Creation of single oxygen vacancy on titanium dioxide surface

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Physical and chemical properties of solid materials are modified by introducing defects, which disarrange the atomic periodic structure. Typical example is oxygen vacancies on titanium dioxide (TiO_2) surfaces. Oxygen vacancies on TiO_2 surfaces provide new physical and chemical surface properties, such as conductivity, catalytic activity, hydrophilicity, etc. To date, annealing, electron-/photo-stimulated desorption, and chemical reaction have been reported to create oxygen vacancies on TiO_2 surfaces. However, these techniques do not allow position control of the defects at the atomic scale. We report the creation of single oxygen vacancy using a scanning tunneling microscope (STM). This technique creates oxygen vacancy at desired site. In addition, based on the experimental findings, we discuss the mechanism of manipulating atomic defects using the STM.

I. INTRODUCTION

Titanium dioxide (TiO_2) has long been paid attention to because of its potential for many important applications such as catalysts, photocatalysts, sensors, and light-switchable amphiphilic films.[1–6] The physical and chemical properties of TiO_2 are strongly affected by the existence of atomic defects such as oxygen vacancies, hydroxyls, and Ti interstitials in its crystal structure.[1–23] Furthermore, controlling the position of atomic defects in the structure is critical in manipulating the properties of TiO_2.

The creation of atomic defects on the TiO_2 surface has been achieved by annealing,[1–6,24] electron-/photo-stimulated desorption,[1,25] and reactions with hydrogen sources (atomic hydrogen or water).[3–5,16,26–28] These techniques are able to control the atomic defects only at the macroscale. A scanning tunneling microscope (STM) has been used for inducing atomic scale diffusion[2,29] and desorption[14,22,26,27,30] of the defects. However, the creation of oxygen vacancies via STM, the most typical defect on TiO_2 at the atomic scale, has not been achieved so far.

Here, we report the creation of single oxygen vacancies at desired sites on the TiO_2 surface using STM. In addition, based on the experimental data, we discuss the manipulation of atomic defects on the TiO_2 surface using STM.

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II. EXPERIMENTAL

All experiments were performed in ultrahigh vacuum at 78 K under conditions that permitted unequivocal identification of each defect. STM experiments were performed using a Low temperature scanning tunneling microscope/scanning tunneling spectroscopy (LT-STM/STS) system (Omicron GmbH, Erlangen, Germany) consisting of two chambers separated by a gate valve. TiO_2(110) single crystals (Furuuchi Chem. Co. Ltd., Tsukuba, Japan) were cleaned in the preparation chamber with base pressure of 8×10^{-8} Pa by cycles of Ar^+ sputtering (3 – 5 keV) and annealing at 900–1000 K. After the surface preparation, the sample was transferred immediately to the STM chamber with the base pressure of 1×10^{-9} Pa to obtain TiO_2(110) surface with O_b vacancies before their reacting with the residual H_2O molecules to form OH.[16,22] STM images were acquired in the constant current mode with a chemically etched W tip.

III. RESULTS AND DISCUSSION

Figure 1 shows a typical example of oxygen vacancy diffusion and desorption of hydroxyl (O_b–H) on a bridging oxygen (O_b) row on TiO_2(110) by applying a pulse of positive sample bias (V_s). The bright spot on the dark line at the center of the STM image in Fig. 1(a) is a vacancy of a bridging oxygen (O_{vac}).[16,22,26,27] After applying a $V_s = +3.5$ V pulse for 1 s with the feedback loop turned off to maintain the tip Z position, the position of the O_{vac} was changed to a lower position (0.30 nm) along the [001]

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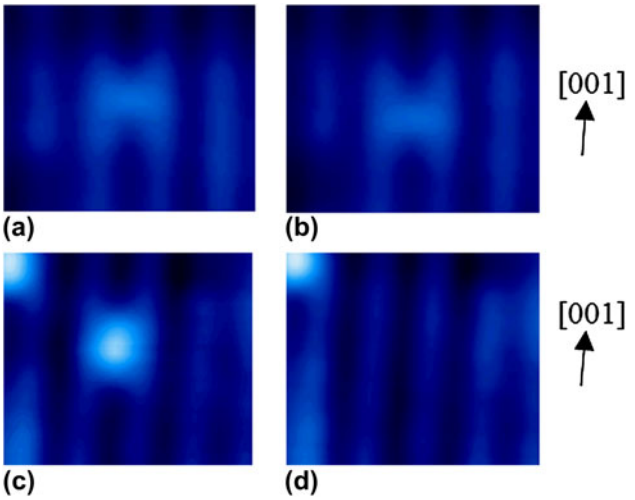


FIG. 1. Constant current STM images (V_s = +1.5 V, I_t = 0.3 nA, T_s = 78 K, 3.5 × 3.0 nm) of TiO_2(110) before (a and c) and after (b and d) applying a pulse on O_{vac} (a and b) and O_b–H (c and d). The applied pulses were V_s = +3.5 and +1.7 V for 1 s. to O_{vac} and O_b–H, respectively, with the feedback loop turned off.

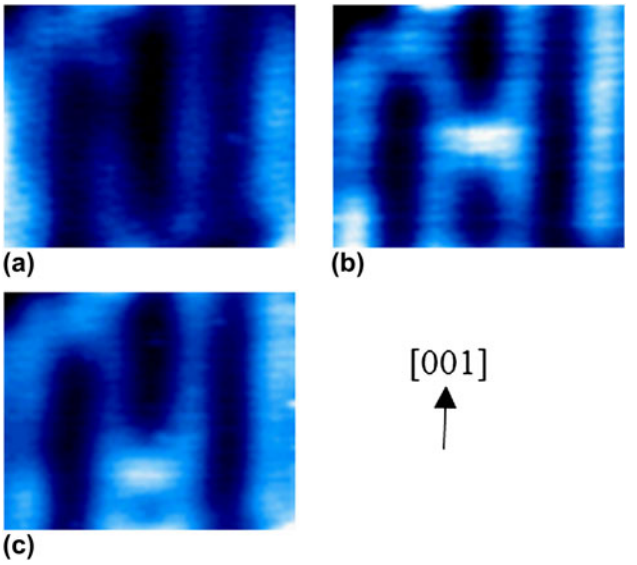


FIG. 2. Constant current STM images of TiO_2(110) before (a) and after (b) pulse injection on O_b. (c) A constant current STM image obtained after applying a pulse on the appeared species at the center of STM image in (b). All STM images were obtained by V_s = +1.5 V, I_t = 0.3 nA, T_s = 78 K, 3.5 × 2.9 nm. The applied pulses were V_s = −2.0 and +4.0 V for 1 s to O_b and the appeared species, respectively, with the feedback loop turned off.

direction as shown in Fig. 1(b). In contrast, after applying a V_s = +1.7 V for 1 s on (O_b–H) [the bright spot at the center of the STM image in Fig. 1(c)], H was removed from the TiO_2(110) surface [Fig. 1(d)]. These reactions agree with previous reports of defect diffusion and desorption on TiO_2(110) using STM.[2,16,22,26,27,29] STM imaging at positive sample bias reveals that the O_{vac} and O_b–H show similar contrast; however, the distinction between O_{vac} and O_b–H is possible via their reaction to the pulse injection of positive sample bias.[16,22,26,27]

Figure 2 shows the reaction to a pulse injection of negative sample bias at O_b. A −2.0 V pulse was applied on O_b [center of Fig. 2(a)] for 1 s with the feedback loop turned off. After the pulse injection, a bright spot appeared at the injection site [Fig. 2(b)]. The apparent height difference from the five-coordinated Ti (Ti_{5c}) of the visible species (0.2 nm) is well matched with one O_{vac}.on TiO_2(110) (0.2 nm). To confirm the assignment of the visible species, a pulse of positive sample bias (V_s = +4.0 V for 1 s with feedback loop off) was applied it. After applying the pulse, the visible species moved toward a lower site along the [001] direction [Fig. 2(c)]. This confirms that the visible species is single $O_{vac.}$ This is the first demonstration of the creation of a single oxygen vacancy at a desired site.

From the experimental results, we infer that diffusion, desorption, and creation of defects on TiO_2(110) are successfully induced in a controlled manner at the atomic scale. However, the mechanism of this STM-induced reaction is unclear. To analyze the reaction mechanism, we investigated the reaction against positive (V_s = +5.0 V for 1 s) and negative (V_s = −2.0 V for 1 s) pulses on O_{vac}, O_b–H, O_b, and Ti_{5c}. As summarized in Table I, O_{vac} and O_b-H react

TABLE I. Reactions of the atomic defects on TiO_2(110) against applying pulse by an STM tip.

Surface species	O_v	O_b–H	O_b	Ti_{5c}[d]
Reaction by a pulse of positive sample	Diffusion[a]	Desorption[b]	×	×
Reaction by a pulse of negative sample	×	×	Desorption[c]	×

[a]Refs. 2 and 29.
[b]Refs. 14, 22, 26, 27, and 30.
[c]If hydrogen is adsorbed on the STM tip, the hydrogen moves from the tip to O_b.[30] Ti_{5c} did not show any reaction with the pulse application. This may originate from the high coordination with the surrounding oxygen atoms.

when a pulse of positive sample bias (electron injection) is applied. At the O_{vac} sites, a voltage pulse is applied to the positively charged Ti ions under O_{vac}. H on O_b is positively charged. Therefore, the positively charged ions react only when a pulse of positive sample bias is applied. In contrast, O_b, which has a negative charge, reacts only with the pulse of negative sample bias (hole injection). Based on these results, we propose that the STM-induced reactions of atomic defects on TiO_2(110) strongly correlate with the electric field between the tip and sample.

The reactions induced by the STM pulses are schematically shown in Fig. 3. By applying a positive sample bias at a O_{vac} site, the neighboring O_b, which has a negative charge (formal charge −2),[1,2] is attracted to the O_{vac} site under the tip. The movement of O_b to the O_{vac} site produces diffusion of O_{vac}. Therefore, the diffusion of

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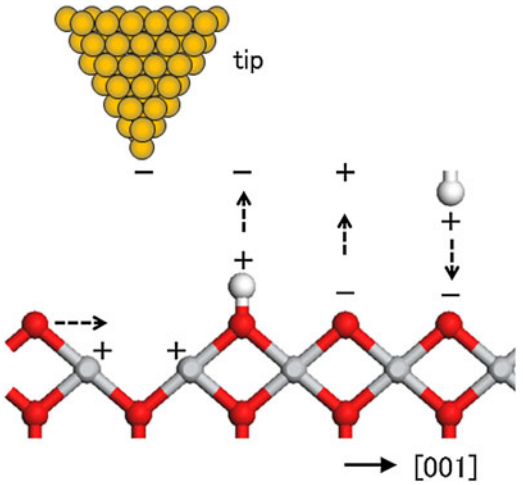


FIG. 3. A schematic image of reactions of atomic defects on TiO_2(110) by a STM tip. Gray, red, and white balls are Ti, O, and H atoms, respectively.

O_{vac} is observed when a pulse of positive sample bias is applied. Conversely, when a pulse of positive sample bias is applied at an O_b–H site, the negative charge on the STM tip attracts H, which has a positive charge on O_b.[1–6] Previous photo-electron spectroscopy and density functional theory studies showed there is no occupied electronic state corresponding to a resonant level with the energy of injected electrons.[1–6] Hence, the desorption of H by a pulse of positive sample bias is considered to be induced by the electric field between the STM tip and the sample surface. As reported by Acharya et al.,[30] the desorbed H is attached onto the STM tip. By applying a pulse of negative sample bias, the H on the STM tip returns to the O_b site.[30] Similarly to the diffusion of O_{vac} and desorption of H, the creation of O_{vac} (desorption of O_b) are induced by the electric field between the STM tip and the sample surface. Because O_b has a negative charge, it is attracted to the STM tip that has a positive charge. As discussed above, we propose that the reactions of the atomic defects on TiO_2(110) are induced by the electronic field between the STM tip and the sample surface.

The above discussion does not deny the effect of electronic/vibrational state excitation induced by tunneling electrons on the reaction. From the polarity dependence of the tip-induced reactions (Table I) and the electronic structure reported in the literature,[1–6] we believe that the electronic field plays an important role in these reactions. The detailed mechanism of electron excitation will be discussed in a future article.[31]

IV. CONCLUSION

In conclusion, we have demonstrated that the creation of single O_{vac} at desired sites is possible by applying a bias pulse by the STM tip. The alignment control of the atomic defects is possible with the combination of diffusion and desorption of the atomic defects. We propose that these reactions are strongly related to the electric field between the STM tip and the sample surface. Applications of this technique can apparently modify the surface and, thus, alter the physical and chemical properties of TiO_2 and related metal oxide materials.

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