# Oxygen deficiency and excess of rutile titania (1 1 0) surfaces analyzed by ion scattering coupled with elastic recoil detection

Kei Mitsuhara, Taishi Matsuda, Hideki Okumura, Anton Visikovskiy, Yoshiaki Kido *

Department of Physics, Ritsumeikan University, Kusatsu, Shiga-ken 525-8577, Japan

## ARTICLE INFO

## ABSTRACT

Oxygen deficiency and excess of rutile titania (TiO$_2$) surfaces are important factors for catalytic activities of metal nano-particles on the TiO$_2$ supports. Medium energy ion scattering (MEIS; 80 keV He$^+$) coupled with elastic recoil detection analysis (ERD; 150 keV Ne$^+$) can determine the numbers of bridging O (O$_{br}$) vacancies (V$_O$) and excess O atoms adsorbed on the 5-fold Ti rows of TiO$_2$(1 1 0) surfaces. The amounts of V$_O$ and adsorbed O were derived by H$_2$O and $^{18}$O$_2$ exposure followed by ERD and MEIS analyses, respectively. The present analysis revealed that only about a half of V$_O$ are filled and a comparable amount of O atoms are adsorbed on the reduced TiO$_2$(1 1 0) surface after exposure to O$_2$ (1000 L; 1 L = 1 × 10$^{-6}$ Torr s) at room temperature (RT). We also detected the adsorbed O for the hydroxylated TiO$_2$(1 1 0) after $^{18}$O$_2$ exposure at RT. Finally, it is shown that the O adsorbed on the Ti rows reacts with CO probably to form CO$_2$ at RT. Based on the results obtained here, we clarify the reason why only a half of V$_O$ are filled by exposing reduced surface to O$_2$ at RT and what is the primary source of subsurface excess electronic charge, which acts as a leading part of the surface electrochemistry and gives the defect state in the band gap seen in the valence band spectra for reduced and hydroxylated TiO$_2$(1 1 0) surfaces.

© 2011 Elsevier B.V. All rights reserved.

## 1. Introduction

Titanium oxide (TiO$_2$) has been widely applied to catalyst as a support of metal nano-particles. In this case, O-deficiency (vacancies) and excess O atoms on the surfaces are important factors for the catalytic activities of metal nano-particels on TiO$_2$ supports. There are still some debatable issues on the atomic and electronic structures of TiO$_2$(1 1 0) surfaces after annealing and gas phase reactions. The local structures of the TiO$_2$(1 1 0) surfaces with bridging O (O$_{br}$) vacancies (V$_O$) and excess O atoms (O adatoms: O$_{ad}$) have been extensively studied by scanning tunneling microscopy (STM) under ultra-high vacuum conditions [1–9]. However, it sometimes meets difficulty of identifying surface species and of following the structures change induced by chemical reactions at relatively high speed in a wide spatial range. In this respect, ion beam analysis sometimes combined with other techniques can be utilized complementarily.

In this work, we analyze quantitatively the structures of rutile TiO$_2$(1 1 0) surfaces which react with O$_2$ and H$_2$O in a gas phase using high-resolution medium energy ion scattering (MEIS) combined with elastic recoil detection (ERD). The absolute amounts of adsorbed O atoms can be derived by MEIS using isotopically labeled $^{18}$O$_2$ and H$_2$$^{18}$O gases. The scattering component from

$^{18}$O is clearly separated energetically from that scattered from $^{16}$O. It is also possible to estimate the absolute amount of V$_O$ by detecting the H$^+$ atoms recoiled from the surface after exposure to H$_2$O, because it is known that all the V$_O$ are filled very quickly with paired O$_{br}$H by exposing H$_2$O [4,7,8]. An H$_2$O molecule is dissociatively adsorbed in a V$_O$ site to create a pair of O$_{br}$H and thus just the half of the detected H corresponds to the amount of V$_O$. Fig. 1 illustrates schematically the rutile (1 1 0) surface with V$_O$, O$_{ad}$, O$_{br}$H and Ti interstitial (Ti-int). We prepared four kinds of surfaces; (i) reduced-($R$-), (ii) hydroxylated-($H$-), (iii) O-rich-($O$-) and (iv) pseudo-O-rich ($O^*$-)TiO$_2$(1 1 0) surfaces. The (1 1 0) surface was reduced by sputtering and then annealing at 870 K for 10 min in ultra-high vacuum (UHV). The $H$- and $O$-TiO$_2$(1 1 0) surfaces were obtained by exposing $R$-TiO$_2$(1 1 0) to H$_2$O at ∼330 K and O$_2$ (1000 L) at room temperature (RT), respectively. The $O^*$-TiO$_2$(1 1 0) surface was formed by exposing an $H$-TiO$_2$(1 1 0) to O$_2$ at RT. All the analysis and sample preparation were performed $in$ $situ$ under UHV conditions (base pressure ⩽2 × 10$^{-10}$ Torr) at the beamline 8 working at Ritsumeikan SR Center [10–12].

The aim of this paper is to show that ion beam techniques work as a very powerful tool to explore gas phase reactions and resultant structure change of reactive oxide surfaces. The reactivity comes from oxygen deficiency and excess in the subsurface region as well as hydroxyl group provided by water deposition. The dissociative adsorptions of O$_2$ and H$_2$O and the reactions of O$_{br}$H with O$_2$ and of adsorbed O with CO are discussed quantitatively based on the surface electrochemistry.

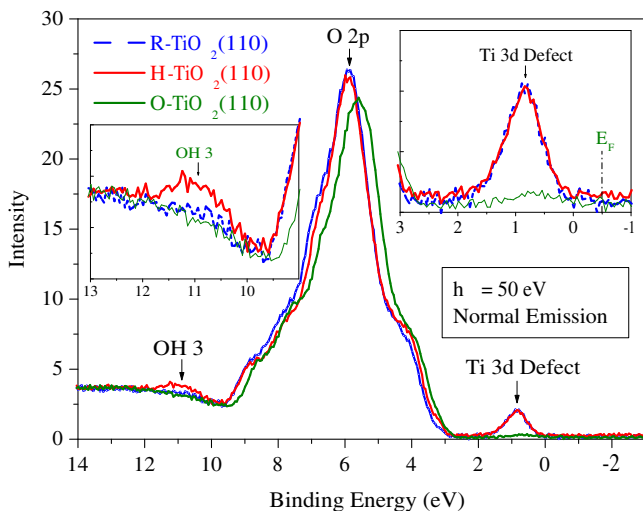* Corresponding author. Tel.: +81 77 561 2710; fax: +81 77 561 2657.
  E-mail address: ykido@se.ritsumei.ac.jp (Y. Kido).
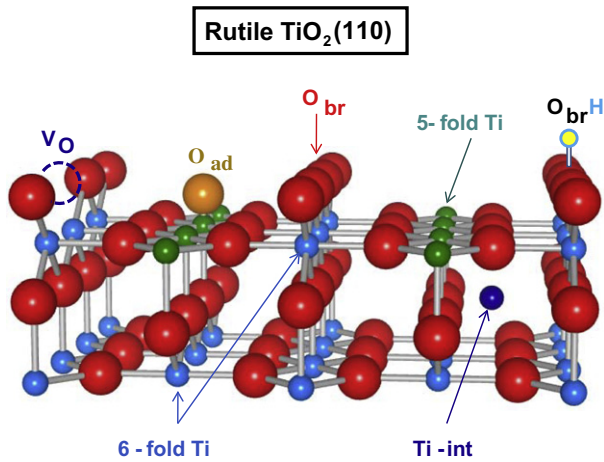
**Fig. 1.** Schematics of a rutile $TiO_2(1\,1\,0)$ surface with $V_O$, $O_{ad}$, $O_{br}H$ and Ti-int. $V_O$ is created on the reduced surface and $O$-$TiO_2(1\,1\,0)$ has $O_{ad}$ and unfilled $V_O$, while $H$-$TiO_2(1\,1\,0)$ surface has paired $O_{br}H$ without $V_O$. All of them involve Ti-int near the surfaces to some extent.

## 2. Experiment

As mentioned before, we prepared four kinds of surfaces, $R$-, $O$-, $H$- and $O^*$-$TiO_2(1\,1\,0)$. Initially as-supplied $TiO_2(1\,1\,0)$ substrates were annealed at 1070 K for 60 min in UHV to be conductive and as a result the color changed into blue from transparency. Such a high-temperature annealing creates O vacancies and Ti interstitials, which act as a color center and an electron donor, respectively [3,13]. The $R$-$TiO_2(1\,1\,0)$ surface was formed by several cycles of 0.75 keV $Ar^+$-sputtering and annealing at 820 K for 5 min in UHV followed by a final treatment of annealing at 870 K for 10 min. The $H$- and $O$-$TiO_2(1\,1\,0)$ surfaces were obtained by exposing $R$-$TiO_2(1\,1\,0)$ to $H_2O$ at ~330 K (10 L, 1 L = $1 \times 10^{-6}$ Torr s) and to $O_2$ ($5 \times 10^{-6}$ Torr) for 100 and 200 s (500 and 1000 L,) at RT, respectively. Fig. 2 shows the UPS spectra observed for $R$-, $H$- and $O$-$TiO_2(1\,1\,0)$ surfaces at a photon energy of 50 eV under normal emission condition ($[1\,\bar{1}\,0]$-azimuth). The left and right insets correspond to magnified spectra around OH $3\sigma$ (hybridization of H 1s and O $2p_z$ orbitals)[7,14] and Ti 3d defect state signals, respec-

tively. From such UPS spectra we can evaluate the presence of the $O_{br}H$ and $V_O$. It is difficult to prepare a stoichiometric surface by annealing in $O_2$ ambience. According to STM observations, Ti interstitials (Ti-int) segregated on the surface react with $O_2$ to create Ti-rich oxide clusters initially and then the surface is renewed by a stoichiometric $TiO_2$ layer [3,7,13]. This cycle is repeated and thus the condition to form a stoichiometric surface depends upon annealing temperature, annealing time, $O_2$ pressure and the density of Ti interstitials. Thus a stoichiometric region can be confirmed locally only by STM. The $H$-$TiO_2(1\,1\,0)$ after exposure to $O_2$ at RT (200 L) is denoted by $O^*$-$TiO_2(1\,1\,0)$, which may have $O_{ad}$ and/or $O_xH_y$ species without $V_O$ and $O_{br}H$. Note that all the samples mentioned above have Ti-int segregated near the surfaces to some extent. The quality of the surfaces prepared here was carefully checked by valence band photoemission spectra (UPS), a $1 \times 1$ pattern observed by reflection high-energy electron diffraction (RHEED) and the shapes of the scattering components from Ti and O near the surface in MEIS spectra, as shown in Fig. 3a and b for $O$-$TiO_2(1\,1\,0)$. Actually, if $TiO_x(x < 2)$ clusters grow on the surface, the scattering components from Ti and O have significantly broad tails in MEIS spectra.
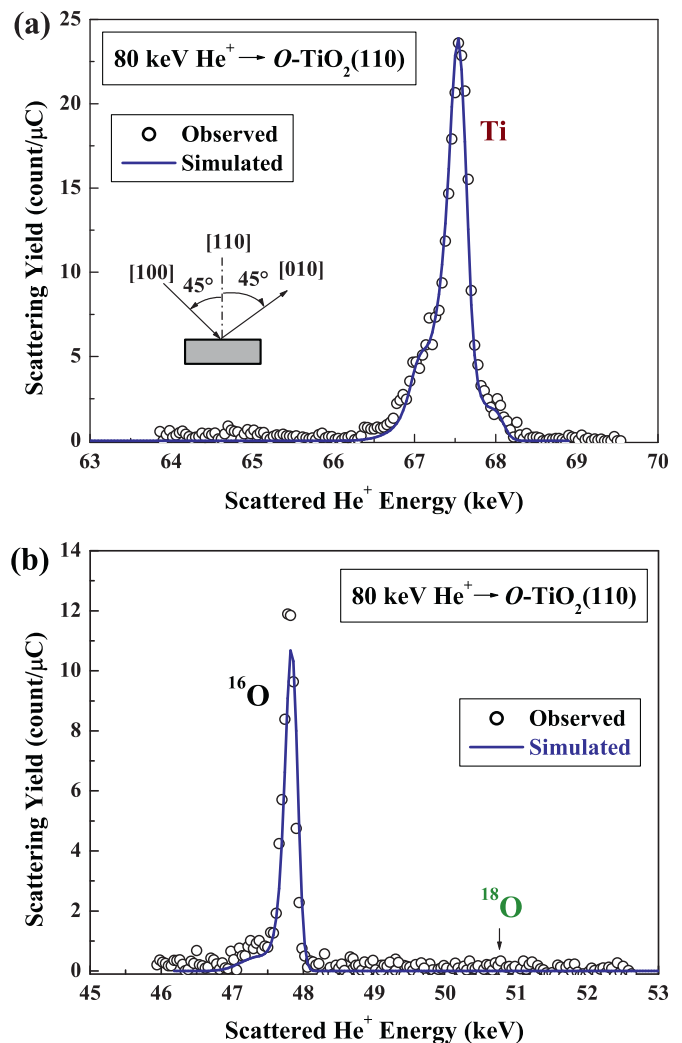


**Fig. 3.** (a) MEIS spectrum (circles) observed for 80 keV $He^+$ ions scattered from Ti atoms of $O$-$TiO_2(1\,1\,0)$ under double alignment condition: $[1\,0\,0]$-incidence and $[0\,1\,0]$-emergence. Solid curve corresponds to simulated spectrum assuming a stoichiometric surface. (b) MEIS spectrum (circles) observed for 80 keV $He^+$ ions scattered from O atoms of $O$-$TiO_2(1\,1\,0)$.



**Fig. 2.** UPS spectra observed at photon energy of 50 eV for $R$-, $H$- and $O$-$TiO_2(1\,1\,0)$ surfaces, which are denoted by dashed, thick and thin solid curves, respectively. The left and right insets are magnified spectra around the signals of OH $3\sigma$ and defect state, respectively.