



Photoresponse of surface oxygen defects on $\text{TiO}_2(1\ 1\ 0)$

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Abstract

Using scanning tunneling microscopy (STM), the local photoresponse of a rutile $\text{TiO}_2(1\ 1\ 0)$ surface was investigated on the atomic scale. While the illumination of 325 nm ultraviolet (UV) light excited almost all the areas on the $(1\ 1\ 0)$ surface, steps and (1×2) ridges that are associated with oxygen deficiencies and a “rosette” structure exhibited higher response intensities. Previously proposed photoexcitation mechanism involving oxygen defect states in the energy band gap is examined by exciting newly created defect sites. These sites did respond to the illumination, but interestingly, when the sites are being paired, only one of them were active for the visible light illumination.

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1. Introduction

Titanium dioxide (titania, TiO_2) is known to catalyze photolysis of water to hydrogen and oxygen [1], as well as decomposition and/or oxidation of hydrocarbons and other organic molecules [2], under ultraviolet (UV) light illumination. Thus, various titania-based materials have been developed for the purpose of water splitting as well as for environmental remediation in recent years.

Recent efforts are directed to extend the wavelength to be absorbed by the photocatalysts from the UV range to visible region where light intensity is much higher in the sunlight as well as household fluorescent light spectra. Various techniques such as NO_x -doping [3], Cr ion implanting [4], and lattice substitution with nitrogen atoms [5] have been proposed.

Despite these efforts to modify titania electronic structures by introducing impurities for the purpose of using it in visible light range, there has been no efforts to identify the geometric structures, or *sites*, that absorbs visible light. This viewpoint is important because the light excitation of semiconductors is normally understood in terms of energy “bands” that

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assumes infinite array of unit cells, whereas catalysis occurs in a very local environment that needs only a few atom assemblies or clusters. The present paper is a part of our attempt to bridge this gap by identifying the geometric structures within pure titania that are responsible for visible light absorption. In our previous papers [6–8] we reported successful observation of local photoexcitation sites on $\text{TiO}_2(1\ 1\ 0)$ with both UV and visible light. The local photoresponse is interpreted in terms of band-gap states associated with surface oxygen defects. The present paper further examines this hypothesis, by examining the photoresponse of other and newly created surface oxygen defects.

2. Experimental

A $(1\ 1\ 0)$ surface of a single crystal rutile titania was used in the present study. The sample surface was cleaned with cycles of Ar^+ ion bombardment at a nominal 2 keV acceleration and vacuum-annealing at 900 K to obtain well-formed (1×1) terraces separated by single height steps. On this cleaned TiO_2 surface He–Cd laser light (TEM_{00} mode, beam diameter $1/e^2 = 1.2$ mm) at the wavelength of 325 or 442 nm (20 and 80 mW, respectively) was illuminated under ultra-high vacuum condition (base pressure of 10^{-8} Pa), through a light chopper that modulates the light on-and-off at frequencies of up to

3 kHz. Scanning tunneling microscopy images of the surface were acquired with constant current mode with positive sample bias, concurrently with the lock-in amplified tunnel-current images that are synchronized with the illuminated light modulation.

3. Results and discussion

Fig. 1(a) shows an STM image of a cleaned $\text{TiO}_2(1\ 1\ 0)$ surface and (b) its photoresponse to 325 nm UV light concurrently taken with (a). Numbers of terrace structures are apparent in Fig. 1(a), separated to each other by single height steps. In the lower right half of the image well-formed (1×1) terraces are visible, with (1×2) “piers” extending from the upper terraces onto the lower terraces. In the upper left half of the image the terraces appear to be covered with globular structures that resemble to the “rosette” structures observed by Li et al. [9].

When this surface is irradiated with 325-nm UV laser light, the entire surface respond to the irradiation, as may be apparent with the non-zero signal (gray color) found across the entire area of Fig. 1(b). It is noted that among the non-zero signal area, some regions show higher response to the light: in the lower right half, areas along the step lines and some of the (1×2) “pier” structures give higher photocurrent. We have reported similar phenomenon previously [8],

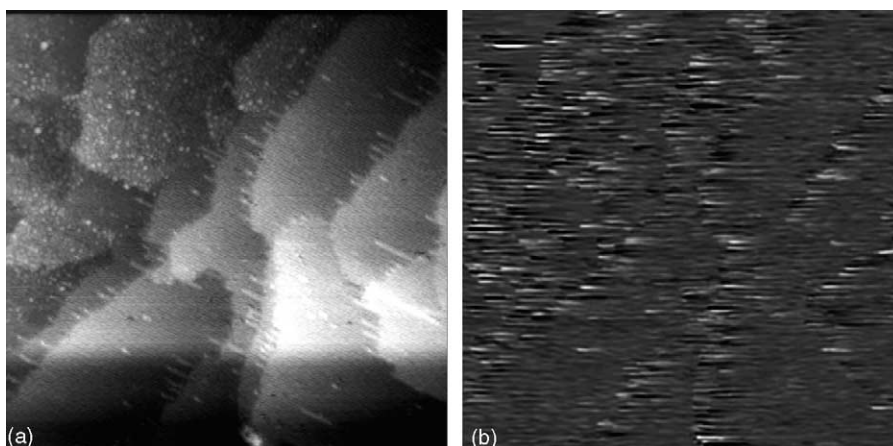


Fig. 1. STM image of a cleaned $\text{TiO}_2(1\ 1\ 0)$ surface (a) and its response to UV light irradiation (b). Both images were concurrently taken. $V_s = 1.7$ V, $I_t = 0.3$ nA and the scan area is $83.2\ \text{nm} \times 83.2\ \text{nm}$.

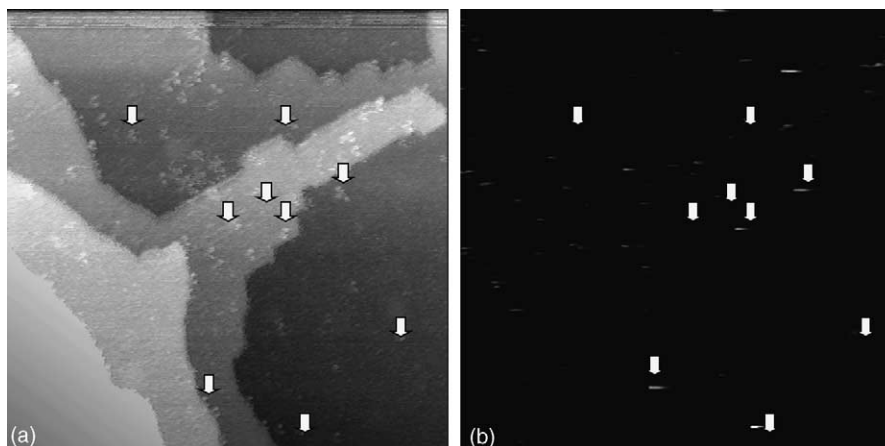


Fig. 2. STM image of oxygen defect surface (a) and its response to visible light irradiation (b). Both images were concurrently taken. $V_s = 1.7$ V, $I_t = 0.3$ nA and the scan area is 96.6 nm \times 96.6 nm.

and it has been interpreted that those higher response areas are characterized with oxygen defects, and the band-gap states created by these oxygen deficiency are responsible for the higher light response.

It is also noted in Fig. 1(b) that upper left area also indicate higher photoresponse, even on the terraces. Apparently these higher photoresponses are associated with the “rosette” structures found in (a), which is considered to be a precursor state to the (1×1) structure with Schottky defects [9]. While the Schottky defect is characterized by a missing pair of cation and anion, the data shown in Fig. 1 may be said consistent with our previous interpretation [8] that the region of higher photoresponse of $\text{TiO}_2(110)$ surface is related to oxygen deficiency.

In order to further examine this hypothesis, we observed the photoresponse of a particular oxygen defect we created on the (110) surface [7]. Fig. 2 shows an STM image of an oxygen-defect surface (a) and its photoresponse (b) concurrently taken under visible laser light illumination at 442 nm. The surface shown in Fig. 2(a) is prepared by irradiating clean $\text{TiO}_2(110)$ surface with 442 nm laser light for 10 min. White dots apparent on the terraces in Fig. 2(a) are attributed to surface oxygen defects. Note that some of these defects are paired, which could be viewed as a local (2×3) structure. The photoresponse of this surface to the visible laser light at 442 nm (Fig. 2(b)) shows that, along the steps as has been reported previously [8], the oxygen vacancies

also respond to the visible light irradiation in addition, as indicated with arrows in the figure.

Detailed comparison between the STM image (a) and its light-modulated tunnel current image (b) indicates that not all the oxygen vacancies thus created are responding to the blue light irradiation. Thus, its photoresponse is not explained with the simple band-gap state hypothesis proposed, and its further examination may be necessary. One possible cause for the inhomogeneous photoresponse may be a shift of the band gap state due to Madelung potential created by the local surface structure [10]. It is further interesting to note that, even when these oxygen vacancies are responding to the blue light, for those that are paired (the local (2×3) structure [7]), only one of them responds to the light irradiation. Further study would be necessary to clarify these points.

4. Conclusions

Local photoresponse of a rutile $\text{TiO}_2(110)$ surface was investigated on the atomic scale using STM. UV light excited almost all the areas on the (110) surface, but steps, (1×2) ridges and “rosette” structures that are associated with oxygen deficiencies exhibited higher response intensities. Previously proposed photoexcitation mechanism involving oxygen defect states in the energy band gap is examined by exciting newly created defect sites. These sites did respond to

the illumination, but interestingly, when the sites are paired, only one of them were active for the visible light illumination.

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