Diffusion and Oxidation of Ti^{3+} Interstitials on a Reduced TiO_2 (001) Surface: A Crystal-face Dependency

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Valence band of a vacuum-reduced TiO_2 (001) surface has been carefully examined using synchrotron x-ray photoelectron spectroscopy to investigate variation of the gap state upon oxidation and thermal diffusion of Ti^{3+} interstitials from the bulk. We compare our results with that obtained from TiO_2 (110) and aim to address a crystal-face dependency in the oxidation and diffusion rates of Ti^{3+} interstitials. We find very similar behaviors in the oxidation and thermal diffusion rate of Ti^{3+} interstitials between the two crystal faces suggesting a negligible crystal-face dependency in this case.

Keywords : Oxidation, Ti^{3+} defects, TiO_2 (001), Photoemission spectroscopy

I. Introduction

TiO_2 is a prominent material for various applications such as photovoltaic solar cells and photocatalysts for hydrogen production and removal of organic contaminants [1]. The success of such applications is determined by factors such as how to adjust the band gap suitable for the application and how to control the defects in the bulk as well as on the surface.

Especially, understanding and controlling the defects in TiO_2 have been a long-term issue since TiO_2 is a reducible oxide with possible bulk (surface) defects such as Ti interstitials and oxygen vacancies [1]. The presence of defects in TiO_2 has a huge influence not only on the electrical properties but also on its photovoltaic and photocatalytic performances.

The presence of defects in TiO_2 has been studied by

UPS, in which a band-gap state in valence band has been assigned to the presence of surface oxygen vacancies [2,3]. Recently, the exact origin of the gap state [4–7] has been intensively discussed and it is generally understood that the gap state is induced by both oxygen vacancies and Ti interstitials, where the ratio between the two can vary depending on the detailed pretreatment conditions [7].

Recent theoretical studies employing DFT calculations also predict that the gap state is originated from excess electrons with a 3d-like character which are localized on either 5-fold [8] or 6-fold [8,9] Ti atoms adjacent to oxygen vacancies on TiO_2 (110). The contribution from Ti atoms in interstitial sites (Ti_{int}) in a 3^+ state with one 3d-like electron has been predicted from spin polarized hybrid DFT calculations [10]. Recent STM [11] and resonant photoemission diffraction [12] studies suggest that the excess charge

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may be delocalized on multiple Ti^{4+} sites.

A further understanding on the exact role of the gap state-related surface charges may be gained by studying the variation of the state upon diffusion and reactions of the defects induced by annealing and oxidation, respectively. The key step in the reoxidation of reduced TiO_2 may involve the diffusion of oxygen vacancies and Ti interstitials [13]. Henderson reported that the diffusion of Ti interstitials play a dominant role in the bulk-assisted reoxidation of ion-sputtered TiO_2 surface [13].

In the present study, we employed synchrotron ultraviolet spectroscopy (UPS) to probe the gap state in valence band for the study of detailed behaviors of defects (oxygen vacancies and Ti interstitials) upon oxidation and subsequent annealing. For such a purpose, we used a (001) plane of a rutile TiO_2 single crystal instead of the well-characterized (110) plane of TiO_2 to find a possible facet-dependent variation in the behaviors of defects. The electrical conductivity is highest along the [001] direction and there might be a chance of observing an enhancement in the diffusion of defects for oxidation near the surface. Our results indicate very similar behaviors of defects on the (001) plane as (110).

II. Experimental Section

A single crystal TiO_2 (001) substrate (0.5 mm thick, one-side polished, MTI) was cut into 5×10 mm in size and a thin Ta foil and was glued on the backside of the substrate using an Al_2O_3 -based glue (Ceramabond 503) before being introduced into a UHV chamber attached to 7B1 beamline (moved to 10D) [14] at Pohang Accelerator Laboratory (PAL). K-type thermocouple was spot-welded on the edge of the Ta foil wrapped around the TiO_2 crystal for a temperature measurement. A well-ordered and clean TiO_2 (001) was obtained by a few cycles of Ar^+ -sputtering

at 1 keV and annealing at 900 K. An ordered TiO_2 (001) surface was confirmed from very sharp integer spots in LEED indicating an atomically long-range ordered domain structure has been obtained.

A detailed information on the atomic structure of the TiO_2 (001) surface has been reported from experimental and theoretical studies [15–18]. Although the pretreatment condition may have a strong influence on the surface structure, theoretical studies show that the (001) facet of rutile TiO_2 crystal has two kinds of surface species of a four-fold Ti^{4+} and a two-fold oxygen, respectively [17]. The high surface free energy of the (001) facet compared to other facets induces the TiO_2 (001) surface to undergo a surface reconstruction involving an outward movement of oxygen atoms and an inward movement of titanium atoms [18]. At above 1,000 K the surface may produce low surface energy facets which contain both 5-fold Ti^{4+} and 4-fold Ti^{4+} sites [16]. Our experimental conditions impose our clean TiO_2 (001) surface to be composed of a reconstructed surface composed mainly of a four-fold Ti^{4+} and a two-fold oxygen.

A well-ordered TiO_2 (001) surface had a typical amount ($\sim 10\%$) of surface defects (oxygen vacancies and Ti^{3+} defects) which could be measured from a gap state in the valence band spectrum. Oxidation of the TiO_2 (001) surface was performed by backfilling the chamber with O_2 (99.999 %) using a variable leak valve up to an O_2 ambient pressure of 10^{-6} torr.

XPS measurements were performed at the 7B1 beamline. Photoemission spectra of Ti 2p, O 1s, and C 1s core levels were taken using a commercial electron analyzer (PHOIBOS 150, SPECS) at a fixed normal emission at RT. Photon energy used for the measurement of valence band was 55 eV. The binding energies of the photoemission spectra were determined by the position of the Fermi edge of Ta foil in contact with the TiO_2 substrate. The C 1s core level spectra are carefully analyzed using a standard nonlinear least-squares fitting procedure with Voigt

functions [19].

III. Results and Discussion

Fig. 1 shows a schematic drawing of the unit cell of rutile TiO_2 crystal. As shown, the basic building block consists of a Ti atom bound to six oxygen atoms in an octahedral geometry. The (110) surface has been calculated to have the lowest surface energy and the (001) surface has the highest surface energy [1]. The high stability of the (110) plane is originated from a compensation of charges between anionic oxygen and cationic titanium on the surface. The surface Ti atoms are either five fold or six fold coordinated. The low stability of the (001) is attributed to the low coordination number of surface Ti atoms; all the surface Ti atoms are four fold coordinated and all oxygen atoms are two fold coordinated. The detailed atomic structure of the (001) plane varies widely depending on the pretreatment condition and is in general not clearly understood because of the instability of the plane.

Fig. 2 shows the valence band spectrum of our clean and ordered TiO_2 (001) surface prepared in a

Figure 1. Schematic unit cell structure of rutile TiO_2 crystal.

UHV chamber after repeated cycles of Ar^+ -sputtering and annealing (~ 900 K). For comparison, the valence band of TiO_2 (110)- 1×1 surface taken at the same condition is also shown. Both spectra are characterized by an intense peak at 4–10 eV and a small peak (labeled as D) 0.9 eV below the Fermi level.

The intense broad peaks from both TiO_2 crystals show a notable difference in the overall shape. The one from TiO_2 (001) is characterized by two distinct peaks at ~ 5 and 7.8 eV, while that from TiO_2 (110) peaks at ~ 6 eV with shoulders on both sides. The origin of the main peak is a band mainly derived from O 2p state [3,4]. Especially, the peaks at 5 and 7.8 eV are characteristic O 2p-derived state of an ordered TiO_2 (001) surface [3]. As the crystal becomes reduced, the coordination geometry of oxygen may change and induce a change in the overall shape of the main O 2p-derived state. The enhanced intensity at ~ 6 eV can be related to the amount of O 2p – Ti 3d hybridization present and the local coordination of O atoms by Ti atoms [3].

The peak labelled as D has been known to be the band gap state. The gap state reflects the presence of Ti^{3+} (3d) state which can be related to reduced Ti

Figure 2. Comparison of the valence band spectra of TiO_2 (001) and TiO_2 (110). D indicates the band-gap state related to the Ti 3d state.

species such as Ti^{3+} interstitials and oxygen vacancies [2–5]. The pronounced intensity of the peak on both (001) and (110) indicates a facile formation of the surface defects (oxygen vacancies and Ti interstitials) on both surfaces after the Ar^+ -sputtering and an-annealing cycle.

The integrated area of the gap state monitored after successive doses of O_2 at RT up to 1,000 L is plotted in Fig. 3. The intensity of the gap state decreases noticeably upon O_2 dose up to a few tens of Langmuir. A further reduction of the gap state however requires an extensive amount of O_2 dose as has been observed on TiO_2 (110) [4]. Fig. 3 indicates that the gap state still remains even after 1,000 L of O_2 dose.

The immediate reduction of the gap state results from oxidation of surface defects such as oxygen vacancies. Ti^{3+} interstitials near the surface may be also reduced by the interaction with O_2 at RT [4]. The

Figure 3. The integrated area of the band-gap state of TiO_2 (001) is plotted against the amount of O_2 dose at RT. The integrated areas of the band-gap state are normalized to that of the initial clean TiO_2 (001) surface. The inset shows a variation in the band-gap state of the initial clean TiO_2 (001) surface after successive oxidation with O_2 dose at RT.

presence of different types of surface defects would make the detailed oxidation reaction kinetics complicated even for the present case where the oxidation is performed under a constant flux of O_2 at a fixed O_2 partial pressure ($\sim 10^{-6}$ torr). Especially, those Ti species in the subsurface region require a substantial diffusion of the interstitials toward surface before being oxidized by oxygen at the surface [4].

The oxidation kinetics of a surface defect may be assumed to be first-order under a constant O_2 flux. In such a case, natural log of the gap state intensity may be plotted against the reaction time (or the O_2 dose) as shown in Fig. 4. The observation of two regions of straight lines with different slopes can be attributed to oxidation of different types of defects which proceed through different reaction rates.

The result indicates that there are at least two separate regions with different oxidation rates. In region I, the oxidation-induced reduction of the gap state proceeds readily up to the O_2 dose of $\sim < 20$ L. The gap state intensity decreases to about half of the initial value. A further decrease in the gap state proceeds rather slowly as depicted as region II. A clear distinction between the two regions of different oxi-

Figure 4. Natural log of the integrated area of the band-gap state in Fig. 3 is plotted against the amount of O_2 dose at RT. Two regions with drastically different oxidation kinetics of surface defects are indicated as Region I and Region II, respectively.

dation kinetics indicates the presence of at least two different surface defects which can be assigned to oxygen vacancies and Ti interstitials, respectively. The oxidation of oxygen vacancies is associated with region I since the uptake of oxygen by oxygen vacancies occurs readily even from the very low temperatures. The oxidation of subsurface Ti interstitials requires a diffusion of the charged species with an energy barrier and is assumed to be related to region II [4].

The oxidized TiO_2 surface may be recovered to the initial reduced state by vacuum-annealing up to successively higher temperatures. Fig. 5 shows our results on the annealing-dependent recovery of the gap state of the oxidized TiO_2 (001) surface. The increase of the gap state is related to a diffusion of shallow Ti interstitials to the near surface region. Our results indicate that the diffusion of Ti interstitials occurs just above 400 K. The result obtained from TiO_2 (110) is compared in Fig. 5. Interestingly, we find a very similar temperature-dependent behavior of the gap

state upon successive annealing within our uncertainty limit. This result may be interpreted to be due to the fact that the diffusion of the near-surface Ti interstitials is not much influenced by the type of crystal orientation between (110) and (001).

IV. Summary

We studied the oxidation kinetics of surface defects on TiO_2 (001) upon O_2 dose at RT. The results are very consistent with that obtained from TiO_2 (110) and indicate the presence of at least two different kinds of surface defects (oxygen vacancies and Ti interstitials) that are related to the gap state. Also, subsequent annealing of the oxidized TiO_2 (001) above 400 K was shown to induce a diffusion of shallow Ti interstitials toward near surface region resulting in a recovery of the gap state, which behavior was found to be very similar to that on TiO_2 (110). Based on our present results, we concluded that the diffusion and oxidation of Ti interstitials had a little crystal-face dependency between (110) and (001).

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Figure 5. Integrated areas of the band-gap state are normalized to that of the initial TiO_2 (001) surface and plotted against annealing temperature. Our result is compared with that of Wendt et al. result [4,20] on TiO_2 (110). The inset shows a change in the band-gap state of the oxidized TiO_2 (001) after successive annealing up to 670 K.

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TiO₂ (001)면에서 Ti 결함의 확산과 산화: 결정면에 대한 의존성

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방사광 가속기에서 얻은 x-선을 이용하여 초고진공에서 열처리를 통하여 얻어진 TiO₂ (001) 단결정 표면의 원자가 전자대에 대한 광전자 분광연구를 수행하였다. 이 연구를 통하여 특히 페르미 준위 0.9 eV 근처에 있는 결함에 기인한 전자 상태의 변화로부터 Ti³⁺ 결함의 산화 또는 열확산 과정에 대한 반응 속도론적 특성을 연구하였다. 본 연구의 결과는 (001)면에서의 Ti³⁺ 결함의 열역학적 특성이 TiO₂ (110) 단결정면에서의 그것과 어떻게 다른지를 규명하는데 큰 의미가 있다. 연구 결과, (001)과 (110) 결정면에서의 Ti³⁺ 결함의 거동은 산화 반응성과 결정 내에서의 열적 확산 특성에서 매우 유사하다는 것을 알게 되었다. 이와 같은 결과를 얻게 된 주된 이유 중의 하나는 관여하는 Ti³⁺ 결함이 주로 표면 근처에 분포되어 있다는데서 찾을 수 있다.

주제어 : 산화, 확산 Ti 결함, TiO₂ (001), 광전자 분광법

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