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A low-energy electron diffraction analysis of the structure of the titanium dioxide (001) surface

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Abstract. LEED $I(V)$ data comprising three non-degenerate beams have been collected at normal incidence from the cleaved (001) surface of TiO_2. Care has been taken to minimize the effects on the $I(V)$ data of electron beam damage to the surface. Analysis of the $I(V)$ data has been carried out using tensor LEED theory and a search strategy designed to minimize the Pendry R-factor. A wide range of possible structures has been examined including a model proposed using energy minimization techniques. The trial structures have included distortions in up to three layers of the surface. Data on two likely structural solutions are presented.

1. Introduction

The $TiO_2(001)$ surface is one of a number of oxide surfaces which are of interest because of their photocatalytic properties (Fujishima and Honda 1972, Boonstra and Mutsaers 1975). Fundamental to the complete understanding of these properties is the arrangement of the atoms at the surface. Recent LEED analyses on oxide surfaces include work on $SrTiO_3(100)$ by Bickel *et al* (1989) and MgO(100) by Welton-Cook and Berndt (1982). The (001) surface of TiO_2 appears to be inherently unstable and it has been shown by Tait and Kasowski (1979) and Firment (1982) to facet upon annealing above about 450 °C. Large shifts in the positions of the atoms at the surface away from the positions that they would have in a bulk-like termination of the solid might therefore be expected. In this work we have carried out a LEED $I(V)$ analysis to determine the positions of the atoms at a cleaved, unannealed and unfaceted (001) (1×1) surface of a crystal of TiO_2.

2. Experimental details

All experiments were carried out in an ultra-high vacuum (UHV) system (de Carvalho *et al* 1984) with a typical operating pressure of 2×10^{-10} mbar. Auger electron spectroscopy (AES) was used to check the cleanliness of the surface. In order to avoid charging of the surface by the beam of electrons, n-type conductivity (about 10^{18} cm^{-3}) was introduced into the TiO_2 crystals by vacuum reduction.

Only about one in three cleaves produced a good (1×1) LEED pattern with a single specular spot. Only these cleaves were used for the collection of LEED $I(V)$ data.

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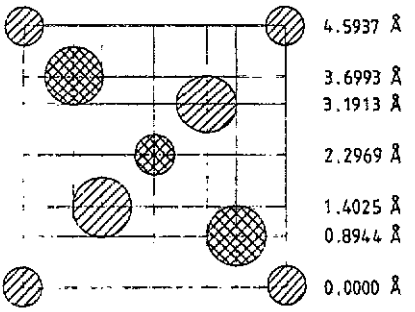

Figure 1. Diagram showing the position of the atoms in the [001] direction for a bulk termination. The hatched atoms belong to the odd-numbered layers and the cross-hatched atoms belong to the even-numbered layers. The small atoms are the Ti atoms. The interlayer spacing is 1.4791 Å.

The electron beam (about 8 μA) damaged the surface quite quickly, resulting in an increase in the diffuse background and, after about 60 min, the disappearance of the LEED pattern. As a result, only one $I(V)$ curve could be collected from a particular area of the surface. Each new $I(V)$ curve was collected from an unused area of the surface. In order to minimize further any effect on the $I(V)$ curves due to beam damage, $I(V)$ curves were collected with both increasing and decreasing energy. Comparison of those $I(V)$ curves collected with increasing energy with those with decreasing energy revealed some changes in the relative heights of peaks well separated in energy but no shifts in the positions of the peaks and no change in the number of peaks. It was therefore concluded that the beam damage introduced disorder into the surface but did not alter the ordered structure of the surface. The subsequent theoretical analysis was carried out on the averages of those $I(V)$ curves collected with increasing energy and those collected with decreasing energy.

If there are no monolayer steps on the surface, it would be expected that the (1, 1) and (−1, −1) beams would be equivalent and that the (1, −1) and (−1, 1) beams would likewise be equivalent but that these two sets of beams would be different. However, all four of these beams were observed to be equivalent. Because of this and the unlikelihood of cleaving along a single (001) layer, it was concluded that the surface consisted of monolayer steps and that, because alternate layers of the crystal are the same but rotated through 90° (figure 1), this would give the observed equivalence provided that the two alternating orientations of the layer unit cell are present at the surface in equal amounts. A similar equivalence was observed for the (2, 2) family of beams.

Good data were obtained at normal incidence for the (1, 1) beam from 43 to 210 eV, the (2, 2) beam from 222 to 330 eV and the (3, 0) beam from 163 to 330 eV (figure 2). The (1, 0), (2, 0) and (2, 1) beams were also observed but were too weak compared with the diffuse background to permit the collection of good data.

3. Theoretical work

A FORTRAN program based upon the theory of tensor LEED developed by Rous *et al* (1986) and derived from the program CAVATN written by Richard Blake was used to analyse the $I(V)$ data. The main idea of tensor LEED is that an accurate full dynamical LEED calculation is done for a base point structure. Perturbations to the structure of the base point are then calculated using a very much faster approximation scheme. The theoretical data generated by the program were compared with the experimental data using the R-factor of Pendry (1980).

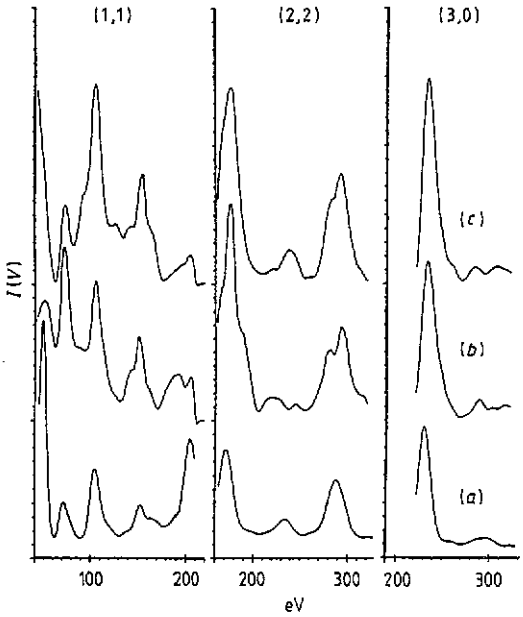

Figure 2. Comparison of the theoretical and the experimental $I(V)$ curves. (*a*) Experiment; (*b*) model 1; (*c*) model 2.

Three parameters P^i_Z, L^i and P^i_D were defined for each of the surface layers that were to be distorted during the analysis of the $I(V)$ data. In the definitions that follow, a is the lattice constant of the layer unit cell in the (001) plane (4.5937 Å), $d_{(002)}$ is the bulk interlayer spacing (1.4791 Å), Z^i_T is the distance (from the vacuum) of the Ti atom in the ith layer, Z^i_O is the distance (from the vacuum) of either of the O atoms in the ith layer and D^i is the least distance between a Ti atom and an O atom in the ith layer. Z'^i_T, Z'^i_O and D'^i are equivalent to Z^i_T, Z^i_O and D^i but they apply instead to the ith layer in a bulk termination of the crystal. P^i_Z is the Z-rumple of the ith layer, P^i_D is the D-rumple (diagonal rumple) of the ith layer and L^i is the relaxation of the ith layer:

$$P^i_Z = (100/d_{(002)})(Z^i_T - Z^i_O)$$

$$P^i_D = 100(D'^i - D^i)/a\sqrt{2}$$

$$L^i = (100/d_{(002)})\,\tfrac{1}{2}(Z'^i_T + Z'^i_O - Z^i_T - Z^i_O).$$

The Ti and the O atoms in each of the layers were constrained to move so as to preserve the symmetry of the layer unit cell.

The program was designed to investigate automatically a large number of possible structures. The investigation contained three parts. The first part consisted of calculating a grid of 289 points in which just two parameters were varied. P^1_Z was varied from −99.4 to +99.4 and L^1 was varied from −49.7 to +49.7. Local minima in the R-factor were identified within this grid and were used in the second part of the investigation which consisted of calculating a new grid of points around each of these minima. The four parameters P^1_Z, L^1, P^2_Z and L^2 were varied in each of these new grids. Local minima in the new grids were then used for the third part of the investigation which consisted of using a search strategy to refine the position of each of these new minima. The six

Table 1. The deviations of the atoms in the surface from the positions that they would have in a bulk termination. The absolute positions of the atoms can be found from adding the deviations to the positions the atoms would have in a bulk termination.

		Model 1			Model 2		
Layer	Atom	Z (Å)	X (Å)	Y (Å)	Z (Å)	X (Å)	Y (Å)
1	Ti	0.052	0.0	0.0	0.013	0.0	0.0
1	O	0.084	0.004	0.004	0.011	0.038	0.038
1	O	0.084	−0.004	−0.004	0.011	−0.038	−0.038
2	Ti	−0.028	0.0	0.0	−0.362	0.0	0.0
2	O	−0.041	−0.014	0.014	0.096	−0.077	0.077
2	O	−0.041	0.014	−0.014	0.096	0.077	−0.077
3	Ti				−0.003	0.0	0.0
3	O				−0.004	0.0	0.0
3	O				−0.004	0.0	0.0

parameters P_Z^1, P_D^1, L^1, P_Z^2, P_D^2 and L^2 were varied during the refinement except in one case in which an extra three parameters P_Z^3, P_D^3 and L^3 were also varied.

4. Results and discussion

The first part of the investigation revealed five minima in the R-factor. Of these, two were initially selected for further study. The first ($P_Z^1 = 0.0$, $L^1 = -6.2$) is the minimum closest to the bulk termination. It is also close to the result of an earlier preliminary study of ours. The new grid around this minimum contained 441 points. P_Z^1 was varied from −12.4 to +12.4, L^1 from −12.4 to 0.0, P_Z^2 from −37.3 to +37.3 and L^2 from −18.6 to +18.6. The second initial minimum ($P_Z^1 = 24.9$, $L^1 = -18.6$) is the one closest to a model proposed using an energy minimization scheme. The new grid around this minimum contained 750 points. P_Z^1 was varied from −12.4 to +37.3, L^1 from −24.9 to +6.2, P_Z^2 from −24.9 to +24.9 and L^2 from −12.4 to +12.4. Further investigation around these two minima produced a total of seven new minima. Of these, only two are significant, both from the first initial minimum. The other five can be rejected on the grounds of unphysically large expansions or contractions of the Ti–O bonds in the surface and relatively poor agreement (and hence high R-factor) between the theoretical and experimental $I(V)$ curves. Details of the two significant models are given in tables 1–3.

The first solution is largely bulk like with only small distortions of the two outermost layers. The second solution involves substantial distortions of the second layer with only very small distortions of the first and third layers. On the basis of the overall R-factor, the second model is preferred and, indeed, visual agreement of the theoretical and experimental $I(V)$ curves is better. However, it is an unusual reconstruction and the R-factor minimum may be the result of the rather limited experimental data. Evidence which may support the first solution exists in the work of Muryn *et al* (1989). Ti 3s core-level shifts were measured for the Ti atoms in a TiO_2(001) surface. One shift is observed close to the value calculated by Kasowski and Tait (1979) for a first-layer Ti atom in a bulk termination. However, the other observed shift (−0.8 eV) is greater than the calculated value (−0.2 eV) for a second-layer Ti atom.

Table 2. Ti–O bond lengths for the atoms in the surface.

Layer of Ti atom	Layer of O atom	Bond length (Å)	
		Model 1	Model 2
1	1	1.99	2.04
1	2	1.89	2.08
2	1	1.86	1.64
2	2	1.96	1.93
2	3		2.23
3	2		1.95
3	3		1.98

Table 3. The minimum values of the R-factors for the two possible structures and the V_{or} values at which these minima were found.

	Model 1		Model 2	
Beam	R-factor	V_{or}	R-factor	V_{or}
(1,1)	0.39	−9	0.36	−9
(2,2)	0.37	−10	0.33	−12
(3,0)	0.40	−5	0.33	−10
Overall	0.42	−8	0.36	−10

5. Conclusions

This work represents a preliminary quantitative LEED study of the cleaved TiO_2(001) surface. A wide range of values for up to nine structural parameters have been examined and two possible structures have been identified. Three local minima from the first part of the investigation remain to be examined in detail but these minima are all far from the bulk termination and experience already gained suggests that any local minima found may be unphysical.

Although it has not been possible to distinguish between the two solutions found, this may be possible with the acquisition of off-normal experimental data.

The investigation has however enabled us to eliminate many possible models (over 2500 different structures were tried). It is also apparent as a result of the investigation that the tensor LEED theory is capable of producing highly consistent results in that almost identical theoretical $I(V)$ curves were obtained when a given structure was reached by perturbation from two well separated base points.

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