(2n × 1) Reconstructions of TiO₂(011) Revealed by Noncontact Atomic Force Microscopy and Scanning Tunneling Microscopy

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ABSTRACT: We have used noncontact atomic force microscopy (NC-AFM) and scanning tunneling microscopy (STM) to study the rutile TiO₂(011) surface. A series of (2n × 1) reconstructions were observed, including two types of (4 × 1) reconstruction. High-resolution NC-AFM and STM images indicate that the (4 × 1)-α phase has the same structural elements as the more widely reported (2 × 1) reconstruction. An array of analogous higher-order (2n × 1) reconstructions were also observed where n = 3–5. On the other hand, the (4 × 1)-β reconstruction seems to be a unique structure without higher-order analogues. A model is proposed for this structure that is also based on the (2 × 1) reconstruction but with additional microfacets of {111} character.

INTRODUCTION

TiO₂ has been investigated intensely since the 1970s when it was discovered that it is an active photocatalyst.¹ Although most surface science studies focus on the most thermodynamically stable rutile TiO₂(110) face,²,³ there is a growing interest in other rutile terminations⁴–¹⁸ as well as anatase TiO₂ surfaces.¹⁹–²¹ The rutile TiO₂(011) surface has received particular interest because of a reportedly enhanced photocatalytic activity.²²,²³

Most studies of TiO₂(011) report a (2 × 1) reconstruction, the structure of which was initially unclear, with two proposed models: a titanyl model⁵ and a microfacet model.⁶ However, three independent diffraction studies have clarified the surface structure,⁹−¹¹ all pointing to the “diffraction model” shown in Figure 1a. Theoretical calculations also find this to be the most stable of the proposed models.⁹,¹⁰ Both the “beanlike” and “zigzag” motifs that appear in scanning tunneling microscopy (STM) images recorded “close to” and “far from” the surface, respectively,¹⁰,¹⁵ could also be reproduced by STM images simulated from the “diffraction model”.¹⁵

In addition to the (2 × 1) phase, Kubo et al.⁶ also report noncontact atomic force microscopy (NC-AFM) and STM images of a coexisting (4 × 1) phase. Ahmed et al.²⁴ also report a (4 × 1) reconstruction following a UHV anneal. Here, we report on a series of (2n × 1) reconstructions that are revealed by NC-AFM and STM images. Two types of (4 × 1) reconstruction were observed, which we refer to as (4 × 1)-α and (4 × 1)-β. The (4 × 1)-α surface has the same structural elements as the widely reported (2 × 1) reconstruction. In an analogous fashion, it is also possible to have an array of such (2n × 1) reconstructions; indeed, we observe a series of (2n × 1)-α reconstructions where n = 2–5. In contrast, the (4 × 1)-β reconstruction seems to be a unique structure without higher order analogues. The proposed structure for (4 × 1)-β has the same structural elements as the (2 × 1) phase but with the addition of {111} microfacets.

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EXPERIMENTAL METHODS

The experiments were performed in Osaka using a custom-built NC-AFM housed in an ultrahigh-vacuum chamber (with a base pressure of \( \sim 5 \times 10^{-11} \) Torr) and operated at room temperature. The TiO\(_2\)(011) crystal (Pi-Kem) was prepared using repeated cycles of Ar-ion bombardment (2 keV) for approximately 5 min and annealing between 1073 and 1273 K for 10–25 min. This gave the \((2n \times 1)\) terminations that we report. Preparation of a different TiO\(_2\)(011) crystal (MaTecK GmbH) with a lower annealing temperature of \( \sim 943–953 \) K led to the more commonly observed \((2 \times 1)\) termination. However, further systematic study is required to establish a definitive recipe for preparation of \((2n \times 1)\) terminations.

NC-AFM images were obtained using the frequency modulation detection method,\(^{15}\) with the cantilever oscillation amplitude kept constant (peak-to-peak amplitudes 176–278 Å). The data presented here were taken with two silicon cantilevers which had resonant frequencies in the range \( \sim 155–156 \) kHz. A DC voltage \((V_{\text{CPD}})\) is added between the tip and sample that minimizes the average tip–sample contact potential difference.

STM images were obtained using the same cantilevers, biased with a voltage \((V_{\text{s}})\), with the oscillation still active such that the current is time-averaged \((I)\). In some cases, the tips were treated by electrical pulses or nanoindentation procedures to ensure sufficient conductivity for STM measurements.

RESULTS AND DISCUSSION

Structure of \((2n \times 1)\) Reconstructions. Figure 2a shows a large-area NC-AFM image of the TiO\(_2\)(011) surface. The image is characterized by a number of bright rows aligned to the [\(0\overline{1}1\)] direction. There are several domains present, which are shaded with different colors in Figure 2b. On the right-hand side, the rows have a \((4 \times 1)\) periodicity. The line profile in Figure 2c is obtained from the green line shown in Figure 2b, which crosses two \((4 \times 1)\) domains. It is clearly evident from the line profile that two types of \((4 \times 1)\) reconstruction are present: on the left-hand side, the corrugation of the rows is about 1.5 Å, whereas on the right-hand side, it is about twice this: \(\sim 3\) Å. We refer to these as the \((4 \times 1)\)-\(\alpha\) and \((4 \times 1)\)-\(\beta\) reconstructions, respectively. Apart from the greater corrugation of the \((4 \times 1)\)-\(\beta\) phase compared with \((4 \times 1)\)-\(\alpha\), the \(\beta\) phase can also be distinguished by its smoother appearance due to a lower density of defects, fixed \((4 \times 1)\) periodicity, and a broader appearance of the rows.

In Figure 2b, the \((4 \times 1)\)-\(\alpha\) regions are unshaded, whereas the \((4 \times 1)\)-\(\beta\) region is shaded light-blue. The center of the image contains rows mostly with a \((6 \times 1)\) periodicity and a very narrow \((2 \times 1)\) domain that is shaded yellow. The \((6 \times 1)\) region is further separated into three domains, shaded light-red and dark-red. The unit cells of the two light-red regions contain two adjacent bright rows, whereas the unit cell of the dark-red region contains only one bright row. It is also apparent that the two light-red regions are out-of-phase with respect to each other, as highlighted by the white guideline in Figure 2b. This suggests that the bright rows in the regions shaded light- and dark-red are the same. In contrast to the \((4 \times 1)\)-\(\beta\) regions, it can also be seen that the other \((2n \times 1)\) regions merge with each other without discernible barriers. For instance, the row highlighted by the black guideline in Figure 2b going from top to bottom straddles \((6 \times 1), (2 \times 1), \) and \((4 \times 1)\)-\(\alpha\) regions.

On the basis that the rows from the \((2n \times 1)\) phases [apart from \((4 \times 1)\)-\(\beta\)] can simultaneously form part of the \((2 \times 1)\) and the higher order \((2n \times 1)\) phases, we propose that with the exception of \((4 \times 1)\)-\(\beta\), all the bright rows from the \((2n \times 1)\) reconstructions have the same structure as that of the \((2 \times 1)\) reconstruction. As such, these phases will be referred to collectively as \((2n \times 1)\)-\(\alpha\). A series of schematic models for these \((2n \times 1)\)-\(\alpha\) structures are shown in Figure 3a. By definition, if the added \((2 \times 1)\) rows are packed with saturation density, then the frequently reported \((2 \times 1)\) reconstruction will be formed.\(^{5–16}\) When the spacing of the added rows is doubled, the \((4 \times 1)\)-\(\alpha\) reconstruction is formed as shown in Figure 3a. Consistent with the NC-AFM image in Figure 2, where two types of \((6 \times 1)\)-\(\alpha\) reconstruction were observed depending on how many bright rows are present (labeled \((6 \times 1)\)-\(\alpha_i\) and \((6 \times 1)\)-\(\alpha_q\) in Figure 2b), two \((6 \times 1)\)-\(\alpha\) models are shown in Figure 3a using either one or two added rows per unit cell.

The high-resolution NC-AFM image in Figure 4a reveals further substructure within the added rows. The rows have a zigzag motif reminiscent of that reported previously in STM images of the \((2 \times 1)\) surface.\(^{5–16}\) The zigzag can be simply defined by a triangle as shown in Figure 4a and highlighted in Figure 4b. The dimensions of the zigzag are shown in Figure 4a in two \((6 \times 1)-\alpha\) triangles. One triangle is isosceles in nature, the equal sides being \(\sim 3.8 \pm 0.4\) Å and the long side being 5.45 Å. The latter side is in line with the unit cell along the [\(0\overline{1}1\)] direction and used to calibrate the measurements. The dimensions of this triangle are remarkably
close to those measured from STM images of the TiO$_2$(011)-(2n × 1)-α phase with zigzag contrast.\textsuperscript{15}

Empty-state STM images taken from a similar area of the surface are shown in Figure 5. The same zigzag motif is discernible, and again, it can be described by an isosceles triangle with a long side of 5.45 Å and equal sides of $\sim 3.9 \pm 0.3$ Å. This gives strong evidence to support our model where the added rows are composed of the same rows that form the (2 × 1) phase.

In empty-state STM, when the tip is relatively close to the sample, a beanlike contrast is found that is dominated by tunneling into O 2p states because the O atoms protrude further out of the surface. On the other hand, when the tip is further from the surface, the zigzag contrast is found. The zigzag contrast is dominated by tunneling into Ti 3d states because of its longer decay length compared to the O 2p states.\textsuperscript{15} Given that the zigzag contrast is electronic in nature, it does not necessarily follow that a similar contrast should be seen in NC-AFM. However, a similar interplay between the decay of the tip–sample potential and the surface geometry could be at play, and theoretical calculations would shed more light on this. Note that at this stage, it is also not clear if the zigzag motif in NC-AFM arises from Ti, and this could be established by simultaneous measurement of NC-AFM and STM.

While evidence has been presented for the structure of the added rows of the (2n × 1)-α reconstructions, the platform on which the added rows sit has not yet been discussed. The models in Figure 3a show these added rows on a (1 × 1) platform simply to highlight the periodicity of the added rows. However, inspection of Figure 4 shows that this is not necessarily the case. Two (6 × 1) units are marked in Figure 4a: one on the left-hand side and one in the center of the image. That on the left-hand side has a darker row (marked with a red line) as well as a bright row in the unit cell. The line profile in Figure 4c also shows this extra darker row clearly, the peak being about 1 Å lower than those of the bright rows.
Figure 6. NC-AFM images and line profiles of TiO$_2$(011)-(2n × 1)-α. (a) Image parameters are 150 Å × 75 Å, Δf = −7.5 Hz, V$_{CPD}$ = 0.6 V. (b) Line profile along the green line marked in (a). (c) Image parameters are 62.5 Å × 30 Å, Δf = −9.1 Hz, V$_{CPD}$ = 0.6 V. (d) Line profile along the green line marked in (c). (e) Image parameters are 70 Å × 35 Å, Δf = −7.5 Hz, V$_{CPD}$ = 0.6 V. (f) Line profile along the green line marked in (e). In (a), (c), and (e), the light-blue lines indicate a 2× spacing with double-ended arrows indicating 4× and 6× periodicities and green crosses marking the position of point defects. For easy comparison, the line profiles are drawn with the same x-axes scales as their corresponding images.

On the other hand, there does not appear to be an extra darker row between the added rows of the (4 × 1) part of the (6 × 1) structure in the center of the image. Figure 6a shows an NC-AFM image with a (4 × 1)-α region adjacent to a (6 × 1)-α region. The (4 × 1)-α region is clearly composed of alternating brighter and darker rows, also highlighted in the line profile in Figure 6b. Figure 6c shows a higher resolution image of the (4 × 1)-α region. The rows have an almost identical appearance, except the upper added rows are slightly broader. This is because they lie topographically higher and therefore part of their side structure is resolved. Likewise, in the NC-AFM image of the (6 × 1)-α region shown in Figure 6e, the unit cell consists of one bright row and two dark rows each with a similar appearance.

We therefore propose that the platform on which the added (2n × 1)-α rows stand can be either the unreconstructed (1 × 1) surface or rows with the (2 × 1) structure, as shown in the schematic models of Figure 3a,b, respectively. When n > 2, there are several configurations in which the (2 × 1)-like rows can be arranged to make the (2n × 1)-α structures. For instance, two types of (6 × 1) structure are shown in Figure 3b: (i) a structure that would appear in NC-AFM as one bright row and one darker row, as seen in Figure 4a, and (ii) a structure with one bright row and two darker rows, as observed in Figure 6e. A ball and stick model of the (4 × 1)-α structure (including a darker row) is shown in Figure 1b that corresponds to the schematic in Figure 3b. All other higher order (2n × 1)-α phases can be visualized using this model and arranging the units as shown in the schematics of Figure 3a,b. We note that while the scanning probe images give good evidence for the general structure proposed, the detailed structure between the rows is unknown (i.e., the region circled in green in the model of Figure 1b) and can probably be addressed by computer modeling given that the structure does not have the long-range order required for quantitative diffraction studies.

Figure 7 shows a high-resolution image of the (4 × 1)-β phase. As with the images presented of the (2n × 1)-α phases, the row again has a zigzag motif. The zigzag can be described by an isosceles triangle similar to those in Figures 4b and 5b: the long side is ∼5.45 Å, and the shorter equal sides are ∼4.3 ± 0.3 Å, similar to that found for the (2n × 1)-α phases here and in STM images of the (2 × 1) termination. The model we propose tentatively is therefore again based on elements of the “diffraction model” for the (2 × 1) phase. However, in this case, we remove every other row of the (2 × 1) model to create a microfaceted structure somewhat similar to that proposed by Kubo et al. and illustrated in Figure 1c.

The proposed model would account for the greater corrugation observed in the NC-AFM images for this phase compared to the (2n × 1)-α phases. Such a microfaceted structure exposes the less stable {111} faces and this could explain why the (4 × 1)-β structure does not develop further higher order structures like (6 × 1) and (10 × 1) because the proportion of the less stable {111} facets increases with the size of the microfacet. For the same reason, the (4 × 1)-β phase is likely to have a higher energy than the (2n × 1)-α phases. This could explain why when starting from an as-purchased crystal, the (4 × 1)-β phase was only observed during the first 21 sputter/anneal cycles, whereas the (2n × 1)-α phases were still observed after 64 cycles. In this scenario, the more stable (2n × 1)-α phases would tend to dominate upon repeated annealing. Note that while the (4 × 1)-β model can be created by removing (2 × 1) units from the (2 × 1) phase, this does not carry any implication on how the phase is formed. It may be that the reconstructions grow out from the surface as has been shown for the rutile TiO$_2$(110) surface.

Defects on the (2n × 1)-α Reconstructions. In the high-resolution STM and NC-AFM images shown in Figures 4–6, several defects (or agglomerations of defects) can be seen, and some of these are marked with crosses and circles.
Figure 8a,b show NC-AFM and STM images, respectively, that are taken from the same area of the surface in the vicinity of the images in Figures 4, 5. This region has a predominantly \((6 \times 1)\) periodicity. Specifically, this region mainly has a \((6 \times 1)\)-\(\alpha\) configuration where two bright rows make up the unit cell.

The green crosses in Figure 8 highlight coincident defects in the STM and NC-AFM image. In one case, a bright defect in the STM appears dark in the NC-AFM image and this defect is marked yellow. Red crosses indicate defects only seen in the STM image and blue crosses mark those that appear only in the NC-AFM image. The majority of crosses are green, indicating that most of the defects are detectable in both images. As the NC-AFM image was recorded 7 min after the STM image, at least some of the defects that cannot be matched between the images may arise from diffusion. Although dark defects that appear in STM images of TiO\(_2\)(011)-(2\(n\times 1\))-\(\alpha\) phases with zigzag contrast have been assigned to oxygen vacancies, bright defects have been assigned to adsorbed hydrogen.\(^{14}\)

In sequential STM images and sequential NC-AFM images taken from the same area of the TiO\(_2\)(011)-(2\(n\times 1\))-\(\alpha\) phase (not shown), several of the bright defects change their positions, indicating that at least some of the defects can diffuse rather easily even at room temperature. On rutile TiO\(_2\)(110) at room temperature, adsorbed hydrogen is known to diffuse either intrinsically or facilitated by molecular water.\(^{51,52}\) On the other hand, diffusion of oxygen vacancies requires elevated temperature.\(^{53}\) Given that the \((2n \times 1)\)-\(\alpha\) phase shares the same basic structure as TiO\(_2\)(011)-(2 \(\times 1\)), the easy diffusion of the defects supports the assignment of the bright defects observed by Tao et al.\(^{14}\) to adsorbed hydrogen.

As with images in STM,\(^{34}\) it is well-known that the contrast obtained by NC-AFM can change depending on the nature of the tip apex.\(^{55–59}\) The contrast changes can be drastic or more subtle. For instance, a subtle difference in contrast can be seen between the images in Figure 6a,c. Both NC-AFM images contain \((4 \times 1)\)-\(\alpha\) regions with bright and darker rows. In the image in Figure 6a, the bright rows have a height of \(\sim 0.6\) Å, and the darker rows have a height of \(\sim 0.2\) Å, so that the height difference between them is \(\sim 0.4\) Å. On the other hand, in the image in Figure 6c, the bright rows have a height of \(\sim 0.5\) Å, and the darker rows have a height of \(\sim 0.3\) Å, with the height difference being only \(\sim 0.2\) Å. As such, the \((4 \times 1)\) periodicity in Figure 6a is clear, whereas the \((4 \times 1)\) periodicity in Figure 6c is only just discernible.

More drastic tip changes can be seen in the series of five NC-AFM images shown in Figure 9. These were recorded sequentially, and each image has a different contrast. In Figure 9a, the bright defects can be seen together with the bright \((2n \times 1)\)-\(\alpha\) rows. In Figure 9b, the contrast is similar, but the defects and rows appear more smeared out. The image appears similar to that in Figure 8a. In Figure 9c, there is a drastic contrast change: the \((2n \times 1)\)-\(\alpha\) rows still appear bright, but the contrast is only dark between rows with \((2 \times 1)\) periodicity. Between rows with a greater periodicity, there is a bright band. The defects are visible as very well-resolved bright spots, but the \((2n \times 1)\)-\(\alpha\) rows themselves are not resolved. In Figure 9d, the
The red guidelines also mark equivalent rows. The green crosses highlight some defects that are visible in (a) and (c). In (d), despite the image being more or less in the same area as (a), the defects are invisible whereas the image in (e) was taken from a slightly different position.

Figure 9. Sequential (200 Å × 60 Å, \(V_{\text{CPD}} = 0.9\) V) NC-AFM images of TiO\(_2\)(011)-(2\(n \times 1\)-\(\alpha\)) with \(\Delta f = (a) -6.1\) Hz, (b) -6.1 Hz, (c) -6.7 Hz, (d) -6.0 Hz, and (e) -5.8 Hz. The light-blue lines indicate a 2\(x\) spacing and in (a)–(d), the red guidelines mark equivalent rows. The red guidelines also mark the [0\(\bar{1}\)1] direction. The green crosses highlight some defects that are visible in (a)–(c). In (d), the defects are invisible whereas the image in (e) was taken from a slightly different position.

CONCLUSIONS

In conclusion, we have used NC-AFM and STM to study the rutile TiO\(_2\)(011) surface. A series of (2\(n \times 1\)-\(\alpha\)) reconstructions were observed, including two types of (4 \(\times 1\)-\(\beta\)) reconstructions: (4 \(\times 1\)-\(\alpha\)) and (4 \(\times 1\)-\(\beta\)). High-resolution NC-AFM and STM images suggest that the (4 \(\times 1\)-\(\alpha\)) phase has the same structural elements as the more widely reported (2 \(\times 1\)) termination. Closely related higher-order (2\(n \times 1\)-\(\alpha\)) phases where \(n = 3–5\) were also observed. The (4 \(\times 1\)-\(\beta\)) reconstruction also has a structure based on the (2 \(\times 1\)) reconstruction but with additional microfacets of \{1\(\bar{1}\)1\} character. Higher-order analogues were not observed for the (4 \(\times 1\)-\(\beta\)) phase. Although not definitively assigned, the same point defects were observed in both NC-AFM and STM images. In sequentially imaged areas, the NC-AFM contrast was subject to changes, and the point defects appeared clearer in some cases and invisible in others. Further study combining theoretical simulations with STM and NC-AFM may be able to explain such tip changes as well as identifying the point defects.

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Notes

The authors declare no competing financial interest.

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