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Characterization of oxygen and titanium diffusion at the anatase TiO_2(001) surface

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ABSTRACT

The diffusion of intrinsic defects in a single crystal anatase TiO_2(001) film was explored by isotopic labeling and static secondary ion mass spectrometry. Using both ^{46}Ti and ^{18}O as isotopic labels, we show that the anatase surface responds to redox imbalances by diffusion of both Ti and O into the bulk under vacuum reduction and (at least) Ti from the bulk to the surface during oxidation. The diffusion of Ti between the bulk and surface in anatase TiO_2(001) closely resembles what was observed in the literature for the rutile TiO_2(110) surface, however the latter is not known to have oxygen diffusion between the bulk and surface under typical ultrahigh vacuum conditions. We speculate that the open lattice of the anatase bulk structure may facilitate independent diffusion of both point defects (Ti interstitials and O vacancies) or concerted diffusion of "TiO" subunits.

1. Introduction

Defects in titanium dioxide (TiO_2) significantly impact its chemical, optical, and electrical properties [1,2]. Experimental studies have examined how surface and subsurface defects impact rutile's surface properties [3–14]. In contrast, fewer studies have assessed how intrinsic defects affect anatase's surface properties [15–19]. A recent scanning tunneling microscopy study found that oxygen vacancies migrate from surface to subsurface sites at temperatures below ~200 K for the anatase TiO_2(101) surface, where different temperature-dependent equilibriums were obtained for various oxygen vacancy densities compared to rutile surfaces [20]. Theoretical investigations have examined the defect stability and diffusion processes in rutile [21–24], and anatase [25–30], with comparisons between the two [31,32]. These results suggest that the atomic and electronic structure of point defects in rutile and anatase are very different. For example, calculations indicate that rutile is more stable than anatase in oxygen deficient conditions, leading to a preference for titanium interstitial formation over oxygen vacancies [31].

Recently the electric field induced drift of defects in TiO_2 has been invoked to explain bipolar resistive switching in memristor devices [33]. It was proposed that a built-in asymmetry of intrinsic defect density in TiO_2 changes the metal/oxide contact resistance, where lower dopant concentrations in the stoichiometric oxide result in a high-resistance Schottky junction, but higher dopant concentrations in the sub-stoichiometric oxide result in a low-resistance Ohmic junction. Applying an electric field causes these intrinsic defects to drift, which then modulates resistance at the corresponding junctions. A second mechanism has been proposed to describe bipolar resistive switching of TiO_2 thin films through the net accumulation of intrinsic defects and the formation/dissolution of sub-stoichiometric titanium oxide conductive filaments (Magnéli phases), depending on the applied electric field and thermal effects due to Joule heating [34]. Joule heating during an electroforming process has been observed to partially convert amorphous TiO_2 films to the anatase phase along with single sub-stoichiometric titanium oxide conductive filaments [35]. The drift of oxygen vacancies and/or oxygen ions in TiO_2 was used to describe the observed switching characteristics of memristors, however the drift of titanium interstitials is rarely considered in regard to memristor switching mechanisms [33–36]. A recent study indicates that chromium and titanium adhesion layers strongly impact memristor device performance, particularly by diffusing through the Pt electrode to the TiO_2 interface [37]. However, the potential for these species to diffuse into the TiO_2 switching layer has not been considered.

In this study, we investigated diffusion of oxygen and titanium at the anatase-TiO_2(001) surface using temperature-programmed secondary ion mass spectroscopy (TP-SIMS). The reduced anatase surface was found to reoxidize by heating above 700 K in ultrahigh vacuum (UHV). Isotopically labeling the surface with ^{18}O or ^{46}Ti reveals that surface reoxidation occurs primarily through the diffusion of titanium interstitials into the bulk of the film. However, SIMS indicates that both O and Ti diffuse into the bulk during UHV reduction.

2. Experimental

A 300 Å epitaxial anatase TiO_2(001) film was grown on conducting Nb-doped $SrTiO_3$(001) crystal by oxygen-plasma enhanced molecular beam epitaxy [38,39]. The sample was transferred to the SIMS system

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through air and was cleaned by cycles of argon bombardment (1 keV Ar^+ at ~0.4 μA) and annealing (850 K), rendering the (4×1)/(1×4) reconstructed, stoichiometric surface [40]. Surface impurities were monitored using Auger electron spectroscopy (AES) and SIMS. The experiments were conducted in an unbaked UHV chamber with a base pressure of ~2×10^{-9} Torr [13]. A 0.5 keV Ar^+ source with an ion current of ~1–10 nA/cm^2 was used for static SIMS analysis. Secondary ions were monitored using an Extrel C50 quadrupole mass analyzer. For temperature-programmed studies, the heating rate was 2 K/s and the temperature was monitored using a thermocouple cemented to the sample. The surface was exposed to oxygen ($^{16}O_2$ or $^{18}O_2$) by chamber backfilling. Enrichment of the surface with ^{46}Ti was performed using an evaporation source containing 96.84% isotopically pure $^{46}TiO_2$ powder, which sublimed as TiO [13,41]. Deposition of $^{46}TiO_2$ on the surface was achieved by subliming in an O_2 background. The surface was restored to its natural isotopic distribution by sputtering. All the TP-SIMS signals were corrected to remove contributions from other isotopic combinations using a deconvolution procedure based on the natural abundance of the titanium and oxygen isotopes [13].

3. Results/discussion

Fig. 1a–c shows SIMS spectra obtained from the anatase TiO_2(001) surface after several different preparation methods. The SIMS spectrum after sputtering with 1 keV Ar ions at 850 K and cooling to 300 K is shown in Fig. 1a. Peaks between 46–50 atomic mass units (AMU) and 62–66 AMU correspond to Ti^+ and TiO^+, respectively, with their relative intensities matching the natural abundances of Ti and O isotopes. (Small additional intensity at 63–67 AMU was due to $TiOH^+$ from trace amounts of background water adsorption on the surface, and. were removed by desorbing water with mild heating.) The TiO^+/Ti^+ ratio correlates with surface stoichiometry and can be used to estimate the surface's oxidation state [12,13,42]. For example, a TiO^+/Ti^+ ratio of ~0.7 after sputtering indicated extensive surface reduction, and a TiO^+/Ti^+ ratio of ~3 after annealing at 850 K indicated surface reoxidation. Similar ratios were obtained after annealing in UHV or in 5×10^{-7} Torr O_2. The SIMS spectrum after deposition of a submonolayer coverage of $^{46}TiO_x$ at 300 K is shown in Fig. 1b. Compared to Fig. 1a, this spectrum shows a significant increase in the $^{46}Ti^+/^{48}Ti^+$ ratio due to enrichment with ^{46}Ti. The ^{46}Ti coverage was estimated at ~0.31 ML [13]. The SIMS spectrum after exposure of the clean surface to 5×10^{-7} Torr $^{18}O_2$ (15 min. at 300 K) is shown in Fig. 1c. The increase in the $^{48}Ti^{18}O^+/^{48}Ti^{16}O^+$ ratio indicates that the surface was enriched with ^{18}O.

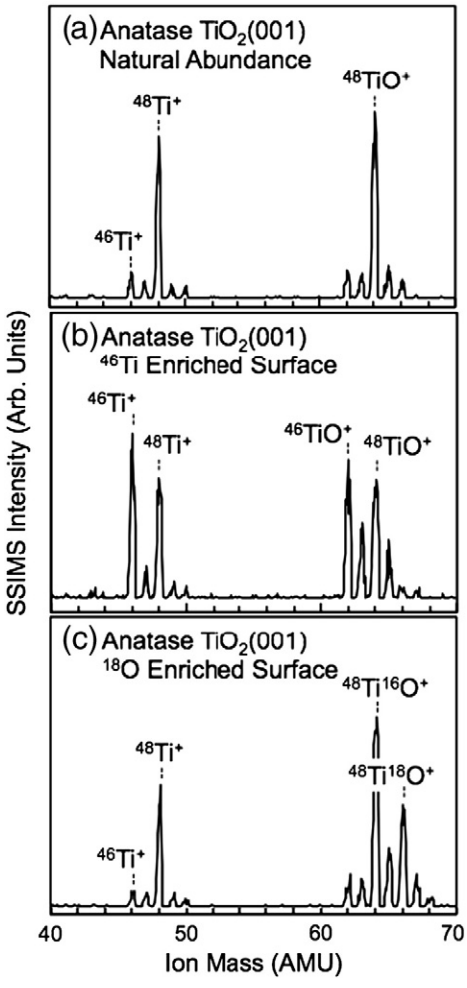

Fig. 1. SIMS data from an epitaxial anatase TiO_2(001) thin film on $SrTiO_3$(001). (a) From the as-grown film. (b) From the ^{46}Ti-labeled surface. (c) From the ^{18}O-labeled surface.

Fig. 2a–c presents TP-SIMS data after enrichment of the surface with ^{46}Ti. The SIMS signals for the $^{48}TiO^+$, $^{48}Ti^+$, $^{46}TiO^+$ and $^{46}Ti^+$ species versus temperature are shown in Fig. 2a. The intensities of all four ions increased between 300 and 600 K, but were different above 600 K. The $^{48}TiO^+$ signal continued to increase until 800 K, at which point it remained constant up to 850 K, whereas the $^{48}Ti^+$ signal decreased abruptly above 700 K. The $^{46}TiO^+$ and $^{46}Ti^+$ signals both decreased above 600 K, but at different rates. To gain more insight into processes occurring during TP-SIMS we plotted the $^{48}TiO^+/^{48}Ti^+$ ratio versus temperature in Fig. 2b. The $^{48}TiO^+/^{48}Ti^+$ ratio stayed fairly constant up to ~700 K, but increased substantially above 700 K indicating a surface stoichiometry change reflective of reoxidation. This surface reoxidation process occurred through a bulk-assisted mechanism since the anneal was performed in UHV. The $^{46}TiO^+/^{48}TiO^+$ ratio versus temperature, plotted in Fig. 2c, provides insight into the reoxidation process. The $^{46}TiO^+/^{48}TiO^+$ ratio stayed fairly constant up to ~600 K, indicating no net change in the ^{46}Ti surface coverage, but decreased substantially above 600 K. The ^{46}Ti surface coverage decreased from ~0.31 ML at 600 K to ~0.12 ML at 750 K, and remained constant up to 850 K. A similar decrease in the ^{46}Ti surface coverage during heating the ^{46}Ti-enriched rutile was assigned to diffusion of Ti interstitials into the bulk [13].

In Fig. 3a–b we show SIMS data versus time for the sample held at 850 K after the TP-SIMS spectrum shown in Fig. 2a. The intensities of the $^{48}TiO^+$, $^{48}Ti^+$, $^{46}TiO^+$ and $^{46}Ti^+$ signals stayed approximately constant up to ~775 s. At this point, oxygen was introduced into the UHV chamber (5×10^{-7} Torr) resulting in an immediate increase in the $^{48}TiO^+$ and $^{46}TiO^+$ signals, but little change in the $^{48}Ti^+$ and $^{46}Ti^+$ signals. The increase in the $^{46}TiO^+$ signal was greater than the $^{48}TiO^+$ signal. This is more clearly seen in a plot of the $^{46}TiO^+/^{48}TiO^+$ ratio versus time (Fig. 3b). The ^{46}Ti surface coverage exhibited a slow decrease during annealing in UHV (from ~0.12 to ~0.08 ML), but addition of oxygen resulted in a ^{46}Ti coverage increase to ~0.16 ML. This addition of oxygen at 850 K resulted in regrowth of TiO_2 on the anatase surface, as observed for rutile substrates [5–7,10]. However, in this study since the TiO_2 film was thin (i.e., not a bulk crystal) the specific Ti isotopic distribution (enriched with ^{46}Ti) that diffused in during vacuum reduction could be returned to the surface during reoxidation.

The TP-SIMS data for the surface enriched with ^{18}O are shown in Fig. 4a–b. The behaviors of the $^{48}Ti^{16}O^+$, $^{48}Ti^+$ and $^{48}Ti^{18}O^+$ SIMS signals as a function of temperature are shown in Fig. 4a. These SIMS signals varied substantially with temperature. For example, the $^{48}Ti^{16}O^+$ intensity increased as the sample was heated to 500 K, at which point it decreased, and then increased again (above 700 K). The $^{48}Ti^+$ intensity increased as the sample was heated to 650 K, above which it decreased. The $^{48}Ti^{18}O^+$ intensity was constant up to 500 K, above which it decreased. A plot of the $^{48}Ti^{16}O^+/^{48}Ti^+$ ratio (not shown) had a shape similar to that in Fig. 2b, reflective of surface reoxidation. To better understand the