

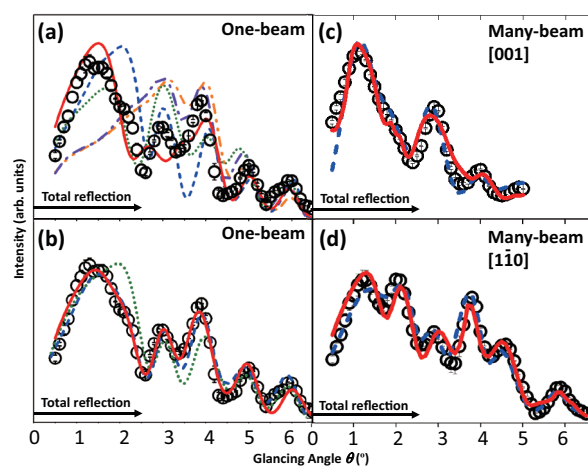
## Structure Determination of the Rutile-TiO<sub>2</sub>(110)-(1×2) Surface Using Total-Reflection High-Energy Positron Diffraction (TRHEPD)

The exact structure of the rutile-TiO<sub>2</sub>(110)-(1×2) surface, which had been under debate for the past 30 years, was investigated using total-reflection high-energy positron diffraction (TRHEPD). The rocking curves of the 00-spot obtained from the experimental diffraction patterns were compared with the curves for various models. The rocking curves matched those for the model consisting of a Ti<sub>2</sub>O<sub>3</sub> composition, originally suggested by Onishi and Iwasawa [1], but with a further modification of atomic positions close to the ones proposed by Wang *et al.* [2].

Titania (TiO<sub>2</sub>) is a transition metal-oxide used in a variety of applications including photo-catalysts, metal-nanoparticle catalyst supports, gas sensors and corrosion-protective coating materials [3-5]. In addition, it is used as a standard material [6] to test the catalytic processes of metal oxides. Knowledge of the structure of the surface where the catalytic processes occur is crucial for studying the fundamentals of the reactivity and reaction mechanisms of solid catalysts [7].

In the present study, we successfully used total-reflection high-energy positron diffraction (TRHEPD) [8-11], which is the positron counterpart of reflection high-energy electron diffraction (RHEED), to determine the atomic arrangement of the rutile-TiO<sub>2</sub>(110)-(1×2) surface [11]; the detailed structure of the surface of the well-known photocatalyst had been under debate for the past 30 years [6].

To prepare the TiO<sub>2</sub> samples [11], the rutile-TiO<sub>2</sub>(110)-(1×1) surface, which is thermodynamically the



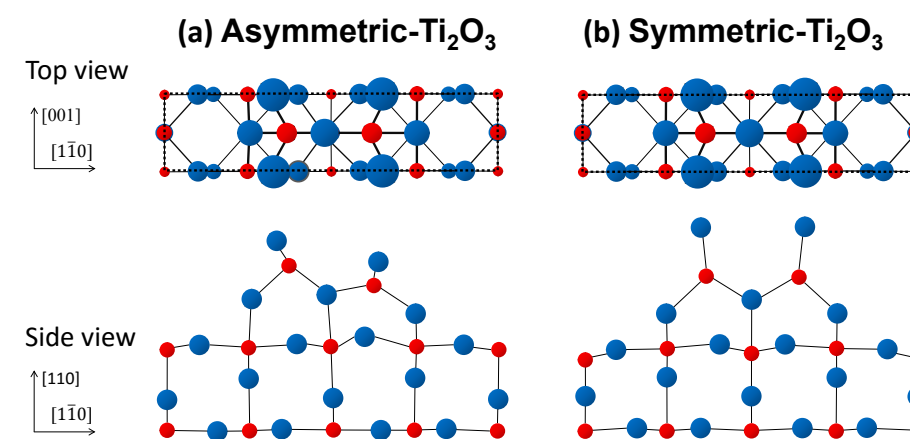
**Figure 1:** TRHEPD rocking curves for the rutile-TiO<sub>2</sub>(110)-(1×2) surface. Open circles in (a) and (b) are the same experimental data, obtained under a one-beam condition. Those in (c) and (d) are the data obtained under many-beam conditions; (c) for the [001] direction and (d) for the [110] direction. The solid (red), broken (blue), dotted (green), double-dotted-broken (orange) and single-dotted-broken (purple) curves are calculated results for the asymmetric-Ti<sub>2</sub>O<sub>3</sub> [2], the symmetric-Ti<sub>2</sub>O<sub>3</sub> [12], the Ti<sub>2</sub>O [13], the missing-row [14] and the Ti<sub>3</sub>O<sub>5</sub> [15] models, respectively, using the atomic coordinates (a) proposed in the original studies and (b)-(d) adjusted to give better *R* values.

most stable phase of this material, was created under an ultra-high vacuum, and then converted to a (1×2) structure by heating to ~1200 K. A high-intensity positron beam was directed onto this surface at a small glancing angle ( $\theta = 0-6^\circ$ ) to obtain a diffraction pattern. Rocking curves were then obtained by plotting the intensity of the mirror-reflected (00) spot of the pattern against the glancing angle, followed by a prediction calculation with the proposed structural models [1, 2, 12-15] so that the experimental results could be explained by any of them.

The open circles in Fig. 1a show the experimental data [11] for the (1×2) surface in the one-beam condition; the 00-spot intensity in this case almost solely depends on the *z* coordinates of the atomic positions. The calculated rocking curves, using the atomic coordinates proposed in Refs. 1, 2 and 12-15 are also shown and are denoted as follows: the red solid curve for the asymmetric-Ti<sub>2</sub>O<sub>3</sub> model [2], the blue broken curve for the symmetric-Ti<sub>2</sub>O<sub>3</sub> model [1, 12]; the green dotted curve for the Ti<sub>2</sub>O model [13]; the orange double-dotted-broken curve for the missing-row model [14]; and the purple single-dotted-broken curve for the Ti<sub>3</sub>O<sub>5</sub> model [15].

Neither the missing-row (orange double-dotted-broken curve) model nor the Ti<sub>3</sub>O<sub>5</sub> (purple single-dotted-broken curve) model reproduces the peak shape in the total-reflection region around  $\theta = 1.5^\circ$ , giving poor values of a reliability factor (*R*) [11], 7.1% and 6.9%, respectively. Therefore, these models were eliminated as possible candidates and are not discussed further.

The asymmetric-Ti<sub>2</sub>O<sub>3</sub> (red solid curve), the symmetric-Ti<sub>2</sub>O<sub>3</sub> (blue broken curve), and the Ti<sub>2</sub>O (green dotted curve) models, giving *R* values of 3.1%, 4.6% and 5.3%, respectively, have a peak in the total-reflection region. Taking these three as the more likely contenders, their rocking curves were recalculated to give better (smaller) *R* values by adjusting the atomic coordinates from those originally proposed [2, 12, 13]; the results are shown in Fig. 1b, using the same keys as in Fig. 1a. The *R* values for the adjusted coordinates are 1.3% for the asymmetric-Ti<sub>2</sub>O<sub>3</sub> model, 1.7% for the symmetric-Ti<sub>2</sub>O<sub>3</sub> model, and 3.1% for the Ti<sub>2</sub>O model. The *R* values for both the Ti<sub>2</sub>O<sub>3</sub> compositional models are small enough



**Figure 2:** Schematic top and side views of the rutile-TiO<sub>2</sub>(110)-(1×2) surface; (a) the optimized asymmetric-Ti<sub>2</sub>O<sub>3</sub> model and (b) the optimized symmetric-Ti<sub>2</sub>O<sub>3</sub> model. The dotted rectangle indicates a (1×2) unit cell. Red and blue circles represent Ti and O atoms, respectively. In the top view, Ti and O atoms at higher positions are depicted by circles with larger diameters.

to be considered as good candidates for the (1×2) structure, while that for the Ti<sub>2</sub>O model is not enough, reflecting the mismatch around  $\theta = 2.0^\circ$  and  $3.5^\circ$ . Thus, it is concluded that the “Ti<sub>2</sub>O<sub>3</sub>” composition, originally suggested by Onishi and Iwasawa [1], is essential for a correct (1×2) structure.

The open circles in Fig. 1c and Fig. 1d show the experimental data [11] obtained under many-beam conditions with incident beams set along the [001] and [110] directions, respectively; the 00-spot intensity in such a case depends on the in-plane coordinates of atomic positions, as well as the *z* coordinates which are already settled by the one-beam analysis. The optimized curves are also shown, using the same keys as in Fig. 1a. The schematic top and side views of these optimized configurations are shown in Fig. 2a for the asymmetric-Ti<sub>2</sub>O<sub>3</sub> model and in Fig. 2b for the symmetric-Ti<sub>2</sub>O<sub>3</sub> model.

The corresponding *R* values in the case of the [110] direction (Fig. 1d) are almost the same (~1.8%) for both the optimized models, while that in the case of the [001] direction (Fig. 1c) for the asymmetric-Ti<sub>2</sub>O<sub>3</sub> model, 1.9%, is better than that for the symmetric-Ti<sub>2</sub>O<sub>3</sub> model, 2.4%. As already mentioned in the case of the one-beam condition (Fig. 1b), that for the asymmetric-Ti<sub>2</sub>O<sub>3</sub> model, 1.3%, is better than that for the symmetric-Ti<sub>2</sub>O<sub>3</sub> model, 1.7%.

If we inspect the optimized structures more carefully, the topmost Ti-O bonds in the symmetric-Ti<sub>2</sub>O<sub>3</sub> model (Fig. 2b) are too stretched to be an energetically stable structure. Our preliminary DFT calculation [11] shows in fact that the optimized asymmetric-Ti<sub>2</sub>O<sub>3</sub> model is more stable by ~1.5 eV per (1×2) unit cell than the optimized symmetric-Ti<sub>2</sub>O<sub>3</sub> model, and is also more stable by ~0.2 eV than the original symmetric-Ti<sub>2</sub>O<sub>3</sub> model [1, 12].

From the results of the present TRHEPD analysis [11] and the theoretical prediction by Wang *et al.* [2] using the global optimization method, called USPEX, allowing for both structural and compositional optimiza-

tions of the surface, it is concluded that the asymmetric-Ti<sub>2</sub>O<sub>3</sub> model is the correct structure for the rutile-TiO<sub>2</sub>(110)-(1×2) surface.

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### BEAMLINE

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