

Geometric structure of $\text{TiO}_2(110)(1 \times 1)$: Confirming experimental conclusions

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Low-energy electron-diffraction and surface x-ray diffraction data acquired from $\text{TiO}_2(110)(1 \times 1)$ are re-analyzed to confirm the integrity of the previously reported optimized geometries. This work is performed in response to *ab initio* density-functional theory calculations that suggest that the atomic displacements determined from low-energy electron-diffraction measurements may be compromised by the limited number of optimized atom positions. Performing structural optimizations as a function of depth into the selvedge, this present study validates the previous experimental structure determinations.

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$\text{TiO}_2(110)(1 \times 1)$ has emerged as the prototypical metal-oxide surface for fundamental studies in ultrahigh vacuum.^{1,2} A key element of the prominence of this substrate is a reliable quantitative description of its stoichiometric geometric structure. Such knowledge has been derived in four contemporary experimental studies,^{3–6} each using a different diffraction technique, i.e., quantitative low-energy electron diffraction (LEED-IV),³ medium energy ion scattering,⁴ photoelectron diffraction,⁵ and surface x-ray diffraction (SXR).⁶ The four independently optimized structures resulting from this body of work exhibit a high degree of agreement, demonstrating experimental consensus. *Ab initio* calculations, however, suggest that the atomic displacements determined from LEED-IV (Ref. 3) may result from the limited number of adjustable atomic layers employed during structure optimization.^{7,8} Here, we demonstrate otherwise, confirming the essential validity of both the previous LEED-IV (Ref. 3) and SXR (Ref. 6) structure determinations.

Thompson and Lewis have employed density-functional theory (DFT) with the generalized gradient approximation (GGA) to calculate the surface energy and geometry of $\text{TiO}_2(110)(1 \times 1)$.^{7,8} Calculations were performed using a series of suitably oriented two-dimensional TiO_2 slabs of increasing thickness to examine the impact of this parameter on both energetic and geometric convergence. Figure 1(a) displays a ball-and-stick model of one of these slabs, which is referred to as a five-trilayer slab in Refs. 7 and 8; the trilayer units are indicated in the figure. It should be noted that all of the slabs considered were centrosymmetric, resulting in their upper and lower halves being equivalent, as indicated by the mirror plane in Fig. 1(a). In accord with pre-

vious work,⁹ it was concluded^{7,8} that a slab consisting of 13 trilayers is required to achieve a fully converged surface energy, i.e., there is no significant variation in surface energy at greater slab thicknesses.

A geometrically converged slab was attained by Thompson and Lewis at nine trilayers. Notably, this relaxed *ab initio* DFT-GGA geometry is not consistent with experimental work.^{3–6} There is, however, good coincidence between the optimized geometry of a thinner, five-trilayer slab [Fig. 1(a)] and the optimized LEED-IV structure;³ the atoms adjusted in Ref. 3 during structure optimization are indicated in Fig. 1(b). It is concluded that this agreement is a result of virtually the same atoms being optimized in both the five-trilayer slab total energy minimization and the LEED-IV structure determination, as can be discerned from Figs. 1(a) and 1(b), remembering that a mirror plane is imposed in Fig. 1(a). On this basis, Thompson and Lewis implicitly suggest that increasing the depth of the optimized selvedge may significantly alter the LEED-IV solution. In this Brief Report, this possibility is addressed by explicitly reanalyzing LEED-IV data collected from $\text{TiO}_2(110)(1 \times 1)$ (Ref. 3) as a function of depth into the selvedge. The SXR data presented in Ref. 6 are similarly re-examined. In both cases, the earlier optimized structures are validated, removing any ambiguity suggested in Refs. 7 and 8.

For this study, the LEED-IV and SXR experimental data sets were identical to those analyzed previously.^{3,6} Surface-structure determination involved generating simulated diffraction data for a potential structure, and then iteratively optimizing the geometry to achieve the best fit between experimental and simulated data. The same software packages that were used in Refs. 3 and 6 were employed for this pur-

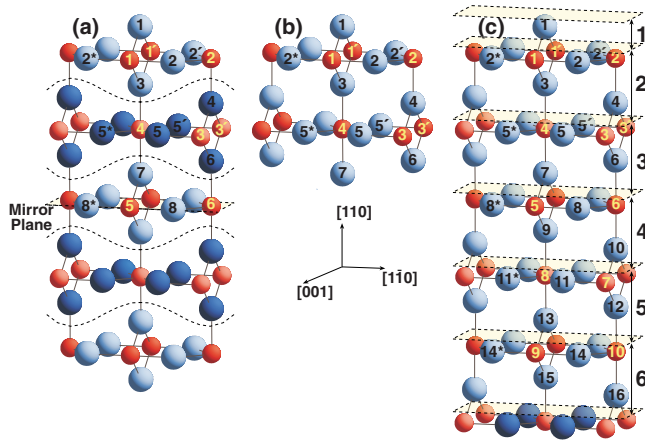


FIG. 1. (Color online) Ball-and-stick models of $\text{TiO}_2(110)(1 \times 1)$. Larger (smaller) spheres are oxygen (titanium) atoms. The numerical labeling of the atoms is to allow identification. Symmetry paired (equivalent) atoms are denoted by * ('). (a) An example of the type of slab used by Thompson and Lewis for their *ab initio* calculations on $\text{TiO}_2(110)(1 \times 1)$ (Refs. 7 and 8). A five-trilayer slab is depicted. The upper and lower halves of the slab are indistinguishable, as indicated by the mirror plane. Trilayer units are picked out by use of alternate darker/lighter shading, along with dashed lines. (b) Atoms optimized in Ref. 3 during determination of $\text{TiO}_2(110)(1 \times 1)$ geometry from LEED-IV data. (c) The layering scheme employed in the present study to investigate how the depth of the optimized selvage impacts upon the LEED-IV/SXRD solutions.

pose, i.e., the Barberi-Van Hove Automated Tensor LEED code¹⁰ and the DL_LEED package¹¹ for LEED-IV, and the ROD software¹² for SXRD. Furthermore, the *self-consistent* phase shifts applied in Ref. 3 were again adopted for generating simulated LEED-IV data. Goodness of fit between experimental and simulated data was quantitatively assessed for LEED-IV and SXRD by the Pendry reliability factor (R_p) (Ref. 13) and χ^2 ,¹⁴ respectively. For both the LEED-IV and SXRD analyses, all nonstructural parameters were constrained to be the same as those used for generating the original best-fit simulated data,^{3,6} except for one LEED-IV parameter, the inner potential, which was allowed to vary freely. As a check on the integrity of the analysis procedures, it was confirmed that the best fits were essentially identical to those obtained previously if the same parameters were employed [LEED-IV: $R_p=0.29$ (Ref. 3) and SXRD: $\chi^2=1.5$ (Ref. 6)].

To investigate how the depth of the optimized selvage impacts upon the LEED-IV/SXRD solutions, structure determinations have been performed as a function of the number of adjustable layers. The layers employed are depicted in Fig. 1(c). As illustrated, the first layer consists simply of the so-called bridging oxygen atoms, whereas each of the deeper layers are composed of an upper Ti-O plane above an O bilayer. This layering scheme was chosen to allow direct comparison with the *ab initio* DFT-GGA slab calculations,^{7,8} as virtually the same atoms are optimized in $(n+1)/2$ LEED-IV/SXRD adjustable layers as in a calculated n -trilayer slab [N.B. Displacements of atoms lying on the mirror plane indicated in Fig. 1(a) are symmetry forbidden during optimi-

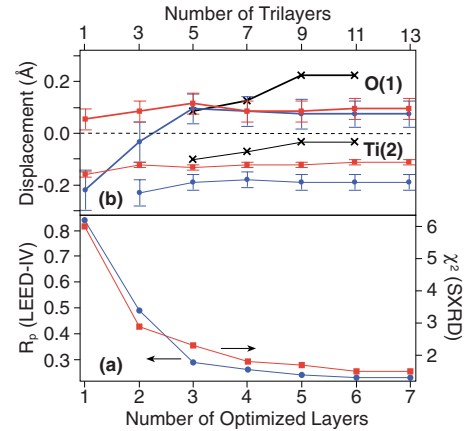


FIG. 2. (Color online) (a) Best fit R_p 's (LEED-IV) (solid circle markers) and χ^2 's (SXRD) (solid square markers) are plotted as a function of the number of layers optimized. The layering scheme is illustrated in Fig. 1(c). (b) Displacement of O(1) (bridging oxygen) and Ti(2) (fivefold titanium) also plotted as a function of the number optimized layers. These two atoms can be identified by reference to Fig. 1(c). There are three plots for each atom, corresponding to the displacements obtained from LEED-IV (solid circle markers), SXRD (solid square markers), and *ab initio* DFT-GGA calculations (crosses) (Refs. 7 and 8). To plot the latter on the same x axis the near equivalence, in terms of adjustable atoms, of $(n+1)/2$ LEED-IV/SXRD layers and an *ab initio* n -trilayer slab was employed. For clarity, an upper x axis showing the corresponding number of trilayers is included.

zation, expect for in-plane shifts of O(8) and O(8*)]. Furthermore, layers 1, 2, and 3 in Fig. 1(c) correspond to the atoms optimized in the original LEED-IV structure determination [Fig. 1(b)].³ Best fit R_p 's (LEED-IV) and χ^2 's (SXRD) as a function of the number of adjustable layers are plotted in Fig. 2(a). As evidenced by the decrease in R_p/χ^2 , it is clear that initially the fits improve considerably as the number of layers optimized increases. Beyond six optimized layers (equivalent to an 11-trilayer calculated slab) there is no further significant improvement in either R_p or χ^2 , i.e., the fits become converged as regards this parameter.

Concerning the LEED-IV analysis, it is striking that the lowest R_p (i.e., 0.23) is appreciably smaller than the value (i.e., 0.29) obtained following optimization of only the atoms considered in the original structure determination.³ Table I lists the atomic displacements away from bulk termination for $R_p=0.23$ (six-layer optimization), along with those presented in Ref. 3 (three-layer optimization). Differences ($\Delta_{\text{LEED-IV}}$) between corresponding atomic displacements are also given. Not all $\Delta_{\text{LEED-IV}}$'s are 0, which is expected from the observed decrease in R_p . However, there are no significant discrepancies between the two optimum structures as all $\Delta_{\text{LEED-IV}}$'s are within experimental error. The least insignificant $\Delta_{\text{LEED-IV}}$'s are for the vertical and lateral displacements of O(2), namely, 0.08 ± 0.11 and 0.07 ± 0.20 Å, respectively. We have explored the possibility that these relatively large $\Delta_{\text{LEED-IV}}$'s are a result of correlation between these two parameters but have found no evidence to support this idea.

Also listed in Table I are the atomic displacements associated with the converged six-layer SXRD optimization. It

TABLE I. Atomic displacements away from bulk-terminated $\text{TiO}_2(110)(1 \times 1)$ obtained from analysis of LEED-IV data optimizing three layers (Ref. 3) reanalysis of the same LEED-IV data optimizing six layers (current work), and analysis of SXR D data again optimizing six layers (Ref. 6) (current work). Also listed are differences ($\Delta_{\text{LEED-IV}}$) between corresponding atomic displacements for the two LEED-IV determinations. Figure 1(c) shows both the layering scheme and the identity of the atoms. A negative value indicates that the atom moves toward the bulk for a displacement perpendicular to the surface plane, and in the $[1\bar{1}0]$ direction for a lateral displacement. (N.B. In Ref. 6, the SXR D derived displacement of O(7) is erroneously given as 0.01 ± 0.04 Å. The value of this parameter should be 0.00 ± 0.04 Å, as stated here.)

| (Å) | | | | |
|-----------------------|----------------------------------|--------------------------------------|---------------------------|---|
| Atom | Displacement LEED-IV (Ref. 3) | Displacement LEED-IV current work | $\Delta_{\text{LEED-IV}}$ | Displacement SXR D current work/Ref. 6 |
| O(1) | 0.10 ± 0.05 | 0.08 ± 0.05 | 0.02 ± 0.07 | 0.10 ± 0.04 |
| O(2) [110] | 0.27 ± 0.08 | 0.19 ± 0.08 | 0.08 ± 0.11 | 0.17 ± 0.03 |
| O(2) [$1\bar{1}0$] | -0.17 ± 0.15 | -0.10 ± 0.13 | 0.07 ± 0.20 | 0.01 ± 0.05 |
| Ti(1) | 0.25 ± 0.03 | 0.24 ± 0.03 | 0.01 ± 0.04 | 0.25 ± 0.01 |
| Ti(2) | -0.19 ± 0.03 | -0.19 ± 0.03 | 0.00 ± 0.04 | -0.11 ± 0.01 |
| O(3) | 0.06 ± 0.10 | 0.07 ± 0.10 | 0.01 ± 0.14 | 0.07 ± 0.04 |
| O(4) | 0.00 ± 0.08 | 0.00 ± 0.08 | 0.00 ± 0.11 | 0.00 ± 0.03 |
| O(5) [110] | 0.06 ± 0.12 | 0.07 ± 0.12 | 0.01 ± 0.17 | 0.04 ± 0.03 |
| O(5) [$1\bar{1}0$] | -0.07 ± 0.18 | -0.04 ± 0.17 | 0.03 ± 0.25 | 0.05 ± 0.05 |
| Ti(3) | -0.09 ± 0.07 | -0.11 ± 0.04 | 0.02 ± 0.08 | -0.08 ± 0.01 |
| Ti(4) | 0.14 ± 0.05 | 0.14 ± 0.03 | 0.00 ± 0.06 | 0.19 ± 0.01 |
| O(6) | 0.00 ± 0.17 | -0.01 ± 0.14 | 0.01 ± 0.22 | 0.01 ± 0.04 |
| O(7) | 0.01 ± 0.13 | 0.03 ± 0.15 | 0.02 ± 0.20 | 0.00 ± 0.04 |
| O(8) [110] | | 0.03 ± 0.11 | | 0.01 ± 0.03 |
| O(8) [$1\bar{1}0$] | | -0.03 ± 0.26 | | -0.03 ± 0.05 |
| Ti(5) | | 0.06 ± 0.09 | | 0.08 ± 0.01 |
| Ti(6) | | -0.07 ± 0.07 | | -0.04 ± 0.01 |
| O(9) | | 0.13 ± 0.56 | | 0.02 ± 0.04 |
| O(10) | | -0.02 ± 1.70 | | -0.02 ± 0.04 |
| O(11) [110] | | 0.00 ± 0.18 | | 0.01 ± 0.03 |
| O(11) [$1\bar{1}0$] | | -0.02 ± 1.02 | | 0.01 ± 0.04 |
| Ti(7) | | 0.10 ± 0.19 | | -0.02 ± 0.01 |
| Ti(8) | | -0.03 ± 0.13 | | 0.07 ± 0.01 |
| O(12) | | 0.01 ± 1.73 | | 0.02 ± 0.02 |
| O(13) | | 0.03 ± 1.76 | | 0.00 ± 0.02 |
| O(14) [110] | | 0.02 ± 1.74 | | 0.03 ± 0.03 |
| O(14) [$1\bar{1}0$] | | $0.06 \pm > 2.00$ | | -0.02 ± 0.03 |
| Ti(9) | | 0.06 ± 1.77 | | 0.02 ± 0.01 |
| Ti(10) | | 0.12 ± 1.74 | | -0.01 ± 0.01 |
| O(15) | | $0.02 \pm > 2.00$ | | 0.00 ± 0.02 |
| O(16) | | -0.14 ± 1.76 | | -0.02 ± 0.02 |

should be pointed out that these displacements are identical to those presented in the original SXR D structure determination,⁶ as the same atoms were optimized in both cases, although the displacements of deeper atoms were not explicitly stated in Ref. 6. As already discussed in Refs. 2 and 6, the agreement between the optimum LEED-IV and SXR D structures is impressive, especially as many of the atomic displacements have been determined rather precisely. As regards precision, one further point to glean from Table I is that the LEED-IV error bars increase much more rapidly with depth than those associated with the SXR D measurements. This phenomenon is to be expected given the greater surface sensitivity of LEED.

On the basis of the above results, it is clear that the original optimum atomic displacements determined for

$\text{TiO}_2(110)(1 \times 1)$ from LEED-IV data³ are not erroneous due to the limited depth of the optimized surface selvedge. It is not disputed that adjusting too few atoms can influence the outcome of such a structure determination. However, this is not the case in Ref. 3. These two points are demonstrated graphically in Fig. 2(b), which displays the displacement of two surface atoms, O(1) (bridging oxygen) and Ti(2) (five-fold titanium), as a function of the number of optimized layers. There are three plots for each atom, showing the displacements obtained from LEED-IV (solid circle markers), SXR D (solid square markers), and *ab initio* DFT-GGA calculations (crosses)^{7,8} (N.B. To plot the theoretically derived displacements on the same x axis the near equivalence, in terms of adjustable atoms, of $(n+1)/2$ LEED-IV/SXR D layers and an *ab initio* calculated n trilayer slab was employed.

TABLE II. Selected bond lengths and bond angles derived from optimized atomic displacements given in Table I. Also listed are bulk-terminated bond lengths and angles. Figure 1(c) provides a key to the identity of the atoms.

| Atoms | Bond length (Å) | | |
|------------|---------------------|-------------------------|--------------------------------|
| | Bulk termination | LEED-IV current work | SXRD current work Ref. 6 |
| Ti(1)-O(1) | 1.95 | 1.84 ± 0.03 | 1.85 ± 0.02 |
| Ti(1)-O(2) | 1.98 | 2.08 ± 0.13 | 1.97 ± 0.05 |
| Ti(1)-O(3) | 1.95 | 2.06 ± 0.07 | 2.07 ± 0.03 |
| Ti(2)-O(2) | 1.95 | 1.92 ± 0.08 | 1.97 ± 0.03 |
| Ti(2)-O(4) | 1.98 | 1.79 ± 0.09 | 1.87 ± 0.03 |
| Ti(3)-O(4) | 1.95 | 2.02 ± 0.06 | 2.00 ± 0.02 |
| Ti(3)-O(5) | 1.98 | 1.95 ± 0.17 | 2.03 ± 0.05 |
| Ti(3)-O(6) | 1.95 | 1.88 ± 0.09 | 1.89 ± 0.03 |
| Ti(4)-O(3) | 1.98 | 1.91 ± 0.10 | 1.86 ± 0.04 |
| Ti(4)-O(5) | 1.95 | 1.97 ± 0.11 | 1.92 ± 0.03 |
| Ti(4)-O(7) | 1.98 | 2.09 ± 0.15 | 2.17 ± 0.04 |

| Atoms | Bond angle (°) | | |
|-------------------|---------------------|-------------------------|--------------------------------|
| | Bulk termination | LEED-IV current work | SXRD current work Ref. 6 |
| Ti(1)-O(1)-Ti(1') | 99 | 106 ± 2 | 106 ± 2 |
| O(1)-Ti(1)-O(3) | 81 | 81 ± 5 | 81 ± 2 |
| Ti(1)-O(2)-Ti(2) | 131 | 128 ± 4 | 131 ± 2 |
| O(2)-Ti(2)-O(2') | 99 | 101 ± 3 | 97 ± 2 |
| O(2)-Ti(2)-O(4) | 90 | 101 ± 6 | 98 ± 2 |
| Ti(3)-O(4)-Ti(3') | 99 | 94 ± 2 | 95 ± 2 |
| O(4)-Ti(3)-O(6) | 81 | 81 ± 7 | 80 ± 2 |
| Ti(3)-O(5)-Ti(4) | 131 | 131 ± 5 | 130 ± 2 |
| O(5)-Ti(4)-O(5') | 99 | 97 ± 5 | 101 ± 2 |
| O(5)-Ti(4)-O(7) | 90 | 88 ± 8 | 86 ± 2 |

For clarity, an upper x axis showing the corresponding number of trilayers is included in the figure). Focusing on the

experimentally derived data, it can be seen that for both O(1) and Ti(2) displacement becomes almost constant for three-layer optimization and beyond. For one- and two-layer optimizations, the displacement of O(1) obtained from LEED-IV, in particular, varies significantly.

Figure 2(b) also shows that the converged *ab initio* DFT-GGA displacements of both O(1) and Ti(2) (Refs. 7 and 8) are not consistent with experiment. Moreover, it is almost certain that the reported^{7,8} coincidence of the five-trilayer *ab initio* DFT geometry and the original LEED-IV solution [three-layer optimization shown in Fig. 2(b)] is simply fortuitous. We note that other *ab initio* DFT calculations of the geometric structure of TiO₂(110)(1 × 1), employing slightly different approximations, more closely match the experimental structural solution.^{15,16} The extreme sensitivity of the computed structure to adopted approximations has previously been analyzed in terms of soft vibrational modes both in the bulk¹⁷ and at the (110) surface.¹⁸

Finally, Thompson and Lewis propose that optimized surface geometries, either computed or experimental, should be reported in terms of bond lengths and bond angles rather than atomic displacements.⁸ They argue that this approach would present the structure “in terms of more physically relevant quantities.” While it is clear one can simply translate atomic displacements into bond lengths and angles, we do agree that for some purposes explicit listing of these latter parameters would give more immediate insight. Thus, a list of bond lengths and bond angles between selected atoms are given in Table II.

In summary, LEED-IV and SXRD data acquired from TiO₂(110)(1 × 1) have been reanalysed to confirm the reliability of the original structure determinations.^{3,6} More specifically, prompted by *ab initio* DFT-GGA calculations^{7,8} structural optimization has been performed as a function of depth into the seldedge. This present study validates the previous structural solutions.^{3,6}

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