

Origin of defect states on the surface of TiO_2

S. Munnix and M. Schmeits

Institut de Physique, Université de Liège, B-4000 Sart Tilman/Liège 1, Belgium

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We have investigated the electronic structure of oxygen vacancies on $\text{TiO}_2(110)$, including atomic relaxation. The study of different defect sites shows that the experimentally observed gap state at 0.7 eV below the conduction-band edge is indeed due to an oxygen vacancy. This state, however, is not due to the removal of an O atom from a surface bridging site, as frequently proposed, but results from a subsurface oxygen vacancy. In this configuration, there is a maximum reduction of the screening between surface cations.

The knowledge of electronic properties of TiO_2 surfaces is of fundamental importance for the understanding of the mechanisms taking place at an atomic scale in a number of practical applications of this material, such as heterogeneous catalysis, the photolysis of water, etc.¹ In particular, the (110) face has been used as an ideal, thermodynamically stable prototype surface in the study of semiconductor-gas interactions. On these surfaces, point defects play a crucial role, as they act as active sites for chemisorption or molecular dissociation.² Experimentally, no states are observed in the gap for defect-free TiO_2 surfaces, but the creation of surface defects by Ar^+ -ion bombardment leads to a nonzero density of states in the 3-eV-wide gap.³⁻⁵ The energetic position of these states, as determined from ultraviolet photoemission spectroscopy (UPS) and electron-energy-loss spectroscopy (EELS) measurements, is at 2.3 eV above the top of the valence band (i.e., 0.7 below the conduction-band edge E_c), with an experimental resolution of typically 0.2 eV. Auger electron analysis shows that the appearance of these states is associated with a reduction of the O/Ti ratio in the surface region, which suggests that they are due to oxygen surface vacancies. However, neither the precise atomic configuration nor the detailed electronic structure of these defects is presently known.

In the present paper, we report the first theoretical study of the electronic structure of single point defects on otherwise perfect $\text{TiO}_2(110)$ surfaces. For the ideal (110) surface, we consider two different models: In the first one (I), the topmost atomic plane contains two Ti and two O atoms per surface unit cell and corresponds to the most compact atomic plane for this crystallographic orientation. In the second model (II), the semi-infinite solid is terminated by an additional O layer; this corresponds to the cutting of a minimum number of Ti—O bonds when creating the surface. These two models are displayed in Fig. 1 and their electronic structure has been studied previously.⁶ The creation of the surface leads essentially to the appearance of O *p* resonances in the conduction band and Ti *d* resonances in the valence-band region. No occupied O *p* states appear in the gap, in accordance with the experimental results quoted above. Only for the type-I surface is there a Ti *d* state following closely the conduction-band edge. The existence of ideal bulk O

mono- or divacancies is not sufficient to create states in the gap.⁷

For both surface types, we have investigated several defect models, corresponding to the removal of one or two O atoms on different surface sites. The defect-induced features obtained for each case allow us to determine unambiguously whether an atomic configuration is able to lead to electronic states inside the gap or not. Using the scattering theoretic method, the electronic structure of the defect can be obtained from the study of the surface-defect Green's function G_d ,^{8,9} just as the surface electronic structure is obtained from the surface Green's function G_s . Detailed formal developments for the TiO_2 case will be given elsewhere. Relaxation of the atoms around the vacancy can be included along the same lines as the relaxation or reconstruction of semiconductor surfaces.¹⁰

Among the various configurations we have considered, we will present here only the results for four of them, which are most relevant to the discussion which will follow. The first corresponds to the removal of an O(0) atom (see Fig. 1 for notations) from a Ti-Ti bridge site on surface II (this model will be labeled II_a in the following). The three other ones correspond, respectively, to the removal of the atoms O(2) (I_a), O(2) and O(2') (I_b), and O(3) (I_c) on surface I. As a typical result, we present in Fig. 2 the Ti-resolved changes in density of states for I_a and I_c . The Ti partial bulk density of states (DOS) is shown for comparison. We have reproduced the surface-induced

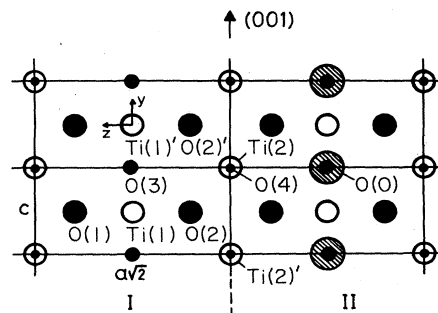


FIG. 1. Atomic configuration of $\text{TiO}_2(110)$ surface terminated by the most compact atomic plane (I, left) or by an additional oxygen layer (II, right).

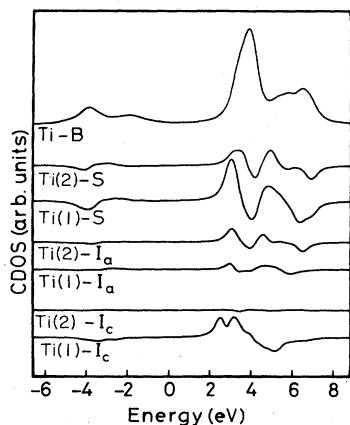


FIG. 2. Bulk partial Ti DOS (B); surface-induced change in DOS on the surface cations Ti(1) and Ti(2) of surface I (S); vacancy-induced changes on the same atoms (I_a, I_c). All DOS's have been calculated with a 0.3-eV Lorentzian broadening. The top of the valence band is at 0 eV and the conduction-band edge at 3 eV.

DOS changes (surface minus bulk) on the cations Ti(1) and Ti(2), next to both vacancies, together with the defect-induced DOS changes (defect minus surface) on the same atoms. Defect-induced changes on O atoms or on more distant Ti atoms are almost completely negligible, as compared to those on Ti(1) and Ti(2). Therefore, the summed changes on the Ti atoms surrounding the vacancy are nearly equal to the total change in DOS. These quantities are shown in Fig. 3 for the four models considered. The analysis of these DOS curves shows that the major trends observed for ideal surfaces remain true for surface defects: The reduction of cation coordination leads mainly to Ti *d*-derived resonances in the conduction-band region and to (weak) O *p*-derived resonances in the valence-band region. Pronounced differences, however, occur with respect to the ideal surface case in the region 2–4 eV. In the defect model II_a, where a bridging anion O(0) has been removed, a strong resonance appears at 3.2 eV. Removal of more O(0) atoms does not lead to a marked downward shift of this resonance, even in the limiting case where all O(0) atoms are removed, reducing the surface II to the model I surface. The I_a vacancy gives rise to a similar change of DOS (CDOS) curve, whose lowest peak is now at 3.0 eV. The removal of a neighboring O(2)' atom to create a divacancy strongly enhances the amplitude of the CDOS peaks, but again produces no Ti *d*-derived state in the gap. When instead a subsurface atom O(3) is removed (I_c), the lower peak splits in two peaks separated by about 1 eV. The lowest of these peaks is at 2.5 eV and is clearly located inside the gap. The orbital-resolved DOS of this state shows that its dominant contribution consists of *d*_{*x*²-*y*²} states on Ti(1) (in the local coordinate system⁶ of Fig. 1); the other peak is mainly composed of the two other orbitals of *t*_{2g} symmetry, *d*_{*yz*} and *d*_{*zx*}.

This analysis allows us to stress the basic mechanism which is responsible for the appearance of surface-defect states. Creation of the ideal surface causes bulk Ti *d*

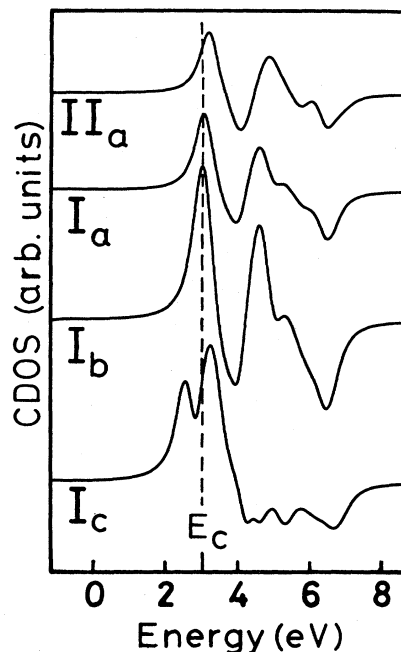


FIG. 3. Summed vacancy-induced DOS changes on Ti atoms next to vacancies II_a, I_a, I_b, I_c.

states to move towards the atomic Ti *d* level, building at the conduction-band edge a DOS whose main composition is of *d*_{*x*²-*y*²} orbital symmetry.⁶ Further displacement of O atoms through defect creation not only lowers the cation coordination, but also reduces the screening of Ti-Ti interactions. As a consequence, the second-nearest-neighbor interaction between Ti atoms is enhanced, leading to a further downward shift of the lower conduction-band states. This effect is most pronounced for the model I_c vacancy: After the removal of the atom O(3), no more oxygen atoms are present in the space between Ti(1) and Ti(1)', allowing a maximum overlap of their *d*_{*x*²-*y*²} orbitals along the [001] direction.

Since the creation of surface O vacancies leaves a wide empty space between surface cations, these atoms are expected to relax. As there is no experimental information on the type and the amplitude of the atomic displacements at the present time, we have considered only the case where the cations experience symmetric displacements around the vacancy, i.e., a breathing-mode relaxation for the three Ti atoms around vacancy I_a and a symmetric displacement along the [001] direction for I_c. The modification of interatomic *d-d* matrix elements with interatomic distance *r* was taken into account by a *r*⁻⁵ scaling law, according to Harrison.¹¹ We have examined the position of the lowest conduction-band-defect feature as a function of *c_r*, which represents the Ti(2)-Ti(2)' [Ti(1)-Ti(1)'] distance for model I_a (I_c). The results are plotted in Fig. 4. For both models, the reduction of the Ti-Ti distance leads to a stronger interaction between *d* orbitals, and henceforth to a downward shift of the CDOS peak, thus reducing the total electronic energy when this state is occupied. For Ti(2)O(3), where the [O/Ti] ratio is also reduced as compared to bulk TiO(2), the lowest interatomic

Ti-Ti distance is 2.6 Å. Taking this value as an estimate of the final relaxation distance would give peak positions at 2.8 and 2.2 eV for models I_a and I_c, respectively.

From the systematic study of the various surface-defect configurations we have analyzed, it can be concluded that for ideal vacancies a well-defined gap state can be found only for model I_c. Relaxation of the atoms around the surface vacancy by about 0.3 Å reproduces for I_c the experimentally observed value of 2.3 eV. For the other vacancy models, however, relaxation by similar distances is not sufficient to produce a strong enough downward shift of the defect level.

In conclusion, we have determined the first electronic structure of surface defects on rutile surfaces. We have shown that defect states inside the gap exist, and which basic mechanism is responsible for their origin. The frequently proposed bridge-site vacancy model (II_a in our notation), however, cannot produce such gap states, but these are due to the removal of subsurface oxygen atoms O(3). The occurrence of such subsurface vacancies is quite possible, since atoms like O(3) are only incompletely protected by surface layer atoms and can thus be removed

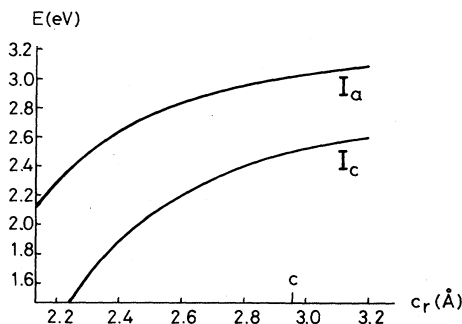


FIG. 4. Energetic position of defect gap state as function of Ti-Ti distance along (001).

by a destructive Ar-ion bombardment. This study shows how the interplay between theory and experiment can lead to a deeper insight in the electronic and atomic structure of semiconducting oxide surfaces.

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