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Structures of the 4×1 and 1×2 reconstructions of $SnO_2(110)$

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Scanning tunneling microscopy (STM) and noncontact atomic-force microscopy (AFM) have been used to investigate the 4×1 and 1×2 reconstructions of $SnO_2(110)$. These terminations were prepared by sequential annealing in UHV at temperatures of 900 and 1075 K, respectively. Two coexisting 4×1 structures are observed with STM, one of which is consistent with previously reported STM images, the other appearing to arise from a SnO(101) overlayer. For the 1×2 phase, a combination of STM and noncontact AFM images point to an added-row morphology.

Tin (IV) oxide is a wide band-gap (3.6 eV), *n*-type semiconductor with the rutile structure. It is used in a wide variety of technologies, including gas sensors, solar cells, and oxidation catalysts. In these applications oxygen vacancies play a pivotal role. There have been a number of experimental[1–11] and theoretical[12–15] studies of $SnO_2(110)$. Three readily prepared reconstructions have been reported, which have 4×1, 1×1, and 1×2 surface periodicity.[1,2,9] These are in addition to the stoichiometric 1×1 termination that can be formed at high partial pressures of oxygen.[1,11] The reduced surface phases can be prepared by sequential annealing in UHV at 900, 950 and 1075 K, respectively.[2]

There is strong evidence to suggest that the $SnO_2(110)$ surface phase transitions are controlled by the concentration of surface oxygen vacancies.[1] SnO_2 surface composition ratios derived by x-ray photoelectron spectroscopy[2] show a straightforward increase in the intensity ratio between O 1*s* and Sn 3*d* peaks as the structure evolves from 4×1 through 1×1 to 1×2, consistent with an earlier Auger electron spectroscopy (AES) study.[1] The simplest model for this 1×1 surface has all the bridging oxygens missing.[1,2] The 1×2 reconstruction has a higher O:Sn ratio than the bare 1×1 structure mentioned above and it has, therefore, been proposed that this surface possesses extra bridging oxygen atoms in alternate rows[2] similar to that initially proposed for $TiO_2(110)1\times2$.[16]

The simplest interpretation of the 4×1 structure involves the removal of every fourth row of in-plane O ions. The difficulty of explaining the stability of this structure led Cox *et al.*[1] to suggest an alternative model consisting of an expanded SnO(101) overlayer which forms a coincidence lattice. An expansion of about 10% in the SnO lattice parameters is required for the two lattices to coincide in the substrate $[1\bar{1}0]$ direction and for the lattice parameter to be $\frac{4}{3}$ that of the substrate in the [001] direction. This structure would account for a 4×1 low-energy electron diffraction (LEED) pattern. Previously reported scanning tunneling microscopy (STM) images[9] are inconsistent with this overlayer model since there is no evidence of a repeat distance in the [001] direction corresponding to $\frac{4}{3}$ of the substrate unit-cell vector. Instead, the STM data were explained in terms of an ordered arrangement of in-plane oxygen vacancies.

Here we use STM and noncontact atomic-force microscopy (NC-AFM) to investigate the structure of $SnO_2(110)$ reconstructions. While STM has previously been used to evaluate the structure of a number of oxide surfaces[17] earlier work with NC-AFM is limited to surfaces of TiO_2.[18–20] Our results for $SnO_2(110)$ indicate the coexistence of two 4×1 terminations. One termination is that observed in the earlier work,[9] while the second is consistent with the SnO(101) overlayer model.[1] For the 1×2 phase, STM and NC-AFM together provide evidence for a similar added-row type structure to that proposed for $TiO_2(110)1\times2$.[21]

All measurements were recorded with a room-temperature ultrahigh vacuum (UHV) STM/AFM instrument (*Omicron GmbH*) operating at a base pressure of $\leq 10^{-10}$ mbar. The STM images were acquired in the constant current mode with the sample positively biased with respect to the tungsten tip. In the NC-AFM mode the feedback source was the frequency shift of the cantilever resonance. A frequency modulation detector measures the frequency difference between the cantilever and a reference oscillator.[22] A NC-AFM topographic image of the sample surface was recorded by measuring the *z* position of the tip with constant frequency shift feedback. For the NC-AFM experiment, a conducting silicon cantilever (*Nanosensor GmbH*) with 10 Nm^{-1} force constant and a resonance frequency of 270–300 kHz was used. The frequency shift used was about -100 Hz. The cantilevers were cleaned *in situ* by Ar-ion bombardment. Vertical and horizontal distances were calibrated using atomically resolved images of Si(111)7×7.

The sample was cleaned *in situ* by cycles of 0.5 keV Ar^+ bombardment followed by annealing in UHV. The annealing temperature was measured using an infrared pyrometer focused on the sample plate, since SnO_2 is transparent. Cleaning cycles were repeated until contaminant levels were less than 1% ML as judged by AES. Annealing to 450 K resulted in a diffuse 1×1 LEED pattern. A faint $c(2\times2)$ pattern was seen on annealing the sample to 500–550 K. The $c(2\times2)$ pattern was removed after annealing to 900 K to leave only the 4×1 structure. After annealing to 1000 K, a 1×1 LEED pattern was observed leading to a 1×2 pattern after annealing to 1075 K. These observations and anneal temperature regimes are similar to those reported by earlier workers[1,2,9] except that a $c(2\times2)$ pattern associated with the 4×1 pat-

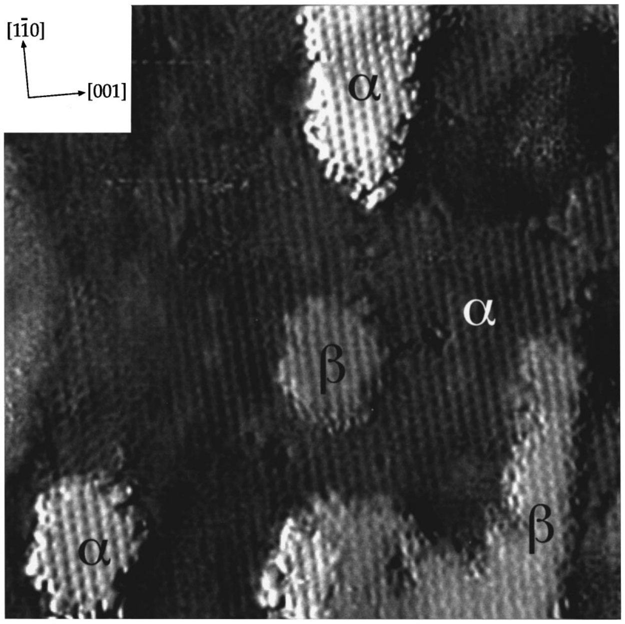

FIG. 1. 300 Å × 300 Å STM image (+1 V, 1.0 nA) of $SnO_2(110)4\times1$. α and β denote the two types of 4×1 reconstruction.

tern was not observed by Jones *et al.*[9] and Shen *et al.*[2]

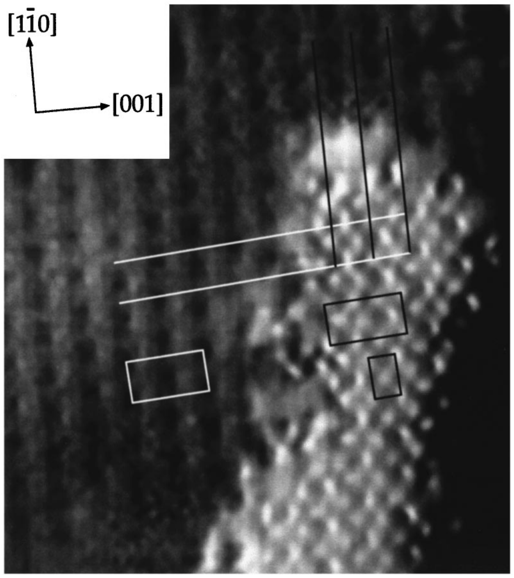

FIG. 2. 78×88 Å^2 STM image taken from Fig. 1, showing the $SnO_2(110)4\times1$ phase previously identified (on the left) and that consisting of a SnO(101) overlayer. The two 4×1 unit cells and the smallest repeat unit for the SnO(101) overlayer are indicated. Lines are drawn to highlight the registry between the two 4×1 surfaces.

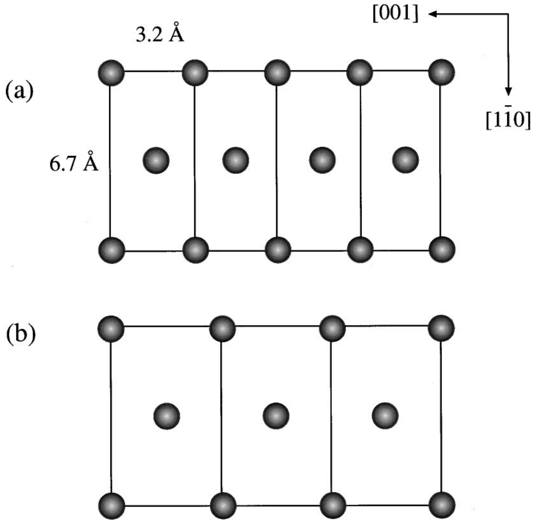

FIG. 3. Schematic representation of the Sn sublattice of (a) $SnO_2(110)$, (b) SnO(101) expanded by about 10% to form a coincidence lattice with $SnO_2(110)$.

Figure 1 shows a large area STM image of the sample surface which exhibited a 4×1 LEED pattern. Two types of terrace are imaged, both of which have 4×1 periodicity. Terrace α covers the majority of the surface whereas only small areas of the upper terrace β were imaged. Figure 2 shows the area in the lower right of Fig. 1 in more detail. Areas of terrace β lie about 1.8 Å above terrace α. Unit cells on each terrace have dimensions 13×6.5 Å^2 in line with the 12.8×6.7 Å^2 expected for the 4×1 unit cell. On terrace α the unit cell has dark areas in the four corners with another dark area at the center. This part of the image is consistent with those images of the 4×1 surface previously published, which were interpreted in terms of an ordered arrangement of in-plane O vacancies.[9] In contrast to earlier work, no significant difference was found between images obtained at a sample bias of 1 and 1.5 V. In the earlier work additional structure was observed in their images at 1 V bias. On occasion we did observe similar features, but it appeared to coincide with a "tip change." Such tip changes, which probably occur by the tip picking up an adsorbate atom or molecule, can strongly affect STM images of metal oxides.[23] We speculate that such a tip change may have been occasioned by the change of bias voltage in the earlier work.

The image of terrace β contains features which have atomic dimensions. Although it has 4×1 periodicity, there is a smaller surface unit cell, marked on the image in Fig. 2, which has the dimensions $\sim4\times\sim6.5$ Å^2. This unit cell possesses a bright feature in each corner and one bright feature in the center. The unit-cell dimensions do not correspond with the $SnO_2(110)1\times1$ surface unit-cell dimensions of 3.2×6.7 Å^2. However, they are consistent with the repeat unit of a Sn containing termination of SnO(101) expanded from 3.80×6.15 Å^2 to give a coincidence lattice having substrate 4×1 periodicity, with three overlayer unit cells of 4.3×6.7 Å^2 in the 4×1 unit cell. Implicit in this assignment is the assumption that the features in the STM image arise from Sn atoms. This is justified on the grounds that the images are accumulated by tunneling into conduction-band states, which have mainly Sn orbitals as a basis. The relationship between the overlayer and substrate lattices, which was suggested by Cox *et al.*,[1] is shown schematically in Fig. 3.

Turning to the registry of the SnO overlayer with terrace α, the lines drawn in Fig. 2 indicate that every fourth $[1\bar{1}0]$ direction row of Sn atoms in the SnO overlayer are in registry with the center of the bright $[1\bar{1}0]$ direction rows of the 4×1 reconstruction on terrace α. Similarly, in the [001] direction, alternate rows of Sn atoms in the SnO(101) overlayer are in registry with every other row of oxygen vacan-

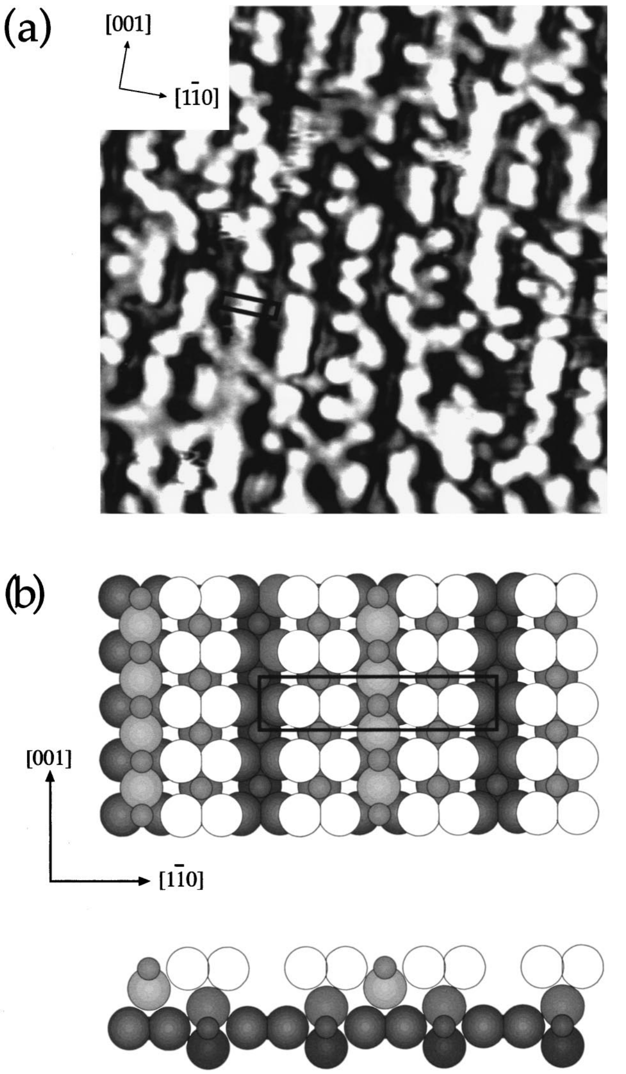

FIG. 4. (a) 150×150 Å^2 STM image (+1.3 V, 0.8 nA) of SnO$_2$(110)1×2,, in which the contrast has been adjusted to view the lower lying [00] direction rows. (b) Top and side views of the added row model proposed for SnO$_2$(110)1×2 on the basis of the STM image. Small circles represent Sn atoms, while large circles represent O atoms.

cies in the 4×1 reconstruction on terrace α. However, superimposing the two lattices with the above registry reveals no obvious coordination between the layers, perhaps suggesting that the SnO(101) overlayer does not grow on top of the SnO$_2$(110)4×1 surface.

At the anneal temperature of 950 K a 1×1 LEED pattern is observed, although we were only able to image featureless terraces with STM. This may arise from disorder. Further annealing to 1075 K gives rise to a 1×2 LEED pattern. Figure 4(a) shows a STM image of the 1×2 structure in which rows 13 Å apart are observed, consistent with the 1×2 unit cell dimension along [1$\overline{1}$0] (13.4 Å). Again assuming that Sn atoms are imaged, the 1×2 images are consistent with an added-row-type model similar to that already suggested for TiO$_2$(110)1×2. [21] A model of one type of added row structure is shown in Fig. 4(b). It consists of added rows along the [001] direction, in which the termination is of a completely reduced 1×1 surface. Since atomic production was not obtained, we cannot provide a definite structural model. However, an alternative, Ti$_2$O$_3$-added-row model proposed for TiO$_2$(110)1×2 (Ref. 24) seems unlikely to be adopted by SnO$_2$(110), since tin does not form a sesquioxide. The NC-AFM results shown in Fig. 5 support an added-row model for the 1×2 reconstruction since the images contain bright rows 8.5 Å wide and separated by 13 Å. On the basis that NC-AFM is less sensitive to local electronic structure effects than STM, in the added-row model we would expect all atoms in the added-1×1 segments to be imaged as bright features. These should be separated by narrow dark strips representing the underlying 1×1 plane. In the case of the 1×2 missing row model only the bridging oxygen atoms would appear bright, giving rise to narrow bright rows separated by broad dark strips.

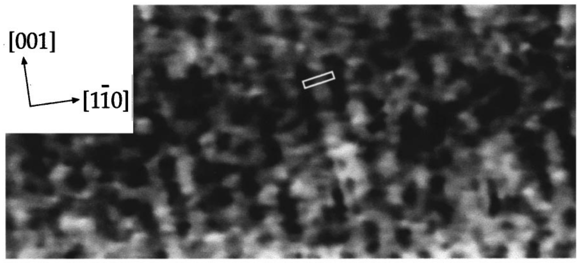

FIG. 5. 300×130 Å^{2}NC-AFM image of SnO$_2$(110)1×2.

In our STM images of SnO$_2$(110)1×2 (Fig. 4), the underlying 1×1 rows can be seen clearly between the 1×2 strips, which is not the case with STM images of TiO$_2$(110)1×2.[21] An explanation for this difference lies in the composition of the conduction band, for SnO$_2$ being largely Sn 5s and 5p states. These orbitals could have greater overlap with tip orbitals than Ti 3d, which forms the basis of the lower conduction band of TiO$_2$.[15] As with TiO$_2$(110)1×2,[25,26] cross-links are seen between the rows which can be explained by the addition of Sn and O atoms in the troughs between the added rows.

In summary, we have imaged the 4×1 and 1×2 reconstructions of SnO$_2$(110) with STM. In addition, we have imaged the 1×2 reconstruction with NC-AFM. A new 4×1 phase is identified which appears to arise from a SnO(101) coincidence lattice. The 1×2 phase resembles the added row structure previously observed for TiO$_2$(110)1×2.

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