

ARTICLE

Suppression of Photoinduced BBO Defects Generation on $\text{TiO}_2(110)$ by Water[†]

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We have investigated creation of variable concentrations of defects on $\text{TiO}_2(110)-(1\times 1)$ surface by 266 nm laser using temperature programmed desorption technique. Oxygen-vacancy defects can be easily induced by ultraviolet light, the defects concentration has a linear dependence on power density higher than 50 mW/cm² for 90 s irradiation. No observation of O₂ molecule and Ti atom desorption suggests that UV induced defects creation on $\text{TiO}_2(110)-(1\times 1)$ is an effective and gentle method. With pre-dosage of thin films of water, the rate of defects creation on $\text{TiO}_2(110)-(1\times 1)$ is slower at least by two orders of magnitude than bare $\text{TiO}_2(110)-(1\times 1)$ surface. Further investigations show that water can be more easily desorbed by UV light, and thus desorption of bridging oxygen is depressed.

Key words: Temperature programmed desorption, Time of flight spectrum, Photo-stimulated desorption, Oxygen vacancy

I. INTRODUCTION

TiO_2 is an abundant material that has been widely used as catalyst support in industry and as photocatalyst for water dissociation [1]. Its surface structure and reactivity have been studied extensively in recent years utilizing single crystals [1, 2], among the single-crystal surfaces, the (110) face is the most stable. The studies on the (110) face have been done with a wide variety of techniques including many ultra high vacuum (UHV)-based surface science techniques. Despite intensive scrutiny, the physical and chemical properties of $\text{TiO}_2(110)$ surfaces remain to be addressed [3].

Defects in transition-metal oxides are believed to play a dominant role in determining their physical and chemical properties. TiO_2 has been well known because of its important roles in catalytic activity, occurrence of the strong metal-support interaction, oxide growth rates in electrochemical cells, and so on [4, 5]. Surface defects can be created by thermal annealing in UHV [6, 7], evaporation of excess Ti [8, 9], Ar⁺ sputtering [6, 7, 10, 11], electron stimulated desorption (ESD) [4, 11], and ultraviolet (UV) photo-stimulated desorption (PSD) [12, 13]. It is well established that thermal annealing in UHV usually creates relatively small quanti-

ties of point defects (reduced $\text{Ti}(\text{Ti}^{3+})$), whereas, Ar⁺ sputtering can produce much higher quantities of defects with mixed Ti oxidation states (Ti^{3+} , Ti^{2+} , and Ti^+). For ESD and PSD, defects on TiO_2 are usually induced by removing bridging oxygen [14]. Early ESD results show that electron stimulated desorption of oxygen ions (and presumably neutral atoms) on bare TiO_2 is generally initiated by the production of a core hole followed by intra-atomic or inter-atomic Auger decay of holes on Ti or oxygen atoms, respectively, with a threshold at about 30 eV [15]. Observations from XPS and SHG suggest that defects (bridging oxygen vacancies) can be created by UV light on $\text{TiO}_2(110)$ surface independent of the photon energy between 3.4 and 4.7 eV and regardless of whether the UV is applied in pulsed or CW form) [16]. However, Li *et al.* reported the STM results that defects created on steps and ridges of $\text{TiO}_2-(1\times 2)$ surface were more easier by UV light [17–20]. Nearly no defects were created on $\text{TiO}_2-(1\times 1)$ surface. To date, the creation of controlled numbers and types of defects on $\text{TiO}_2(110)-(1\times 1)$ surface has been well studied by ESD method. In contrast to ESD on bare $\text{TiO}_2(110)-(1\times 1)$, it is less known about whether defects can be created on $\text{TiO}_2(110)-(1\times 1)$ surface by UV light. In this work, we have investigated the method of controllable creation variable concentrations of defects (bridging oxygen vacancies) on $\text{TiO}_2(110)-(1\times 1)$ surface by 266 nm.

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II. EXPERIMENTS

Briefly, the UHV chamber used for TPD experiments has a base pressure of 6×10^{-11} Torr. A quadrupole mass spectrometer (Extrel) is used to detect desorbed products. An extremely high vacuum of 1.5×10^{-12} Torr in the electron-impact ionization region can be achieved and maintained during the experiment. Details of the TPD apparatus have been described elsewhere [21]. The rutile TiO₂(110)-(1×1) crystal (Princeton Scientific Corp., 10 mm×10 mm×1.0 mm) was mounted on a gold-coated Ta metal plate attached to a liquid nitrogen cooled sample holder for cooling to ~100 K and resistive heating to >1000 K. K type thermocouple was glued directly to the TiO₂(110)-(1×1) surface using a ceramic adhesive (Ceramabond 503, Aremco Products, INC) to provide accurate temperature measurement. The surface was cleaned through cycles of Ar⁺ sputtering (1 keV, 4 μA, 20 min) and UHV annealing (850 K, 30 min) until any contamination was below the detection limit of the Auger electron spectroscopy (AES), and a sharp (1×1) LEED pattern was observed. More cycles of Ar⁺ sputtering (500 eV, 1.5 μA, 20 min) and UHV annealing (850 K, 30 min) were carried out to flatten the surface. After this preparation procedure, the crystal color became blue and an oxygen vacancy population of 3%–4% was created on surface as gauged by water TPD. Daily cleaning was accomplished by annealing the crystal at 850 K for 30 min in UHV. Water with purity of >99.9%, was purchased from Sigma-Aldrich. Before use, it was further purified by several freeze-pump-thaw cycles. The surface was dosed with different coverage (1 ML = 5.2×10^{14} molecules/cm²) of water using a home-built, calibrated molecular beam doser at 110 K. A frequency tripling Ti: Sapphire femtosecond laser at 266 nm (Coherent, repetition rate 1 kHz) was the light source. UV light irradiation was performed at a sample temperature ~100 K with an incident angle of 30° to the surface. The maximum power of the light source at 266 nm used in this work was about 300 mW/cm². The laser had a pulse width of ~50 fs, and a band width of ~20 nm. TPD experiments monitoring H₂O desorption ($m/z=18$) were carried out at a ramp rate of 2 K/s. The TiO₂(110) surface was annealed in vacuum at 850 K for 20 min between TPD experiments to flatten the highly defective surface.

III. RESULTS

Figure 1 depicts TPD spectra from multilayer coverages ($\theta=2.9$ ML) of water dosed on the pre-irradiated TiO₂(110)-(1×1) bare surface as a function of irradiation time by 300 mW/cm² 266 nm laser. Several desorption features are shown in the spectrum: the 157 K peak is assigned to multilayer, the 179 K peak is assigned to second layer H₂O, the 263 K is assigned to first layer H₂O, and H₂O recombination at oxygen vacancy defects at ~500 K, which is similar to Henderson's re-

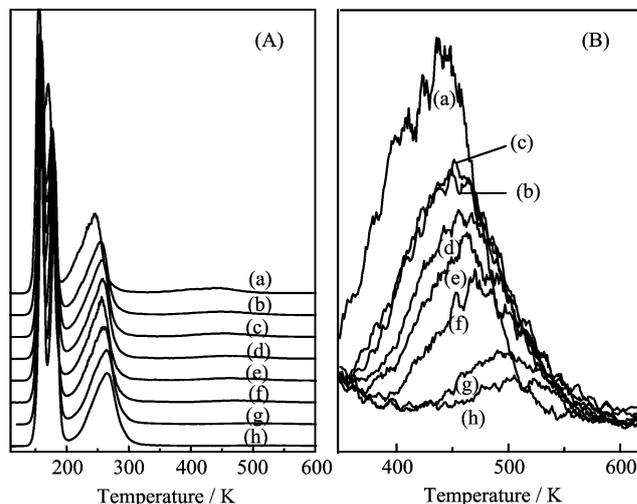


FIG. 1 (A) TPD spectra from multilayer coverages ($\theta=2.9$ ML) of water dosed on the pre-irradiated TiO₂(110)-(1×1) bare surfaces as a function of irradiation time. (B) A close up view of the evolution of features of the dissociative adsorption of water at bridging oxygen vacancy defect sites with increasing time. Irradiation time: (a) 240 s, (b) 120 s, (c) 95 s, (d) 70 s, (e) 40 s, (f) 24 s, (g) 6 s, and (h) 0 s.

sults [22]. The peak shape and desorption temperature of the various water TPD states from TiO₂(110)-(1×1) are very sensitive to laser irradiation time. Figure 1(B) shows the changes of the 500 K peak. The most obvious and expected change resulting from laser irradiation is the enhancement and shift of the 500 K TPD peak. The area of the 500 K peak increased with laser irradiation time, indicating that O-vacancy defects have been produced with laser irradiation. After long time irradiation, the 500 K TPD peak shifts from 520 K to 450 K. The first layer state shifts from 263 K to 258 K, commensurate with the enhancement of the vacancy peak (500 K). There are little shifts in the multilayer peak and the second layer peak. The two peaks becoming less defined is a sign of the merging of the two peaks. The “valley” between the first and second layer states remains well defined, implying that the regular Ti⁴⁺ rows are nearly not affected by UV irradiation. The first layer peak shifts to lower temperature and sharpens after irradiation, that is due to the increased intensity of H atoms on bridging oxygen rows [24]. The increased 450 K peak intensity indicates that controllable creation of defects on TiO₂(110)-(1×1) by UV light is feasible.

Defects produced by 300 mW/cm² 266 nm for various irradiation durations with 1 ML water covered TiO₂(110) was investigated as well. As shown in Fig.2, the changes of the peak shape and desorption temperature of the various water TPD peaks with 1 ML water covered TiO₂(110)-(1×1) after UV irradiation are consistent with that of the bare TiO₂(110)-(1×1). The difference is that longer irradiation time is needed for

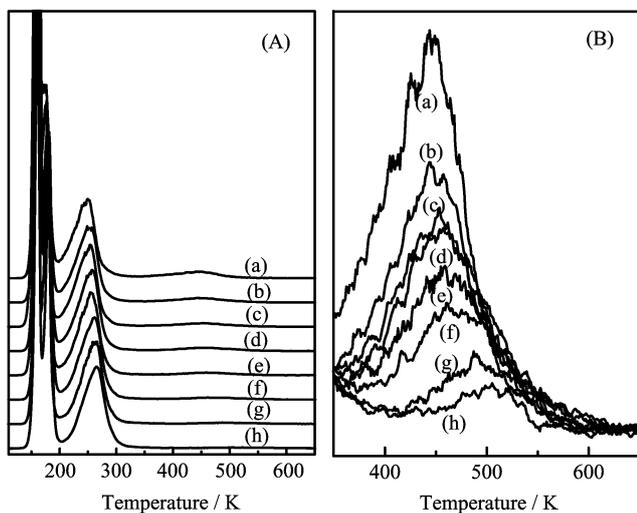


FIG. 2 (A) TPD spectra from multilayer coverages ($\theta=2.9$ ML) of water dosed on the pre-irradiated $\text{TiO}_2(110)-(1\times 1)$ 1 ML water covered $\text{TiO}_2(110)-(1\times 1)$ surfaces as a function of irradiation time. (B) A close up view of the evolution of features of the dissociative adsorption of water at bridging oxygen vacancy defect sites with increasing time. Irradiation time: (a) 3600 s, (b) 1800 s, (c) 1200 s, (d) 900 s, (e) 600 s, (f) 360 s, (g) 90 s, and 0 s.

creating the same amount of bridging oxygen defects for 1 ML covered $\text{TiO}_2(110)-(1\times 1)$ surface. The defects concentrations calculated from Fig.1 and Fig.2 are shown in Fig.3. The defects concentration increased on 1 ML water covered $\text{TiO}_2(110)-(1\times 1)$ is slower by two orders of magnitude than that on bare $\text{TiO}_2(110)$ surface, implying that water seems to protect the surface from avoiding removing bridging oxygen.

To further confirm the TPD result, a time-of-flight (TOF) mass spectrometer was used to collect the desorption products from the $\text{TiO}_2(110)-(1\times 1)$ surface when the surface was irradiated by 266 nm (Fig.4). For bare $\text{TiO}_2(110)-(1\times 1)$ surface, O-atom emission from $\text{TiO}_2(110)-(1\times 1)$ during irradiation with 266 nm was clearly observed at the beginning, no O_2 and Ti atom TOF signals were detected, which is similar to the electron stimulated desorption results [23]. We can conclude that only bridging oxygen was removed during UV irradiation and UV light has little effect on regular Ti^{4+} rows. When 1 ML H_2O covered $\text{TiO}_2(110)-(1\times 1)$ surface was irradiated by 266 nm, O-atom emission signal increased slowly in the first few seconds, and H_2O was the main desorption product (not shown). Even at long irradiation time, O-atom emission signal still kept at a low level. The observation is consistent with the result shown in Fig.3, which implies that desorption of H_2O and bridging oxygen competes with each other, and H_2O seems to be easier to be desorbed. Previous theoretical studies suggest the adsorption energy for H_2O is about 0.7 eV [24], while the adsorption energy for bridging oxygen is more than 2 eV [25]. The

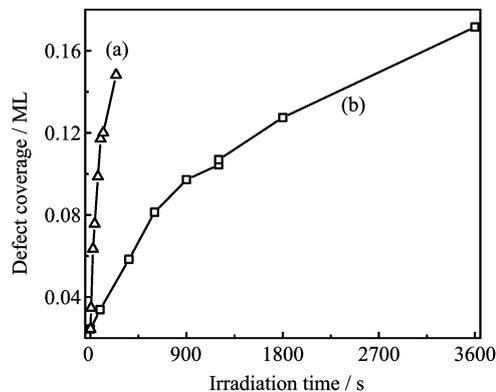


FIG. 3 Defects concentrations produced by 266 nm $300 \text{ mW}/\text{cm}^2$ as a function of irradiation time. (a) Bare $\text{TiO}_2(110)-(1\times 1)$ surface, and (b) 1 ML water covered $\text{TiO}_2(110)-(1\times 1)$ surface.

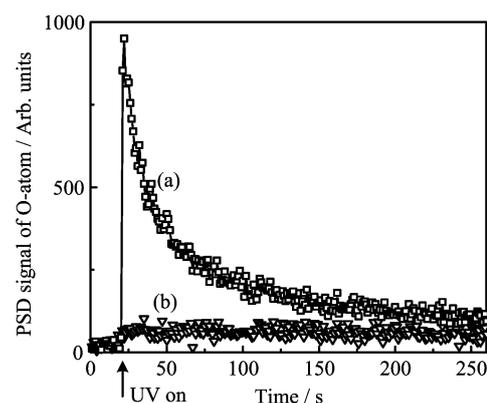


FIG. 4 Photo-desorption signals for O-atom as a function of irradiation time from (a) bare $\text{TiO}_2(110)$ and (b) 1 ML water covered $\text{TiO}_2(110)$.

big difference in desorption energy clearly shows that H_2O can be more easily desorbed than bridging oxygen. Recent ESD results of Kimmel *et al.* show that after ESD, the concentration of oxygen defects decreased and the first layer peak shifted to higher temperature with 1 ML water covered $\text{TiO}_2(110)-(1\times 1)$ surface [26], which was due to O_2 production from water splitting by ESD. In comparison with their results, our observations implied that no O_2 was produced from 1 ML covered $\text{TiO}_2(110)-(1\times 1)$ during UV irradiation.

In order to unravel the relationship of defects concentration and 266 nm photon flux, defects produced by 266 nm 90 s as a function of irradiation power was carried out on bare $\text{TiO}_2(110)-(1\times 1)$ surface. As shown in Fig.5, the trends of the peak shapes and desorption temperatures of the various water TPD states with laser power increasing are consistent with the bare $\text{TiO}_2(110)-(1\times 1)$ with increasing irradiation time. The defects concentrations after various photon flux of 266 nm irradiation were calculated, as shown in Fig.6. When power density is lower than $50 \text{ mW}/\text{cm}^2$, there

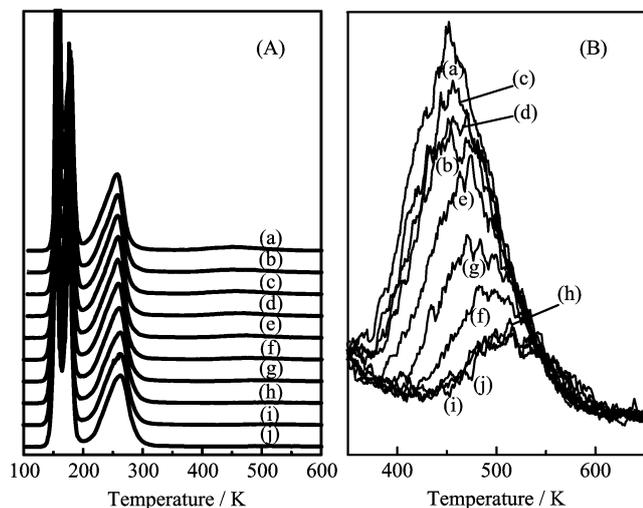


FIG. 5 (A) TPD spectra from multilayer coverages ($\theta=2.9$ ML) of water dosed on the 90 s pre-irradiated TiO₂(110)-(1 \times 1) bare surface as a function of irradiation power. (B) A close up view of the evolution of features of the dissociative adsorption of water at bridging oxygen vacancy defect sites with increasing power. Irradiation power: (a) 290 mW/cm², (b) 260 mW/cm², (c) 240 mW/cm², (d) 200 mW/cm², (e) 165 mW/cm², (f) 120 mW/cm², (g) 80 mW/cm², (h) 51 mW/cm², (i) 23 mW/cm², (j) 0 mW/cm².

is little changes in defects concentration; it seems to be a threshold for defects creation. This is consistent with previous observations in contact angle measurements of water on TiO₂ surface during UV irradiation [14]. With higher photon flux, the defects concentration increasing shows a linear relationship with photon flux. More work is needed to unravel the mechanism of photo induced bridging oxygen desorption to produce surface defects.

IV. DISCUSSION

In this work, UV light can create controllable number of defects by controlling irradiation time or photon flux from low concentration (<4%) to high concentration (more than 20%, not shown here), similar to previous ESD results [4, 11] and PSD results as gauged by X-ray photoemission spectroscopy (XPS) [12, 13]. However, due to the high photo energy of X-ray, it can also make bridging oxygen desorbed from the surface, the results is not so accurate.

As discussed in the introduction, UV photon irradiation of bare TiO₂ (110) reduces the surface by desorbing O, thus produce surface defects. Here, with 2 ML water covered TiO₂(110)-(1 \times 1) surface (see in Fig.7), it seems that desorption of water comes from the second layer first, and no increasing of surface defects is observed. According to previous ESD work [27], the H₂O on first layer can be rapidly exchanged with the H₂O

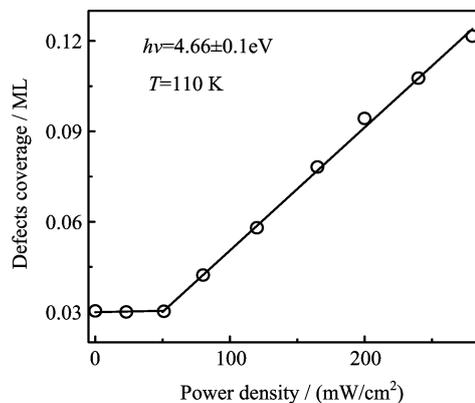


FIG. 6 Defects concentrations produced by 266 nm irradiation for 90 s as a function of power density, which were calculated from water TPD of Fig.5.

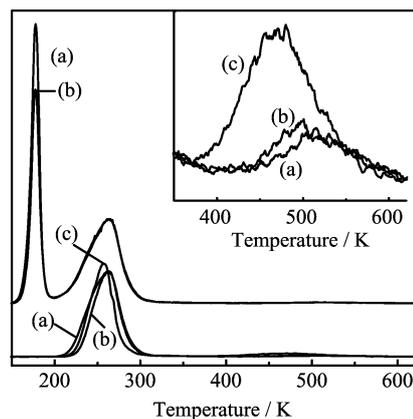


FIG. 7 Water TPD spectra after 1 and 2 ML water films covered TiO₂ (110)-(1 \times 1) surface with 266 nm 40 mW/cm² irradiation at 110 K for 30 min. (a) TPD without irradiation, (b) TPD with irradiation, (c) the water TPD following the bare TiO₂(110)-(1 \times 1) irradiated with 266 nm 40 mW/cm² at 110 K for 30 min.

on the second layer at $T>120$ K due to the hydrogen bond between the H₂O of the two layers, and the second layer H₂O can be desorbed more easily by ESD, which is consistent with their desorption energies. Meanwhile, the bridging oxygen rows are totally covered with 2 ML water covered surface, which hints that desorption of bridging oxygen can be largely inhibited when bridging oxygen is covered by water. Whereas, with 1 ML water covered TiO₂(110)-(1 \times 1) surface, the desorption of bridging oxygen is depressed. That's a little different from 2 ML covered TiO₂(110)-(1 \times 1) surface.

The hydrophilicity of TiO₂ has been shown to be largely enhanced with increasing concentration of bridging oxygen defect [12] and higher bridging oxygen defects on the TiO₂(110) surface make the formation of hydrogen relatively easier than water formation, enhancing the efficiency of hydrogen production [28]. Meanwhile, the existence of bridging oxygen defect can

also enhance the interaction of reactants and surface, such as formaldehyde CH_2O , NO , CO . Of course, the bridging oxygen defect can also inhibit reactions, and lower the photoactivity of $\text{TiO}_2(110)$ [29]. Thus, the role of bridging oxygen defects should be carefully investigated to confirm whether it can promote reactions or inhibit reactions.

V. CONCLUSION

We have investigated surface defects creation on bare $\text{TiO}_2(110)-(1\times 1)$ surface and thin water films (<3 ML) covered $\text{TiO}_2(110)$. With bare $\text{TiO}_2(110)-(1\times 1)$ surface, UV light can create controllable number of defects very easily. When thin water films (<3 ML) are initially adsorbed on $\text{TiO}_2(110)-(1\times 1)$ surface, photo irradiation results primarily in desorption of H_2O . After prolonging irradiation, O PSD becomes significant. With 1 ML water covered $\text{TiO}_2(110)-(1\times 1)$ surface, PSD of H_2O competes with bridging oxygen, which makes the rate of bridging oxygen desorption slower by two orders of magnitude than bare $\text{TiO}_2(110)-(1\times 1)$ surface. With such a method to produce controllable defects on $\text{TiO}_2(110)-(1\times 1)$ surface, the role of oxygen defects in molecules adsorptions, thermal reactions, and photo-catalytic reactions can be widely investigated in future.

VI. ACKNOWLEDGMENTS

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