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Electronic properties of rutile TiO_2 ultrathin films: Odd-even oscillations with the number of layers

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The dependence of the surface properties of thin rutile $TiO_2(110)$ films on the number of layers in two-dimensional slab models has been investigated with first-principles methods based on density-functional theory. A pronounced oscillation of the interlayer distances, surface and adhesion energies, and electronic structure as a function of the number of layers has been found. The effect can be explained by surface-induced hybridization of Ti 3*d* and O 2*p* orbitals among the layers. This leads to reinforced interactions between the first and second layers and to weaker bonding and longer distances between the second and third layers of the films. By removing the 3*d* orbitals from the Ti basis set we found that TiO_2 behaves almost exactly as the isostructural $SnO_2(110)$ surface. The results are of importance for the properties of epitaxial ultrathin films grown on metal substrates as well as for single crystal surfaces.

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I. INTRODUCTION

Titanium dioxide is an important material for heterogeneous catalysis, and is widely used as a model system in the surface science of oxides either in the form of single crystals or of supported films on metal substrates.[1,2] Thin oxide films epitaxially grown on metal substrates are attracting an increasing interest because of their similarity to single crystal surfaces and of the possibility to tune their properties as function of the defectivity of the surface or of the thickness of the films. The scope of the present study is to analyze the electronic and energetic properties of TiO_2 rutile thin films as a function of film thickness. Experimental information is available only for the atomic structure of rutile (110) for the atomic positions in the first two layers.[3]

Previous theoretical studies showed a slow convergence of the adsorption and other surface properties with the number of layers in rutile (110) films.[4–7] Oscillations of the surface energy and vacancy formation energies have been observed as a function of film thickness. A similar trend was observed for the addition of TiO_2 rows in a study of the rutile (110) 1×2 reconstruction.[8] On the other hand, no such oscillation occurs in the case of the rutile (100) surface.[9] For the isostructural nontransition metal oxide $SnO_2(110)$ surface a much less pronounced dependence of calculated surface properties on the number of layers was observed.[10,11] Here we provide new insight and we show that ultrathin TiO_2 layers exhibit a significantly different behavior depending on their composition, in particular on the odd or even number of TiO_2 layers in the film.

The rutile (110) surface was modeled with the band structure approach using periodic boundary conditions. Two complementary methods were employed in order to better control the dependence of the results on the technical aspects of the calculations. One approach is based on localized atomic orbital basis sets (CRYSTAL03[12]) and the other one uses plane waves (VASP[13,14]). The general trends are the same within the two approaches although small quantitative differences have been found for some of the properties considered.

II. SURFACE MODELS AND METHODS

A. Models of rutile thin films

TiO_2 rutile films with (110) orientation which contain up to 10 TiO_2 layers (30 atomic layers; Fig. 1) have been studied using a fixed bulk lattice parameter for x and y directions corresponding to the optimized values for each method, while the atomic positions were completely optimized within the slab symmetry group. The optimizations have been considered converged when the forces are smaller than 0.02 eV/Å. Particular attention has been given to the convergence of the electronic properties as function of the number of layers in the film. In particular we have considered properties like the band gap, E_g, the position of the top of the valence band, E_{VB}, and the bottom of the conduction band, E_{CB}, the relaxation energy, E_{rlx}, defined as the difference of the total energies of the film with truncated bulk and fully relaxed structures, the interlayer distances, the interlayer adhesion energies, E_{adh}, and the surface energy, E_s.

For comparison, analogous films of SnO_2 with (110) rutile structure containing up to six layers have been considered. Since TiO_2 and SnO_2 have similar crystal structures but different electronic structures, this comparison is useful to understand the dependence of the properties on the film thickness in a transition metal oxide compared to a simple metal binary oxide.

B. Computational details

The calculations have been performed at the DFT level using the Perdew-Wang generalized gradient approximation (GGA) exchange-correlation functional, PW-GGA.[15] This functional has been shown to give reliable results for energetic and structural properties for various metal oxides.[16] The same functional has been used in connection with all electron atomic orbital basis sets (CRYSTAL03) and with pseudopotential plane waves basis sets (VASP).

In the crystalline orbital program CRYSTAL03 the Bloch functions are linear combinations of atom-centered basis functions.[12] The accuracy of the results is therefore dependent on the quality of each atomic basis set. In the present

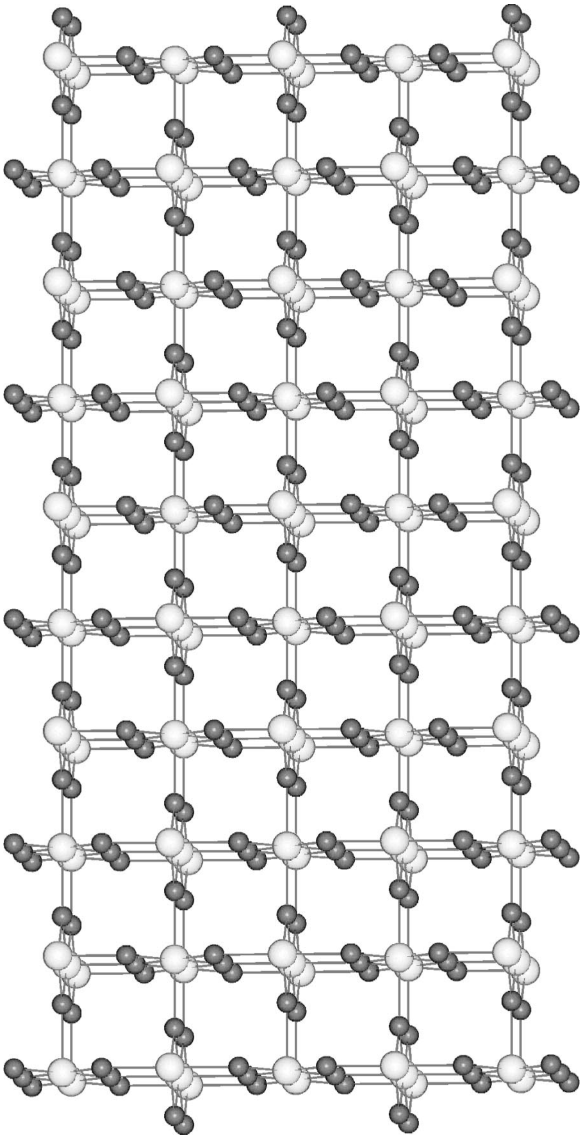


FIG. 1. Side view of a 10 layers $TiO_2(110)$ film.

study we used the recommended all-electron basis sets for Ti (8-6411G31d) and O (8-411G$*$), that have been optimized in previous studies of rutile and NiO, respectively.[17,18] The integral accuracy was increased with respect to the standard values, as suggested by recent Hartree-Fock CRYSTAL studies on rutile (110).[19] Cut-off values of 10^{-7} and 10^{-14} were used for the overlap and exchange integrals, respectively. The surface was modeled with isolated two-dimensional slabs, and no three-dimensional periodicity was imposed. A rather dense 8×8 Monkhorst-Pack mesh was employed, corresponding to 25 k points in the first Brillouin zone. This was necessary to overcome SCF convergence problems for the slabs with 7 and more layers and has been applied to the smaller models as well. For the smaller slab models the difference between 4×4 and 8×8 meshes was negligible. All symmetry-allowed atomic coordinates were optimized using analytical energy gradients and an updated Hessian procedure. The optimized bulk lattice parameters are $a=4.633$ Å, $c=2.981$ Å, $u=0.305$ to be compared to the experimental values of $a=4.594$ Å, $c=2.958$ Å, $u=0.305$.[20] These lattice parameters are used for the slab calculations and are fixed throughout.

TABLE I. Electronic and energetic properties of TiO_2 films as a function of the number of layers; CRYSTAL03 results; band gap E_g, top of the valence band, E_{VB}, bottom of the conduction band, E_{CB}, relaxation energy E_{rlx} (eV), surface energy E_s (J/m^2).

nL^a	E_g^b	E_g^c	E_{VB}	E_{CB}	E_{rlx}	E_s
2	2.50	2.45	−7.48	−4.98	−2.61	0.47
3	1.45	0.88	−7.35	−5.90	−1.86	0.91
4	2.19	1.82	−7.37	−5.18	−2.62	0.58
5	1.71	1.34	−7.27	−5.56	−2.19	0.74
6	2.09	1.72	−7.30	−5.21	−2.55	0.63
7	1.77	—	−7.22	−5.45	−2.34	0.72
8	2.06	—	−7.26	−5.20	−2.41	0.63
9	1.85	—	−7.22	−5.37	−2.36	0.65
10	1.98	—	−7.20	−5.22	−2.40	0.63

[a] Number of layers in the film.
[b] CRYSTAL03 results; corresponding bulk value 1.93 eV.
[c] VASP results; corresponding bulk value 1.74 eV.

In the VASP code a supercell approach is used, together with a plane wave basis set.[13] We used ultrasoft pseudopotentials[21,22] and a kinetic energy cut-off of 396 eV. Within this approach, the optimized bulk lattice parameters are $a=4.658$ Å, $c=2.977$ Å, $u=0.305$. For the TiO_2 slabs a $(2\times 4\times 1)$ Monkhorst-Pack mesh was used, corresponding to 4 k-points in the irreducible part of the first Brillouin zone. Test calculations with a three times finer k-sampling have shown no changes in the slab geometry and a 1% change in the computed band gap. The slabs were separated by at least 9 Å of vacuum. The positions of all atoms of the supercell were optimized by means of a conjugate gradient optimization algorithm. For the electronic structure calculations a Gaussian broadening of the electronic levels with $\delta=0.2$ eV was applied.

III. RESULTS AND DISCUSSION

The properties of TiO_2 films containing from 2 to 10 layers, corresponding to a film thickness of up to 32 Å, are reported in Table I as a function of the number of layers (CRYSTAL03 results). It is apparent that properties like the band gap show strong oscillations with film thickness. In particular, the gap is largest for a 2L film, 2.50 eV, and smallest for a 3L film, 1.45 eV. Both values are far from the bulk gap which is estimated to be 1.93 eV, i.e., about 1.2 eV smaller than the experimental value, 3.06 eV,[23] a typical effect in DFT studies of solids and surfaces.[24]

By adding more TiO_2 layers, the calculated gap slowly approaches the bulk value, with the films containing an even number of layers showing a larger gap than the bulk, while the opposite is true for the films containing an odd number of layers. This is clear from Fig. 2 where the odd-even oscillation of the band gap is shown. The 9L and 10L films, with gaps of 1.85 and 1.98 eV, respectively, are sufficiently close to the bulk value. It should be mentioned, however, that the

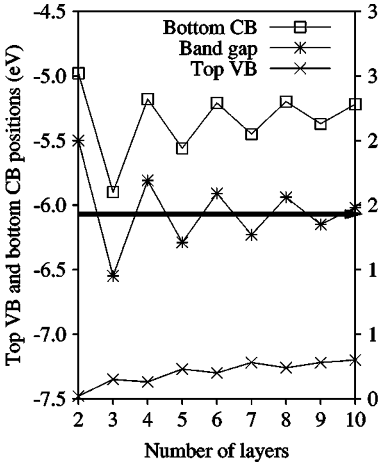


FIG. 2. Dependence of electronic properties of rutile $TiO_2(110)$ thin films on the number of layers.

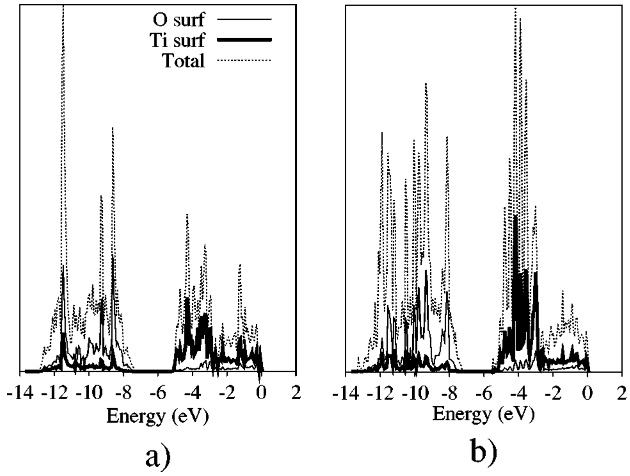
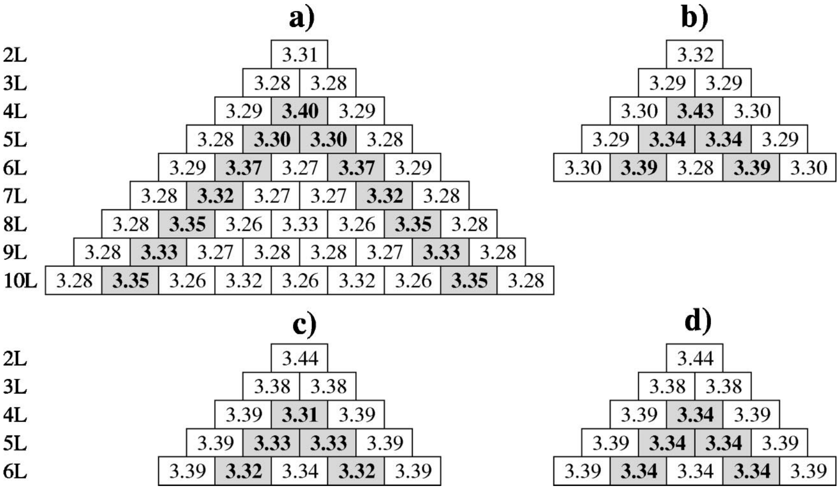


FIG. 3. Density of states for (a) 4L and (b) 5L slab models of rutile $TiO_2(110)$ (CRYSTAL03 results). Thin solid lines: first layer O atoms; thick solid lines: first layer Ti atoms. Dotted line: total DOS. The energy levels (eV) are referred to the vacuum level equal at zero.

value of the band gap for a thin film does not necessarily converge to the bulk value, given the presence of two surfaces in the film. Experimentally no evidence for surface states has been found for rutile (110).[2] Similar (but not identical) results are obtained when plane waves are used, Table I (VASP results). Here the analysis has been restricted to films containing up to six layers. Also in this case the odd-even oscillation of the band gap is found, and a slow convergence towards the corresponding bulk value, 1.75 eV, is observed. Notice that the band gap in the plane wave approach is about 0.2 eV smaller than with localized orbitals. This is probably due to the use of ultrasoft pseudopotentials in the plane wave calculations.

A closer analysis of the oscillations in the band gap reveals that these are almost entirely due to changes in the position of the bottom of the conduction band, while the top of the valence band remains stable (Fig. 2). Since the bottom of the conduction band is largely composed of Ti 3*d* orbitals (Fig. 3), the strong oscillation as function of the number of layers suggests that the largest contribution comes from 3*d* orbitals with component normal to the surface, like the $3d(z^2)$, or the $3d(xz)$ and $3d(yz)$ orbitals. An analysis of the density of states in fact shows that the lowest unoccupied bands originate from the coordinatively unsaturated Ti_{5c} surface atoms. Here the positions of the low-lying $3d(z^2)$ and $3d(xz)$ orbitals are different in the 4L and the 5L slab models.

The changes in position of the bottom of the conduction band, E_{CB}, are a direct consequence of the different structural rearrangements occurring in the films as function of the number of layers. In Fig. 4(a) the average distances between the TiO_2 layers as obtained with CRYSTAL03 are given, taking as a reference the average of the *z* coordinate of each Ti ion in a given layer. A 2L TiO_2 film has an interlayer distance of 3.31 Å, slightly longer than that of the bulk, 3.28 Å. In a 3L slab, the two external layers have a distance of 3.28 Å from the central one. An interesting effect occurs when we consider a 4L slab. Here in fact the first and second layers are separated by 3.29 Å, while the distance between the second and the third layers is considerably larger, 3.40 Å, Fig. 4(a). This suggests that a 4L TiO_2 film can be seen as composed by two weakly interacting bi-layers. This is supported by the analysis of the energy required to separate a 4L film into two 2L slabs, 0.37 J/m^2, Fig. 5. This value is six times smaller than the energy required to separate the 4L film into a 3L and a 1L slab, 2.33 J/m^2, Fig. 5. The tendency to show a longer distance between the second and the third layers is not restricted to the 4L film and is present also in thicker films, Fig. 4. It is found also using a plane wave approach; actually in this case the changes in the interlayer distances with the number of layers are even more pronounced than with a localized basis set, Fig. 4(b). In general, films containing an even number of layers show a large separation between second–third layers, while the films containing an odd number of layers show a smaller second–third layer distance, Figs. 4(a) and 4(b). For instance, in 6L, 8L, and 10L films the second–third layer distance is of 3.37, 3.35, and 3.35 Å, respectively; in 5L, 7L, and 9L films it is between 3.30 and 3.33 Å. Notice that the largest oscillations are always between the second and the third layers. The distance between the first two layers is stable, 3.28 Å (except the 2L film which however has no "bulk"), while the distance of the inner layers stays more constant and is closer to the bulk distance. Still, for films with an even number of layers, an oscillation for the interlayer distance and the adhesion energy can be observed even for the largest system studied, the 10L slab, Figs. 4(a) and 5(a). From this analysis it emerges that the first two layers in a TiO_2 film are less tightly bound to the rest of the film, and that this tendency is more pronounced when the film has an even number of layers. A direct proof of this conclusion comes from the energy E_{adh} required to detach the top 2L film from the rest: the value converges towards 0.5 J/m^2, an energy which is about one half of that required to detach a 3L film from the rest, about 0.95 J/m^2, Fig. 5(a) (CRYSTAL03 results). These values differ from the extrapolated value for the surface energy E_s, 0.64 J/m^2, Table I, while the adhesion energies for inner layers slowly converge to E_s. Very similar values of the interlayer adhesion



a)

2L	3.31								
3L	3.28	3.28							
4L	3.29	**3.40**	3.29						
5L	3.28	**3.30**	**3.30**	3.28					
6L	3.29	**3.37**	3.27	**3.37**	3.29				
7L	3.28	**3.32**	3.27	3.27	**3.32**	3.28			
8L	3.28	**3.35**	3.26	3.33	3.26	**3.35**	3.28		
9L	3.28	**3.33**	3.27	3.28	3.28	3.27	**3.33**	3.28	
10L	3.28	**3.35**	3.26	3.32	3.26	3.32	3.26	**3.35**	3.28

b)

	3.32				
	3.29	3.29			
	3.30	**3.43**	3.30		
	3.29	**3.34**	**3.34**	3.29	
	3.30	**3.39**	3.28	**3.39**	3.30

c)

2L	3.44				
3L	3.38	3.38			
4L	3.39	**3.31**	3.39		
5L	3.39	**3.33**	**3.33**	3.39	
6L	3.39	**3.32**	3.34	**3.32**	3.39

d)

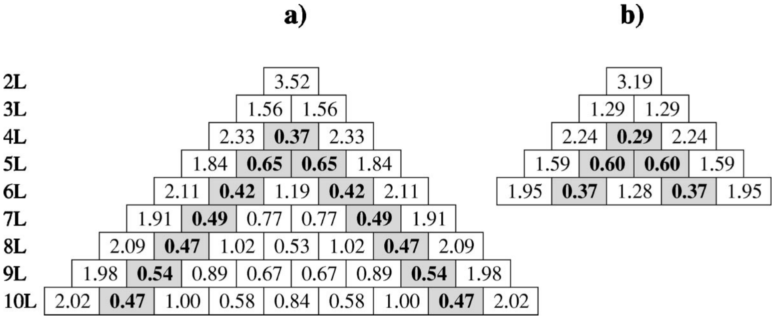
	3.44				
	3.38	3.38			
	3.39	**3.34**	3.39		
	3.39	**3.34**	**3.34**	3.39	
	3.39	**3.34**	3.34	**3.34**	3.39

FIG. 4. Interlayer distances (Å) of thin rutile TiO_2 and SnO_2 films as function of the number of layers. (a) $TiO_2(110)$ CRYSTAL03 results; (b) $TiO_2(110)$ VASP results; (c) $TiO_2(110)$ without Ti 3*d* orbitals, CRYSTAL03 results; (d) $SnO_2(110)$ CRYSTAL03 results. Each number in the figure corresponds to the distance between a layer and the following one. Layers are represented by vertical lines. The values in bold refer to the distances between second and third layers.

energies have been obtained with the plane wave approach, Fig. 5(b). Also the calculated surface energy E_s oscillates with the number of layers as observed in previous calculations. The surface energy calculated with CRYSTAL03, converged to $0.64\pm0.01\ \mathrm{J/m^2}$, Table I, is smaller than that obtained in previous studies based on LDA,[25] $0.83-0.90\ \mathrm{J/m^2}$, or on the PW-GGA functional, $0.73\ \mathrm{J/m^2}$.[5] Note, however, that this latter value has been obtained with a 7L model; our value for a 7L thick film is very close, $0.72\ \mathrm{J/m^2}$.

Despite the non-negligible geometric changes in almost all layers of the slab models, the relaxation energy, E_{rlx}, does not increase with the number of layers and converges to a value close to 2.40 eV ($0.98\ \mathrm{J/m^2}$). This indicates that the main contribution to the relaxation energy comes from the surface and sub-surface layers.

Which is the origin of the structural changes with the number of layers and in particular of the odd-even oscillations in the electronic properties? A first answer comes from the analysis of the density of states projected onto specific atoms and orbitals and from the inspection of the charge density maps. In Fig. 3 we report the density of states (DOS) curves for 4L and 5L slabs, projected onto the O 2*p* and Ti 3*d* contributions of the surface atoms. In the 4L DOS, Fig. 3(a), there is a clearly visible pronounced peak in the bottom of the valence band (−12 eV) which is composed of O $2p_z$ orbitals strongly hybridized with surface Ti_{6c} $3d_{xz}$ orbitals. This hybridization reinforces the interaction between the first and the second or the third and the fourth layers, but results in a weaker interaction between the second and the third layer, with a consequent increase of the interlayer distance. This weaker interaction is the consequence of the absence of a symmetry plane in the film, and is clearly visible in the charge density plots where the formation of O-Ti hybrid orbitals within the first and fourth layers is apparent (Fig. 6). There is an increased electron density between six-fold coordinated titanium atoms, Ti_{6c}, in the fourth layer and the bridging oxygen atoms of the same layer (Fig. 6). A larger electron density is also observed between the first layer Ti_{5c} atoms and the oxygens below. A similar observation was made by Diebold *et al.*[26] for the electron density of the first three layers of a rutile surface. This hybridization would lead to a dipole moment along the surface normal direction which is destabilizing according to Tasker's rules for polar surfaces.[27] Therefore, the dipole moment is compensated by a hybridization in the opposite direction in the following layers. In this way the bonding between the first and second layer is increased while that between the second and third layer is weakened. The distance between layers 2 and 3 increases as described above, and the third layer becomes "surface-like." A similar although less pronounced effect occurs between layers 3 and 4, and so on. As can be seen from the oscillation of interlayer distances and adhesion energies in the 10L model, this effect extends rather deep. We also did a calculation with a 10L film where the bottom five layers are frozen to the bulk geometry while the top five layers are completely relaxed. The results show that the interlayer distances for the first four layers are almost identical to those obtained by fully relaxing the 10L film. This shows unambiguously that the large second third layer distance is a surface property intrinsic to rutile TiO_2 in both single crystal and thin film forms. The situation is quite different when we consider the 5L film. Here, the intense DOS peak with an O $2p_z$-Ti $3d_{xz}$ character [Fig. 3(b)] is not present because the



a)

2L	3.52								
3L	1.56	1.56							
4L	2.33	**0.37**	2.33						
5L	1.84	**0.65**	**0.65**	1.84					
6L	2.11	**0.42**	1.19	**0.42**	2.11				
7L	1.91	**0.49**	0.77	0.77	**0.49**	1.91			
8L	2.09	**0.47**	1.02	0.53	1.02	**0.47**	2.09		
9L	1.98	**0.54**	0.89	0.67	0.67	0.89	**0.54**	1.98	
10L	2.02	**0.47**	1.00	0.58	0.84	0.58	1.00	**0.47**	2.02

b)

	3.19				
	1.29	1.29			
	2.24	**0.29**	2.24		
	1.59	**0.60**	**0.60**	1.59	
	1.95	**0.37**	1.28	**0.37**	1.95

FIG. 5. Adhesion energies, E_{adh} ($\mathrm{J/m^2}$), of thin rutile TiO_2 and SnO_2 films as function of the number of layers. (a) $TiO_2(110)$ CRYSTAL03 results; (b) $TiO_2(110)$ VASP results. Each number in the figure corresponds to the energy required to detach the first *n* layers from the rest of the film. Layers are represented by vertical lines. The values in bold refer to the adhesion between the top two layers and the rest of the film.

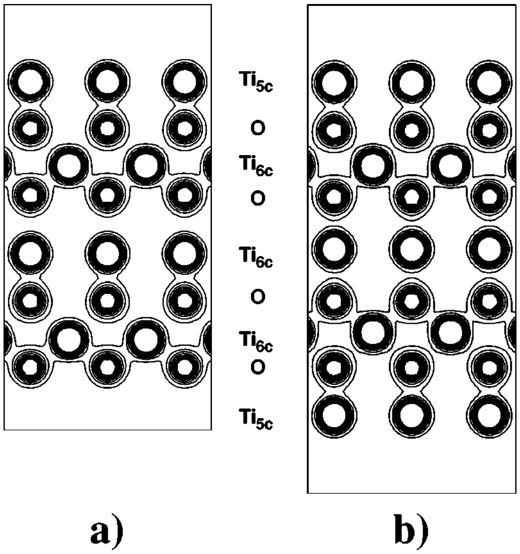


FIG. 6. Electron density maps (in steps of 0.1 $e^-/\mathrm{a.u.}^3$) for (a) 4L and (b) 5L slab models of rutile $TiO_2(110)$. Cut along the Ti_{5c} surface atoms.

corresponding state is not localized between the first and second layers but is delocalized over the entire system, Fig. 3(b). This reflects also in the charge density plots that show a substantial similarity of the Ti-O interactions along the z direction of the film, Fig. 6(b). The key aspect determining the difference between the 4L and the 5L films (and in general of thin films containing an even and an odd number of layers) is the presence of a symmetry plane. Notice, however, that the tendency to form stronger interactions between the first and the second layer, and weak interactions between the second and the third layer, is common to all films, no matter of how many layers are present.

The previous discussion of the changes in the interlayer distance and energy gap related to the number of layers in the films suggests that this is due to the different hybridization along the z direction of the O 2p and Ti 3d states. In general, the effect could be due to multipole moments present on the TiO_2 films containing an even number of layers or to other spurious effects due to the absence of a symmetry plane. However, this is not the case. To show this, we have performed a structural optimization for TiO_2 films containing up to six layers removing the 3d orbitals from the Ti basis set. In this way, the only orbital mixing which is possible is between the O 2p states and the Ti 4s and 4p levels. This situation, in which Ti is forced to behave as a nontransition metal, is compared with that of SnO_2 films with the rutile structure and the same film thickness, Figs. 4(c) and 4(d). The results show two very clear trends. First of all, without 3d orbitals the distance between the first and second layers becomes longer than in the bulk, 3.39 Å, opposite to what occurs in "real" TiO_2, while the distance of the inner layers is stable, 3.33 Å ± 0.01, Fig. 4(c). Thus, there is no sign of the formation of a stable bilayer weakly interacting with the rest at the top of the film. Second, and more important, the structure of the TiO_2 film without 3d orbitals is almost identical to that computed for SnO_2 [Fig. 4(d)], proving unambiguously the peculiar behavior of TiO_2. Without d orbitals, rutile TiO_2 behaves as SnO_2, at least in terms of geometrical structure.

IV. CONCLUSIONS

In this paper we have analyzed the geometric and electronic properties of thin rutile $TiO_2(110)$ films as a function of the number of layers in the films. Oscillations of surface properties with the number of layers have been discussed in previous theoretical studies, but so far the focus has been more on the number of layers in a slab needed to obtain a good representation of the rutile single crystal surface. Here we have shown that the strong oscillations are an intrinsic property of thin rutile TiO_2 films and that they are largely connected to the presence of an even or odd number of layers in the film. The convergence of the structure and properties towards the bulk is rather slow, and not completely reached, even with a film of ten layers (>30 Å thickness). The main reason for the oscillations is the change in O(2p)-Ti(3d) interlayer hybridization along the film. In films with an even number of layers, which do not contain a symmetry plane normal to the z direction, the O-Ti hybridization causes the formation of a series of tightly bound TiO_2 bi-layers with weaker interactions between a bi-layer and the following one. In an extreme view, a thin TiO_2 film with an even number of layers can be viewed as a layered system. On the contrary, a thin TiO_2 film with an odd number of layers has a symmetry plan at the center of the film and develops O(2p)-Ti(3d) hybrid orbitals which extend along the entire thickness of the film, thus reducing the tendency to form weakly interacting bi-layers. The tendency to form strong O-Ti bonds is always present for the surface and the subsurface layers. This results in a short first–second layer distance, and consequently in a longer second–third layer separation. This effect is present also in models of single crystal rutile surfaces where the bottom five layers are fixed at the bulk geometry and the top five layers are completely relaxed, showing that it is an intrinsic surface effect.

The fact that these oscillations, which determine both the geometric and the electronic structure of the rutile TiO_2 films, are due to the mixing of the O 2p and Ti 3d states is clearly shown by a computational experiment in which the Ti 3d orbitals have been removed from the calculations, forcing Ti to behave as a simple metal. When this is done, TiO_2 does no longer exhibit the odd-even oscillations and behaves almost exactly as the isostructural SnO_2 oxide.

These results are of importance not only for an accurate modeling of rutile TiO_2 single crystal surfaces, but also for the study of ultrathin TiO_2 epitaxial films grown on metal substrates to model catalytic reactions in controlled conditions.

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