Geometric Structure of TiO$_2$(011)(2×1) Surface by Low Energy Electron Diffraction (LEED)

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Abstract

A structural study has been performed on the TiO$_2$(011)(2×1) surface by quantitative low energy electron diffraction (LEED), using a delay-line-detector (DLD-LEED) system. The atomic coordinates obtained are in good agreement with recent studies using surface x-ray diffraction (SXRD). The best-fit Pendry R factor is 0.29. This effectively rules out the other models previously proposed, which have significantly higher R factors. Contrary to a previous study for the TiO$_2$(110)(1×1) surface, it was also found that calculating the sample potentials self-consistently had little effect on the results.

Key words: Electron solid interactions, scattering, diffraction, low energy electron diffraction, titanium oxides, surface reconstruction

1. Introduction

The surface of titania (TiO$_2$) has been extensively studied since the discovery in 1972 that its acts as a photocatalyst for the water-splitting reaction [1]. The majority of the studies have focused on the thermodynamically most stable face, TiO$_2$(110) [2]. However, other faces are almost as important. For example, the (011) face may have enhanced activity towards water dissociation [3], but is less studied. A scanning tunneling microscopy (STM) and density functional theory (DFT) investigation of TiO$_2$(011)(2x1) has suggested a surface terminated by titanyl (Ti=O) groups, possibly a cause of the enhanced photo-catalytic activity [4]. Another similar study suggested a microfaceting missing-row model [5]. More recent surface x-ray diffraction (SXRD) studies, however, found that their data are inconsistent with these two models and favored a structure terminated by zigzag rows of twofold coordinated oxygen atoms asymmetrically bonded to fivefold titanium atoms [6, 7]. The purpose of the present work is find out which, if any, of these three models are supported by quantitative low energy electron diffraction (LEED). There have been very few quantitative

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LEED studies on insulating oxide surfaces because beam charging has always
presented a challenge to LEED experiments. This is overcome either by charge
compensation, or by using a low electron beam current [8]. Most of the pre-
vious quantitative LEED studies have been confined to unreconstructed oxide
surfaces. Corresponding studies on reconstructed surfaces are even fewer [9],
mainly due to the major obstacle presented by multiple scattering to the inver-
sion of LEED data. The delay line detector LEED system used in the current
study had been used previously for a structural analysis of the MgO(111)(1x1)
surface [10]. TiO$_2$(011)(2x1) provides us with the first opportunity to study a
more complicated oxide surface with significant reconstruction. There has been
some discussion in the recent literature as to whether non-self-consistent sample
potentials are good enough for oxide surfaces [11]. This question will also be
addressed in the following.

2. Experimental Details

The experiment was performed under ultra-high vacuum (UHV) at a base
pressure of 1 x 10$^{-9}$ torr. A polished TiO$_2$(011) sample was cleaned by sputter-
ing and subsequent annealing in the range of 500-650 °C. LEED measurements
were performed with a low-current, pulse-counting and high-count-rate delay
line detector (DLD-LEED) system. This apparatus uses a low-current elec-
tron gun, microchannel plates for charge amplification, and delay line anode
planes for signal detection, allowing for the minimization of charging effects
and electron beam induced damage. Of particular concern to this study is an
STM experiment which has established that bombardment of the TiO$_2$(011)
(2x1) surface with electrons results in surface oxygen desorption [12]. Using
300 eV electrons, the vacancy concentration increased with increasing electron
dose from 35% (2.3x10$^{16}$ electrons cm$^{-2}$) to 70% (1.8x10$^{17}$ electrons cm$^{-2}$) of a
monolayer. Under the present experimental conditions, the sample was exposed
to 1x10$^9$ electrons in the duration of one energy scan (20 - 200 eV, 2 eV step
size). Since the electron beam of the DLD-LEED has an energy-dependant di-
ameter ranging between 50 and 250 microns [8], the sample will be exposed to,
at most, a dose on the order of 1x10$^{15}$ electrons cm$^{-2}$ per energy scan. When
compared to the results of Dulub et al. [12], it is determined that this limited
electron dose should not significantly alter the TiO$_2$(011) (2x1) surface. The
details of the DLD-LEED system and the comparisons with other systems can
be found in [8]. Other details about the extraction of I-V curves from the raw
data are given in [10]. The energy range of the I-V curves is limited by both
the size of the detector and noise at high electron energies. It was found that
the electron intensities generally decreased after about 200 eV, and the data
quality rapidly deteriorated with energy. The high energy end of the data was
therefore capped at 200 eV. Because of the dead zone on the detector [8], some
of the beams were missing in the LEED pattern. Therefore, the detector was
rotated to make all the beams detectable. Data were collected at 4 different
detector orientations of 267.5°, 290°, 312.5° and 335°. The data were then av-
eraged over equivalent beams and detector orientations to minimize errors due to noise and possible slight deviation from normal incidence.

3. Glide Plane Symmetry

We will next consider the effects of glide plane symmetry on the LEED pattern of a surface. Since the surface has a $(2\times1)$ rectangular unit cell of dimensions a and b, the LEED spots also form a rectangular pattern. At normal incidence, the reflection matrix for an electron with energy E to be scattered in the direction $\vec{g} = (g_x, g_y) = 2\pi(\frac{nx}{a}, \frac{ny}{b})$ can be written as

$$M(g_x, g_y) = C \sum_i f^{(i)}(g_x, g_y) e^{-i(k_{g\perp} - k)z_1} e^{-ig_xx_1 - ig_yy_1}$$

(1)

where C is a constant, $k = \sqrt{2E}$ and $k_{g\perp} = \sqrt{2E - g_x^2 - g_y^2}$. In Eq. 1, $(x_i, y_i, z_i)$ is the position of the $i^{th}$ atom relative to an origin chosen to be on the glide plane. The real and imaginary parts of the inner potential are usually absorbed into E. In the kinematic approximation, $f^{(i)}(g_x, g_y)$ is just the atomic form factor for an electron scattered from an incident direction into the direction specified by the wavevector $\vec{g}$. In LEED, where multiple scattering cannot be ignored, Eq. (1) will remain of the same form except that $f^{(i)}(g_x, g_y)$ will be renormalized by the multiple scattering paths involving the $i^{th}$ atom and its neighbors.

For a surface with glide plane symmetry, the atoms can be grouped into pairs which are related to each other by the symmetry operation. Let’s consider a particular pair with indices $i=1,2$. Since they are located on opposite sides of the glide plane, $x_2 = x_1 + \frac{a}{2}$, $y_2 = -y_1$, $z_2 = z_1$ and $f^{(2)} = f^{(1)}$. The last equality follows from the fact that each member of the pair have symmetrically-related atomic environments and therefore each kinematic form factor will be modified in the same way by their respective multiple scattering paths. The contribution of the pair can be written as

$$M(g_x, g_y) = C \sum_i f^{(i)}(g_x, g_y) e^{-i(k_{g\perp} - k)z_1} e^{-ig_xx_1} e^{-ig_yy_1} \left( e^{-ig_yy_1} + (1)^{n_x} e^{ig_yy_1} \right)$$

(2)

where $g_x a = 2n_x \pi$ has been used. From Eq. (2), it follows that $M(g_x, -g_y) = (-1)^{n_x} M(g_x, g_y)$. Another consequence of (2) is that if $g_y = 0$ and $n_x$ is odd, then $M(g_x, 0) = 0$. The conclusions remain valid when the sum is performed over all the atoms. Therefore if the surface has glide plane symmetry, the LEED spots at normal incidence will exhibit a rectangular pattern in which the beams $(n,0)$, for odd $n$, are missing for all energies and the LEED pattern has reflection symmetry with respect to a mirror plane passing through the x axis. The observed LEED pattern from the sample is consistent with the presence of glide plane symmetry, and an image at 98 eV is shown in Fig. 1. Since the bulk-terminated structure (see Fig. 2) contains 2 different glide planes within
the (2x1) cell, it is expected that at least one of them will be preserved when the surface undergoes reconstruction. After taking into account the symmetry, there are a total of 20 inequivalent beams. The cumulative energy range of the averaged data collected for the 20 beams is about 2200 eV.

4. LEED intensity calculations

For the LEED intensity calculations up to electron energies of 200 eV the phase shifts were generated from a self-consistent potential calculated from the FLEUR program [13] with angular momentum quantum numbers up to \( l_{\text{max}} = 7 \). Electron attenuation was simulated by an imaginary part of the inner potential equal to a constant value of \( V_{0i} = 5.0 \text{ eV} \). The real part of the inner potential, \( V_{0r} \), was also constant and initially set equal to 10.0 eV. It was treated as an adjustable parameter in the calculation. The best fit thermal-vibration amplitude was 0.12 Å for Ti and 0.14 Å for O. For the intensity calculation we used the combined space [14] option in the tensor LEED package of Barbi-eri and Van Hove [15]. The code was modified in order to preserve the glide plane symmetry during the optimization of atomic coordinates. The Pendry R-factor (\( R_{p} \)) [16] was applied for the quantitative comparison of experimental and computed intensity spectra. The optimization was stopped when the atomic coordinates converged within 0.01 Å vertical to the surface and 0.03 Å parallel to the surface.

5. Results and Discussion

The structural search for the TiO\(_2\)(011)(2x1) surface was initialized with the following models from the literature: (a) the Brookite model [6, 7], (b) the microfaceting missing-row model [5] and (c) the titanyl model [4], as shown in Fig. 3. The Brookite model was obtained from SXRD data. It is a full model, with the same number of atoms as the bulk-terminated surface, while the other models are not. The surface Ti atoms in this model are five-fold coordinated and the top oxygen atoms are 2-fold coordinated. In the microfaceting missing-row model, 2 out of 4 of the oxygen atoms are removed from the first layer and 2 out of 4 of the titanium are removed from the second layer. The bright spots seen in STM images were attributed to the surface five-fold coordinated Ti atoms and the dark region to missing Ti atoms. In the titanyl model, an additional 2 oxygen atoms are missing. The top oxygen atom is bonded to only one surface Ti atom with a Ti-O bond length 0.3 Å shorter than the bulk, which leads to the speculation that these atoms form a titanyl group with a double bond. This model is also consistent with the observed STM images with bright spots corresponding to the positions of the titanyl groups. The Brookite model, while consistent with STM results, actually has a lower surface energy than the two other models [6]. In the LEED calculation, the atoms were allowed to move from their initial positions. The optimized Pendry R-factors (\( R_{p} \)) were found to be 0.29 for the Brookite model, 0.54 for the microfaceting missing-row model.
and 0.66 for the titanyl model. The theoretical $I$-$V$ curves for the Brookite model compared with experimental data are shown in Fig. 4. Comparisons for all the models with the experimental data for two selected beams are shown in Fig. 5. The statistical errors can be estimated by [16]

$$\frac{\Delta R}{R} = \frac{1}{N^{1/2}}$$

where $R$ and $\Delta R$ are the $R$-factor and its standard deviation and $N$ is the effective number of data points given by

$$N = \frac{\Delta E}{4V_i}$$

where $4V_i$ is the peak width, $V_i$ is the imaginary part of potential. $\Delta E$ is the cumulative energy range.

In the present case, $\Delta E = 2200$ eV and $V_i = 5$ eV. Therefore $N \approx 110$. Since only the top 3 layers were allowed to relax in all directions while the next 3 layers were constrained to move vertically, there are 24 structural parameters to be determined, which means that the number of effective data points is sufficient to solve the structure.

By combining Eqs. 3 and 4, we get $\Delta R = 0.028$. From this, the errors in the atomic coordinates may be found. Since any deviation of greater than $\Delta R = 0.028$ from the value of $R = 0.29$ found for the Brookite model is statistically significant, the titanyl and microfacet missing-row models are inconsistent with the LEED data. We show in Table 1 the atomic coordinates of the unreconstructed bulk-terminated surface. The atomic displacements from the bulk positions in the present work compared with previous SXRD and DFT results [6, 7] are summarized in Table 2. The errors are about 0.05 Å for vertical coordinates near the surface and larger for deeper layers. The errors in the Ti-O bond lengths between the top two layers are larger: around 0.1 Å. As seen from the table, the atomic coordinates found by the first set of SXRD data [6] and the LEED experiment agree quite well. The maximum difference in the $z$ coordinates is about 0.04 Å while the deviation in the $x$ and $y$ directions are less than 0.12 Å. The maximum deviations of the LEED results from the second set of SXRD data [7] are bigger. They are 0.19 Å perpendicular to the surface and 0.47 Å along the surface.

Next we will consider the effect of charge self-consistency on LEED analysis. With the easy access of user-friendly, full-potential DFT codes and major improvements in computer performance, calculation of self-consistent potentials have become much easier. Therefore, the question of self-consistency should not be of great practical concern. In most surfaces previously studied by LEED [14, 17], which consist mostly of metals and semi-conductors, non-self-consistent phase shifts, typically calculated by the Mattheiss prescription [18], have tended to produce spectra in good agreement with experiments. However, in recent work on TiO$_2$(110)(1x1) [11], it has been suggested that LEED calculations with self-consistent charges significantly affect the Pendry R-factor, compared with non-selfconsistent calculations. This naturally raises the question of whether
self-consistency, though unimportant for non-insulators, may be necessary for insulating oxide surfaces, where charge transfer between cations and anions is relatively large. In contrast, a previous LEED study on MgO(111)(1x1) \[10\] suggested this effect did not have a noticeable effect on LEED calculations. If so, it is hard to see why self-consistency would have a greater effect for a less ionic surface like TiO\textsubscript{2}. In fact, according to our DFT calculations, the charge transfer between Ti and O muffin-tins is less than 1/2 of an electron. We compare in Fig. 6 the phase shifts for Ti and O muffin-tins obtained from both self-consistent and non-self-consistent potentials with the muffin-tin radii exactly the same as what was used in reference [11]. The self-consistent phase shifts were obtained by FLEUR \[13\] and the non-self-consistent phase shifts by the MUPPOT program \[17\] on the basis of the Mattheiss prescription. The difference between the two sets of phase shifts is seen to be quite small. We have also repeated our structural search with the non-self-consistent phase shifts. It was found that the R-factor changes from 0.29 to 0.28, and the change in the optimized atomic coordinates are within the error limits. This contradicts the large effect of charge self-consistency found in the LEED analysis of the TiO\textsubscript{2}(110)(1x1) surface, which dramatically improves the R-factor from 0.64 to 0.29 \[11\]. Our findings confirm the common belief that due to the fact that LEED electrons need to approach the atomic nuclei to have their momenta changed sufficiently to be detected in backscattering, they are more sensitive to the inner-core atomic potentials, which are little affected by self-consistent-potential calculations. Our conclusion is that the potential may have some small effect on the R factor but will not have a significant effect on the final optimized structure, even for oxides. A recent LEED study \[19\] also reaches essentially the same conclusion. It points out that parameters such as the muffin-tin radii and energy dependence of inner potentials actually may have larger effects on the R-factor than charge self-consistency.

6. Conclusion

We have performed a structural search on the 2 × 1 surface of TiO\textsubscript{2}(011) by quantitative LEED analysis of data from a low beam current DLD-LEED system, which allows study of insulating oxides. The present study confirms the Brookite model found by surface x-ray diffraction, with agreements in atomic displacements within 0.04 Å perpendicular to the surface, and 0.12 Å parallel to the surface. This definitively rules out the other previously proposed models in the literature which have significantly higher R factors, and opens the way to the study of complicated reconstructed oxides using quantitative LEED. It was also found that self-consistency in the potential has little effect on the structural results for oxide surfaces, contrary to claims elsewhere.

Acknowledgments: HCP and DKS (PI) acknowledge support for this work from the U.S. Department of Energy (Grant No. DE-FG02-84ER45076). We thank Ulrike Diebold for useful discussions.
References

Table 1: The atomic coordinates of the unreconstructed bulk-terminated surface. Only half of the unit cell is given. The other half can be generated by glide plane symmetry.

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<th>x (Å)</th>
<th>y (Å)</th>
<th>z (Å)</th>
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<td>0.76</td>
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<tr>
<td>O</td>
<td>2.73</td>
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<td>0.76</td>
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<tr>
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<td>0.00</td>
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<tr>
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<td>1.15</td>
<td>-2.49</td>
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<tr>
<td>Ti</td>
<td>5.89</td>
<td>3.44</td>
<td>-2.49</td>
</tr>
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Table 2: The atomic displacements from the bulk positions in the present work compared with previous SXRD and DFT results [6, 7] for the TiO$_2$(011)(2x1) surface. Note that our x-y coordinate system is orthogonal to the references.

<table>
<thead>
<tr>
<th>atom</th>
<th>O</th>
<th>O</th>
<th>Ti</th>
<th>Ti</th>
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</table>

- O: 2.99 3.00 3.12 2.90 2.71 -2.61 -2.48 -2.48 -2.52 -2.20 0.63 0.78 0.87 0.62 0.82
- Ti: 0.39 0.32 0.42 0.32 0.32 -0.47 -0.59 -0.59 -0.56 -0.62 0.39 0.59 0.66 0.43 0.36
- Ti: -1.75 -1.77 -1.66 -1.76 -1.77 0.02 -0.11 -0.10 -0.09 -0.14 -0.77 -0.74 -0.73 -0.80 -0.73
- O: 0.31 0.26 0.35 0.27 0.27 -0.09 0.04 -0.07 0.00 -0.27 -0.08 -0.03 0.01 -0.06 -0.06
- O: 0.36 0.40 0.49 0.42 0.58 -0.27 -0.15 -0.15 -0.15 0.20 -0.01 -0.06 -0.06 -0.01 -0.14
- O: -0.11 -0.14 0.00 -0.06 -0.09
- O: -0.03 -0.01 -0.15 -0.06 -0.17
- Ti: -0.12 -0.03 0.07 -0.06 -0.08
- Ti: -0.05 -0.04 -0.09 -0.07 -0.05
Figure 1: LEED pattern of TiO$_2$(011)(2x1) surface at 98 eV
Figure 2: (a) top view and (b) side view of bulk-terminated TiO$_2$(011)(1x1) surface. Ti atoms are represented by smaller white spheres and O atoms by larger gray spheres. The two lines in (a) indicate the positions of the glide planes.
Figure 3: Side view of (a) Brookite model [6, 7] (b) microfaceting missing-row model [5] and (c) titanyl model [4] for TiO$_2$(011)$(2\times1)$ surface. Ti atoms are represented by smaller white spheres and O atoms by larger gray spheres.
Figure 4: Comparison of the experimental (dashed line) and best-fit calculated (solid line) spectra of 20 non-equivalent beams for the Brookite model in Fig. 3a. The average Pendry R-factor is 0.29.
Figure 5: Comparison of the experimental (dashed line) and best-fit calculated (solid line) LEED spectra of 2 selected beams for all the models in Fig. 3.
Figure 6: Comparison of phase shifts for Ti and O calculated from self-consistent (solid line) and non-self-consistent (dashed line) potentials. $l$ is the angular momentum of the incident electron wave.