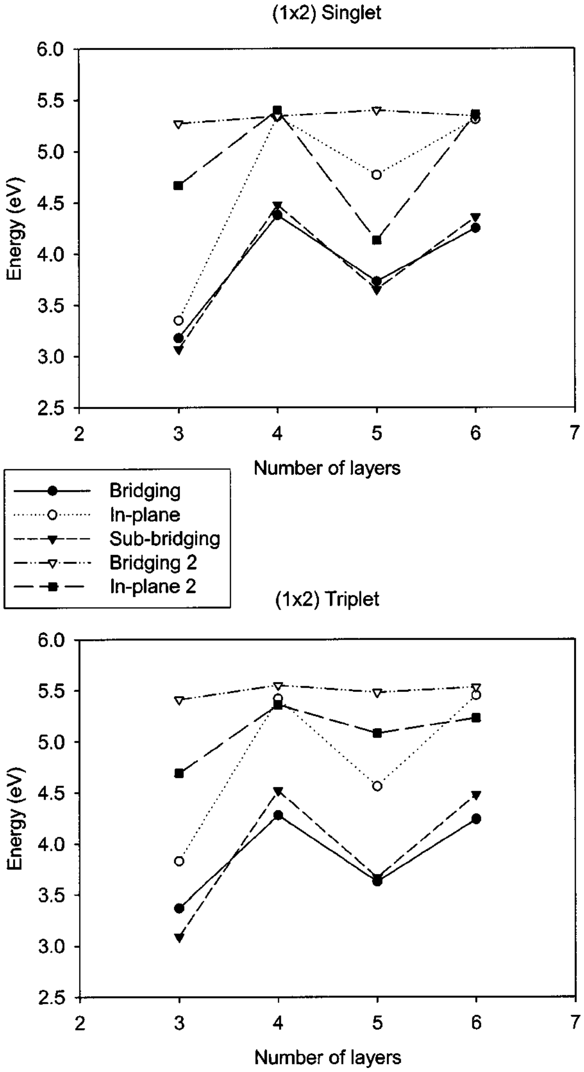


FIG. 5. Vacancy formation energy for several kind of vacancies vs the number of layers. Results for the (1×2) model in its singlet and triplet states are shown.

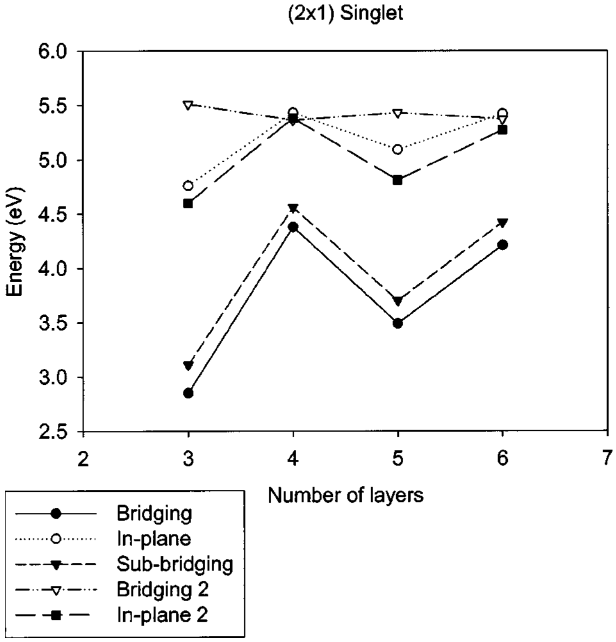


FIG. 6. Vacancy formation energy for several kind of vacancies vs the number of layers. Results for the (2×1) model in its singlet state are shown.

layers and a full convergence can only be reached for slabs with a considerable number of layers. It is worth noticing, as we mentioned above, that the average values converge rapidly, and only the energy for 3.5 layers is slightly lower than the converged number. From these results we suggest the use of averaged values higher than 4.5 layers to obtain representative energy values.

Second, energies are remarkably independent from the spin state. In an earlier study Lindan *et al.* found a significant difference in energy vacancy formation between singlet and triplet states.[9] However, the same author has recently claimed that they used a nonadequate pseudopotential which led to unrealistic results.[13]

Third, the formation energy is not sensitive to the two different arrangements considered. Our results show a small energy difference (<0.2 eV) between the (2×1) and (1×2) reconstructions that agrees well with previous theoretical works.[7,9] This might be an indication of a weak interaction among vacancies.

One aspect that has usually been neglected in previous calculations is a systematic study of the formation of different kind of vacancies compared to the bridging ones. We have extended our models to explore this possibility and considered the creation of vacancies within the outermost layers (see Fig. 1 for vacancy identification). In Fig. 5 we show vacancy formation energies versus number of layers. We have considered an (1×2) arrangement for two different spin states. From the figure, we first notice the same oscillating behavior for models with odd/even number of layers and a slow convergence, in particular, for vacancies in the outermost layers (i.e., bridging, in-plane and sub-bridging vacancies). This fact is a clear warning that one should be cautious when deriving conclusions from single model calculations (i.e., in-plane vacancies are almost as stable as bridging vacancies for three layer slabs). In any case, it is clear from the converged energy values that it is easier to remove oxygen atoms from the first layer and, among the atoms in the same layer, the less demanding process is to create bridging and sub-bridging vacancies. This is in disagreement with results from[7,12] that concluded that an in-plane vacancy in the second layer could be approximately as stable as a bridging one. However, this conclusion was indirectly drawn from calculations with four-layer slabs, partially relaxed, and/or in the presence of adsorbed molecules. It may be possible that the

TABLE I. Vacancy formation energy for $\theta=0.25$ using a (4×1) model. Calculations were performed for four- and five-layer slabs in the singlet state for several kind of vacancies: bridging, sub-bridging, in plane within the first layer, and bridging and in plane in the second layer. (see Fig. 1 for nomenclature).

No. layers	Bridging	In-plane	Sub-bridging	Bridg2	In2
4	3.77	5.14	4.16	5.32	4.93
5	2.36	4.69	2.94	5.40	4.23
4.5	3.07	4.92	3.55	5.36	4.58

TABLE II. Ionic displacements in defective surfaces with bridging vacancies. Calculations were performed for four- and five-layer slabs in the singlet state. The displacements are computed as a difference in *z* coordinate respect to the equivalent ions in the relaxed stoichiometric surface. Only displacement for some selected ions are included (see text).

	(1×2)		(2×1)		(4×1)	
Atom	Four layers	Five layers	Four layers	Five layers	Four layers	Five layers
Ti	−0.52	−0.47	−0.28	−0.20	−0.37	−0.31
O in plane	+0.24	+0.26	+0.11	+0.16	+0.04	+0.08
O sub-bridging	−0.16	−0.09	+0.11	+0.32	+0.02	+0.07

presence of adsorbates could alter the relative stability of vacancies. It can also be seen that plots look very similar for both spin states as noted before.

In Fig. 6, we have included graphs for a (2×1) model in the singlet state (results for triplet states are similar and are not shown). The numbers and behavior are comparable to the (1×2) model although the energy fluctuations for in-plane oxygen atoms are smaller.

In addition, we have performed calculations at a lower vacancy density (i.e., $\theta=0.25$) using a (4×1) model. Table I reports the energy values for this model using four- and five-layer slabs in the singlet state. We have also included average values that we think are more representative for comparisons. We did additional calculations in some selected cases and checked that results for triplet states are again quite similar to those presented here. We recall that these values represent our best effort to reproduce experimental findings. The vacancy formation energy values (≈ 3 eV) are higher than those found for the (110) surface in $SnO_2(\approx 2.3\,\mathrm{eV})$.[23] This is expected since it has been determined experimentally that the oxygen vacancy density is considerably higher in SnO_2 than in TiO_2 (Ref. 35) what implies that the Ti-O bonds are stronger than the Sn-O bonds.

We must notice that the energy to create a sub-bridging vacancy is surprisingly similar to the energy of a bridging vacancy, and the stability is even reversed for a three layers model. We estimate the energy difference between the two kinds of vacancies to be about 0.1–0.2 eV for $\theta=0.5$ and the gap increases to about 0.4−0.5 eV for $\theta=0.25$. In experimental conditions, vacancy formation is stimulated by annealing at temperatures higher than 1000 K, followed by cooling to room temperature for measurements. Preliminary calculations[36] show that transitions barriers are low enough to allow vacancy transformations between bridging and sub-bridging vacancies at typical annealing temperatures. We speculate that if a thermodynamic equilibrium is reached at such temperatures, the distribution of vacancies would follow a Boltzmann distribution, and would be maintained at room temperature, where transitions are not further possible. In that case, we estimate the proportion of sub-bridging vacancies to be about 1%. To the best of our knowledge there is no positive experimental identification of subbridging vacancies. However, this fact might be related to the low vacancy density and/or a similarity with the properties of the bridging vacancies.

C. Defective surface relaxation

We have also analyzed the ionic displacements in the defective surfaces for the relaxed structures. Tables II and III report the displacements computed as a difference in *z* coordinate respect to the equivalent ions in the relaxed stoichiometric surface, and includes values taken for several models. Positive values indicate that atoms move outwards and negative values correspond to inward relaxation. We have only considered the bridging and the sub-bridging vacancies since, as we discussed above, are the most stable and the only ones that might be experimentally observed.

A. Bridging vacancy

When a bridging oxygen atom is removed, the Ti atom which was previously bonded to it moves inwards in order to increase its coordination number and the oxygen atoms in plane relax outwards. We find the same general trend using any model, but different displacements of the sub-bridging oxygen atoms, which move downwards in (1×2) and upwards in (2×1) and (4×1). This discrepancy is not surprising because as can be seen from Fig. 3 the vacancy arrangement in the (1×2) model, is drastically distinct including alternating whole rows of vacancies. This arrangement represents

TABLE III. Ionic displacements in defective surfaces with sub-bridging vacancies. Calculations were performed for four- and five-layer slabs in the singlet state. The displacements are computed as a difference in *z* coordinate respect to the equivalent ions in the relaxed stoichiometric surface. Only displacement for some selected ions are included (see text).

	(1×2)		(2×1)		(4×1)	
Atom	Four layers	Five layers	Four layers	Five layers	Four layers	Five layers
Ti	+0.75	+0.97	+0.18	+0.23	+0.09	+0.10
Ti second layer	−0.52	−0.43	−0.50	−0.38	−0.40	−0.43
O bridging	+0.68	+0.91	−0.08	−0.08	−0.31	−0.36
O in plane	+0.03	+0.12	+0.02	+0.06	0.00	+0.01

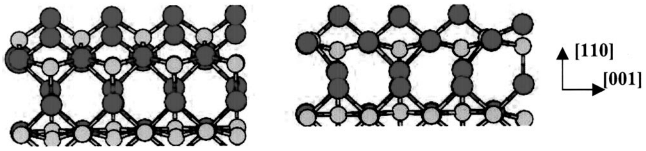


FIG. 7. Sideviews of relaxed sub-bridging oxygen defective surfaces using (a) (1×2) and (b) (4×1) models.

quite an unrealistic model of real surfaces since the low density of vacancies on them makes rather improbable such a vacancy alignment.

Absolute numbers are similar for the (2×1) and (4×1) models. However, at θ=0.25, the Ti atoms move inwards more significantly than at θ=0.5, while the in-plane and subbridging O atoms move out more appreciably at θ=0.5. In general, at a lower vacancy concentration we have got a less strained surface and the relaxation is mainly restricted to the vacancy surroundings.

B. Sub-bridging vacancy

The removal of an oxygen atom from the surface can modify more or less strongly the positions of the neighboring atoms depending on the model used. This is particularly seen when creating a sub-bridging vacancy. In Table III we show the ionic displacements for several models. For (1×2) model the ionic displacements are significantly different from those for the other models. Figure 7 shows a view of the relaxed surface using (1×2) and (4×1) models. In the (1×2) model both the Ti atom row and the bridging oxygen row relax moving out above the missing sub-bridging O atoms. However, in (4×1) model the surface is stabilized when bridging O atoms relax inwards. Thus, the Ti atom above the vacancy is seen to relax outwards by 0.97 Å in (1×2) but only 0.23 Å in (2×1) and 0.10 Å in (4×1). Furthermore, the O bridging bonded to that Ti moves out by 0.91 Å, while, it moves inwards for the other models [0.08 Å in (2×1) and 0.36 Å in (4×1)].

These results show that one has to be cautious when choosing limited models in order to mimic defective surfaces, not only because we cannot computationally afford a low vacancy density but also because results could be strongly dependent on the particular arrangement of vacancies.

IV. CONCLUSIONS

In the present work we have carried out a systematic study of oxygen vacancy formation on the TiO_2 (110) surface by means of plane-wave pseudopotential density functional theory calculations. We have focused in comparing the formation energy of several kind of vacancies in the outermost layers of the surface and analyzing the influence that different technical parameters and model size could make on the results.

We have noticed that energies that are based on slab calculations show an oscillating behavior with the number of layers, therefore it is recommended to use average values between slabs with odd and even number of layers. In particular, energies are almost converged when using average values higher than 4.5. Energies from calculations with three-layer slabs could contain errors as high as 1 eV.

We have performed calculations with several arrangements of vacancies. We have not found significant differences between singlet and triplet states. Furthermore, the formation energies for (1×2) and (2×1) models are similar, which could imply a weak interaction among vacancies.

Among the several vacancies we have tested, we find that the most stable is the bridging vacancy that agrees with experimental data. However, the formation of subbridging vacancies might be possible at moderate temperatures.

Regarding atomic displacements caused by surface relaxations, we find that one has to be specially cautious when deriving conclusions. For example, a (1×2) model reproduces well the formation energy of a bridging vacancy but could lead to quite an unrealistic structure of the reduced surface. Since surface stress is a long range effect, in order to reproduce realistic displacements around a vacancy, the use of very large unit cells might be necessary.

ACKNOWLEDGMENT

This work was funded by the Spanish DGESIC, Project No. MAT2002-576.

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