Surface Reconstructions of $TiO_2(110)$ Driven by Suboxides

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Scanning tunneling microscopy and density functional theory are used to develop a new structural model for surface reconstructions driven by Ti interstitials on $TiO_2(110)$. Ti interstitials form the edge- or face-sharing octahedra that serve as building blocks for (1×1) reconstruction. Thus, contrary to conventional wisdom, the 1×1 periodicity is insufficient to establish the correct surface stoichiometry. Furthermore, in our structural and compositional model the reversible oxidation or reduction between (1×1) and (1×2) is entirely achieved by transfer of the added rows.

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Remarkable catalytic activity by highly dispersed gold on titanium oxide [1,2] recently has renewed interest in the fundamental properties of the surfaces of TiO_2. Because defects are believed to play a crucial role in the formation of nanoclusters on the surface, both theoretical and experimental studies [3] have examined in detail the interactions between surface defects and metal clusters such as nucleation sites, the nature of bonding, bonding geometry, and local charge redistribution. A part of the challenge in understanding defects is that transition metal oxides including TiO_2 can accommodate a range of stoichiometry and structure [4]. The inherent complexity thus requires one to determine the local stoichiometry and structure, which dictate the electronic and the chemical properties of the oxide surfaces.

For over three decades, the surfaces of rutile TiO_2 have been considered as model systems to investigate structures and properties of transition metal oxides as high purity, single crystals are widely available. A high quality surface can be prepared using conventional surface preparation techniques such as sputtering and annealing [5]. Defects generated by sputtering have been thought to migrate to the bulk during annealing [6,7]. Consequently, the restoration process of the reduced surface has been viewed as reoxidation by the bulk.

Many studies especially from the surface science community have focused on oxygen vacancies as the origin of defects [8]. However, there has been growing speculation about the role of Ti interstitials in the reoxidation processes [9]. For commonly observed double strands, which many believe to be a precursor to Ti-rich (1×2) reconstruction of $TiO_2(110)$, double rows of Ti were proposed to occupy interstitial sites in stoichiometry of Ti_2O_3 [10]. A recent calculation using density functional theory (DFT) indicated that these strands might even be regarded as quasi-one-dimensional atomic wires displaying metallic character [11]. By tracking isotopically labeled ^{18}O and ^{46}Ti, Henderson [9] suggested that more diffusive Ti interstitials rather than O vacancies played the key role in restoring stoichiometry of ion-sputtered surface during annealing. McCarty and Bartelt [12] further concluded that the transfer of Ti interstitials and O vacancies to or from the surface in equilibration with bulk was responsible for step motion and the reversible phase transition from (1×1) to (1×2) on $TiO_2(110)$ with varying temperature.

While the previous studies offer strong support for the major role of Ti interstitials in reoxidation, there has not been a direct observation of Ti interstitials. In this Letter, we present a scanning tunneling microscopy (STM) image of a row of adatoms on (1×1) $TiO_2(110)$ that is interpreted using first principles DFT calculations. From the comparison between experimental and theoretical studies, a structural model is proposed for a single row of Ti atoms accumulated at specific interstitial sites. The Ti row easily dissociates molecular oxygen and becomes oxidized to TiO in partially complete octahedra, which share faces with the substrate octahedra. We further propose that the formation of face-sharing octahedra is a mechanism through which a "bulklike" (1×1) surface can be restored in substoichiometry: 2(TiO) instead of $2(TiO_2)$ per unit cell. When the row of 2(TiO) is reduced, the remaining structure relaxes into a Ti-rich double row of Ti_2O, which exhibits key characteristics consistent with previously reported double strands [10].

The experiment was carried out using a variable temperature STM in an ultrahigh vacuum (UHV) chamber (base pressure $< 10^{-10}$ Torr). A rutile $TiO_2(110)$ sample (Commercial Crystal Lab.) was cleaned by several cycles of Ar-ion sputtering with the ion currents of about 0.5 μA at the sample for 15–20 minutes followed by annealing it up to $\sim 650\,^{\circ}$C for 15 minutes. A constant current topographic mode was employed for imaging. Sample biases were usually chosen between $+1.0$ and $+2.2$ V, and within this bias range no significant effect of bias on image was noticed. All STM images presented here were obtained at room temperature.

Theoretical modeling, based on DFT, was used for both the investigation of the energetics of defect structure in Ti as well as for molecular dynamic simulations [13]. The calculations were carried out using a conventional (2×1) 20 Å thick slab model, keeping the atoms of the bottom layers at bulk positions to simulate the semi-infinite crystal. Core atomic states were represented by projector augmented wave pseudopotentials [14] within the local density approximation for the exchange-correlation functional [15]. A plane-wave basis with energy cutoff up to 400 eV, a fine k-point sampling of the surface Brillouin zone, and a large vacuum region extending to 25 Å were chosen after careful convergence studies of the total energy. For each structure, energy convergence down to 0.1 meV and forces smaller than 1 meV/Å were systematically reached.

After cycles of sputtering and annealing, the surface exhibits strands terminated with bright spots on (1×1) terraces, as observed before [10]. The STM image of a row of what appears to be adatoms is shown in Fig. 1(a). On $TiO_2(110)$, the STM image contrast has been understood predominantly through electronic rather than geometric effect: Bright rows are assigned to 5-coordinated Ti^{4+} atoms and dark ones are identified to bridging oxygen rows [3]. Thus, the line of adatoms along [001] is located right next to a row of the Ti^{4+}. They are believed to be Ti atoms and about 1.1–1.4 Å above the surface Ti^{4+} atoms. By ignoring the impact of electronic effect for both Ti atoms [16], this height difference can be thought of as a real structural feature. The distance between the line defect and the nearest row of Ti^{4+} is about 1 Å, positioning the defect right above the 3-coordinated oxygen row [Fig. 1(b), top]. The spacing between two adjacent adatoms within the strand along [001] is 3.3 Å on average, equal to that between two adjacent Ti^{4+} atoms of the surface. However, the position of each adatom in the line appears to be shifted by 0.8 Å along [001], compared to that of Ti^{4+} in the adjacent row, placing it close to the 3-coordinated, surface oxygen atom.

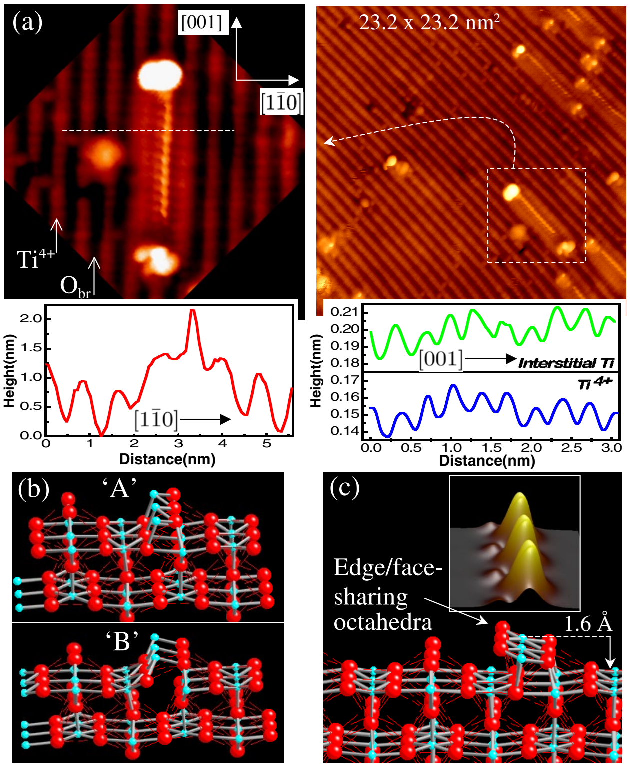

FIG. 1 (color online). (a) STM image of a strand (1.2 V; 0.5 nA) with the height profiles across (left, dotted line) and along (right) the line defect. (b) DFT-relaxed structures of an interstitial Ti row on $TiO_2(110)$: at A above 3-coordinated surface O (the favored geometry); at B for Ti interstitials aligned to bridging O along $[1\bar{1}0]$ (unfavored). Only the top few layers of the actual system are shown here. (c) The most stable structure of Ti interstitials after forming TiO (Ti: small, O: large in ball-and-stick models) and simulated STM image of the structure (inset).

Supporting the experimental observation, the DFT-based geometry relaxations of a periodic Ti row added onto 6 layers of TiO_2 indicate that the most stable position for added Ti is found at an interstitial site "A": above the 3-coordinated surface oxygen [Fig. 1(b), top]. A second symmetric position for adding Ti is also found at another interstitial site "B" when Ti is shifted along [001], by half the lattice constant [Fig. 1(b), bottom], but the energy for this position is found to be 290 meV per unit cell (i.e., per added Ti) higher than that for the former. While both positions would be equivalent in bulk ("c" in $P42/mnm$) [17], on the (110) surface the Ti interstitial atom clearly prefers the former position to the latter."

Ti interstitials at both A and B have significant influences on the underlying oxygen octahedral structure. The row of the bridging oxygen and the row of the 3-coordinated oxygen relax toward Ti interstitials and away from the 6-coordinated Ti row underneath the bridging oxygen, increasing the Ti-O bond lengths. On the other hand, the oxygen atoms on the opposite side of the coordination octahedron move toward the 6-coordinated Ti, decreasing the Ti-O bond lengths. For the most stable geometry (A), the largest distortion is observed for the bond length between the bridging oxygen and the 6-coordinated Ti, which increases from 1.81 to 2.13 Å after adding the Ti interstitials. The volume of the oxygen octahedron also increases by 6.6%. With Ti interstitials placed at B, more severe deformation of the octahedron takes place. The row of the 3-coordinated surface oxygen atoms is pulled up toward the Ti interstitials. The bond length between the oxygen and the 6-coordinated Ti underneath the bridging oxygen is increased from 2.03 to 2.56 Å, and the octahedron volume is enlarged by 8.5%.

Ab initio spin polarized molecular dynamics calculations show that the added row of Ti interstitial atoms easily dissociates molecular oxygen. The predicted property of interstitial Ti to be oxidized is compatible with the reported reactivity properties of adsorbed Ti on the surface of TiO_2 [18]. A detailed discussion of the subsequent oxidation of the Ti row will be presented in a longer paper. After the oxidation, the A position for the Ti interstitial remains the most stable. A fully relaxed structure of the oxidized TiO strand on 6 layers of $TiO_2(110)$ is shown in Fig. 1(c). The oxygen atoms surround the Ti interstitials to complete the equatorial O plane of a partial octahedron. The simulated STM image of the Ti-O structure supports the experimental observation: The row of interstitial Ti appears bright, next to the surface Ti^{4+} row [Fig. 1(c), inset] [19]. Because the simulations of both rows of Ti and oxidized TiO show that there is practically no distinction in STM images, we determine that the line of adatoms in the high-resolution STM image is either a row of Ti or TiO with its Ti coordinated at the interstitial site.

The partially complete octahedra centered on interstitial Ti share the edges of the equatorial O plane with each other along the row and share faces with the substrate octahedra. The edge- or face-sharing geometry provides means to coordinate the Ti cation octahedrally with oxygen in substoichiometry [4]. In fact, it is well known in bulk rutile that the oxygen vacancies can be removed through crystallographic shear planes, for which corner- and edge-shared octahedra in stoichiometric rutile TiO_2 slip to form face- and edge-shared octahedra [20]. More recently, using grazing incidence x-ray diffraction data, Landree *et al.* [21] proposed a model for the (1×3) reconstruction on $TiO_{2-x}(100)$, which consisted of edge- and face-shared octahedra.

The edge- or face-sharing, substoichiometric octahedra can generate (1×1) $TiO_2(110)$ under an oxygen-deficient environment such as annealing in UHV after sputtering. Figure 2 shows a STM image of many strands several tens of angstroms long, growing out of step edges. The image further reveals a "raft" of bright strands with the single periodicity along $[1\bar{1}0]$, forming a small terrace. The line profile reveals that the step height of this small terrace is 1.6 Å, only half that expected from corner-shared octahedra of bulklike termination. Moreover, the alignment of the bright row of the small terrace is best estimated between the Ti^{4+} (bright) and the bridging oxygen (dark) rows of the lower terrace, whereas in bulk the Ti^{4+} row is located directly above the bridging oxygen row of the lower terrace. The half-step height and the placement of the Ti^{4+} row between the Ti^{4+} and the bridging oxygen rows of the lower terrace are the hallmarks of the slipped and stacked octahedra [3].

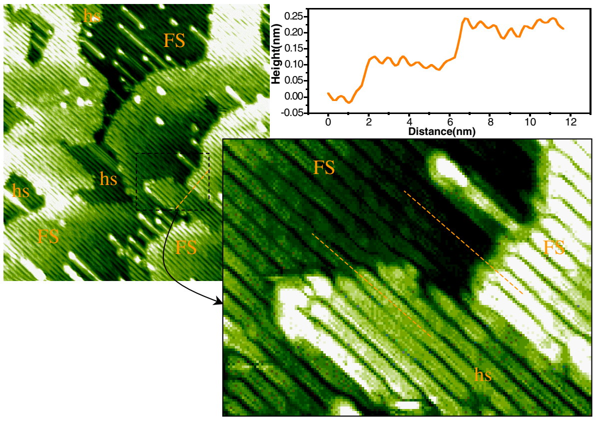

FIG. 2 (color online). STM image (50×50 nm^2; 1.80 V; 0.5 nA) of strands and 1×1 terraces with half-step (hs) as well full-step (FS) height with a line profile on $TiO_2(110)$.

In order to theoretically account for the (1×1) surface generated from edge- or face-sharing octahedra, additional rows of Ti and O were added to the TiO strand in Fig. 1(c). The most stable structure of the Ti_2O_2 row is shown in Fig. 3(a). The added Ti adopts the geometry so that Ti is coordinated with surrounding O to form an octahedron with the equatorial plane vertically oriented. At the same time, the second O row becomes the bridging O row of the surface, which is only about 1.6 Å higher than the lower terrace. Therefore, we determine the small terrace as the direct experimental evidence of generating a (1×1) surface with edge- or face-shared octahedra of suboxides. Moreover, this study further illustrates that the 1×1 periodicity of $TiO_2(110)$ alone is not sufficient to correctly establish surface stoichiometry of TiO_2, as generally implied in literature.

The reduction of the Ti_2O_2 row was also investigated theoretically by removing the bridging O row. The total

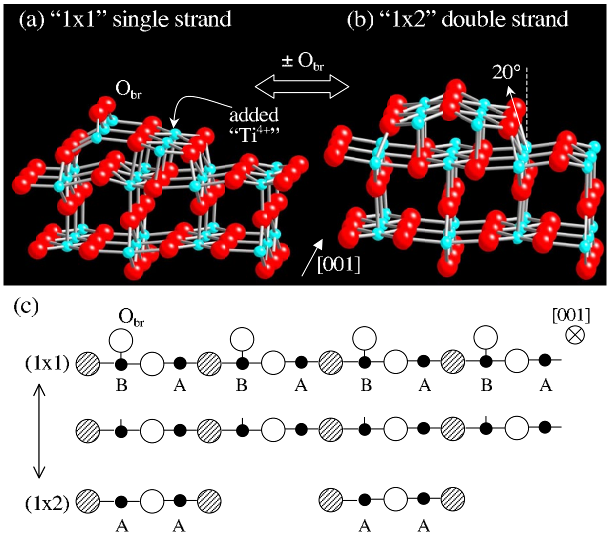

FIG. 3 (color online). DFT-relaxed structures of (a) the Ti_2O_2 single strand with (1×1) periodicity and (b) the Ti_2O double strand. After the removal of the bridging O row, the Ti row beneath shifts by half the lattice constant along [001]. (c) Schematic diagrams for the phase transition between (1×1) and (1×2) via diffusion of the added rows. [Solid circles: added Ti (A or B); open circles: added O; hatched circles: bridging O of the substrate.] Each step is for illustration only, not necessarily reflective of the actual redux processes.

energy of the structure is the lowest when the reduced Ti row (previously underneath the bridging O) is shifted along [001], by half the lattice constant [Fig. 3(b)]. Both Ti rows form partially complete octahedra with the O equatorial plane horizontally oriented, and both rows of the octahedra are buckled symmetrically about the oxygen row in the middle. The top view of the structure also shows that the arrangement of Ti and O is reminiscent of that in TiO rocksalt [22]. The bond distance between Ti and O is 2.07 Å in the double row structure, close to 2.09 Å expected from the simple cubic TiO ($a = 4.1815$ Å). The lattice constant of 2.96 Å along [001] on TiO(110) is exactly the same as the nearest neighbor distance for Ti-Ti and O-O in TiO. This Ti_2O structure possesses the same key attributes of experimentally observed double strands as the previous model of Ti_2O_3 [10,23] does, albeit with a clear distinction. It is centered on the Ti^{4+} row of the surface and about 1.6 Å high [3], due to Ti at the interstitial site A instead of B as in the Ti_2O_3 model. The bridging O rows are pulled toward the Ti interstitials, resulting in the tilt angle of 20° from surface normal, which is consistent with the observed angular distribution of electron-stimulated, O^+ ion emission [24]. Thus, both single and double strands are the manifestation of Ti interstitials of different stoichiometry.

Finally, the proposed conversion of a Ti_2O_2 strand to the double row structure provides a simple, yet specific structural and compositional model for reversible phase transition from (1×1) to (1×2) of $TiO_2(110)$, reported earlier [12]. It was proposed that the (1×2) structure resulted from the diffusion of Ti and O into the bulk, which accommodated much less Ti than O, leaving the surface Ti-rich. The transition from (1×1) to (1×2), based on our model, is realized by the transfer of two added Ti interstitials rows and three added O rows into the bulk [Fig. 3(c)]. The Ti-rich surface stoichiometry is thus the direct consequence of more O rows diffusing into the bulk than Ti rows. The structural transformation, evidenced by the single bright row to double rows in STM, is the outcome of both Ti interstitial rows occupying at the interstitial site A. The doubled periodicity of the (1×2) surface results from the fact that two units of a single strand are necessary for the transformation into a double strand in periodic fashion due to both bridging O rows bowing symmetrically inward toward the double Ti rows. The reversible reduction or oxidation is achieved entirely by the added rows moving along [001], with the substrate rows fixed.

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