SLAC-PUB-10163

February 19, 2003
Submitted to the proceedings of ISCSI-4 (October 21-25, 2002, Karuizawa)
Abstract No. 188

(Revised manuscript)

Real-time monitoring of oxidation on the Ti(0001) surface by synchrotron radiation photoelectron spectroscopy and RHEED-AES

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Abstract

The oxidation kinetics on the Ti(0001) single crystal surface was investigated by real-time Auger electron spectroscopy combined with reflection high-energy electron diffraction (RHEED-AES) and high-resolution photoelectron spectroscopy using synchrotron radiation. The RHEED specular reflection spot intensity showed an oscillatory behavior, at the maxima and minima of which the oxygen uptake curve obtained by O KLL Auger electron intensity shows breaks. This agreement indicates that growth of oxides progresses with changing the surface morphology and the oxygen uptake rate. The O_2 dose dependence of Ti 2p photoelectron spectrum measured at photon energies of 574.6 eV (surface sensitive) and 1549 eV (bulk sensitive) revealed that (1) oxidation of metallic Ti atoms with growing Ti_2O and TiO on the surface makes the surface morphology roughened up to ~17 L, (2) the roughened morphology is recovered by oxidation of Ti_2O and TiO into Ti_2O_3, Ti_3O_5 and TiO_2 up to ~45 L,

Work supported in part by the Department of Energy contract DE-AC03-76SF00515.
Contributed to ISCSI-4:
Fourth International Symposium on the Control of Semiconductor Interfaces,
Karuizawa, Japan, 10/21/2002 - 10/25/2002

(3) after almost saturation of TiO_2 growth in the surface layer the surface morphology is roughened again by further oxidation at the interface up to ~140 L, and (4) then the oxygen uptake rate is considerably suppressed due to the passivation effect of grown oxides.

Keywords: Titanium; Oxidation; Auger electron spectroscopy; Reflection high-energy electron diffraction; Photoelectron spectroscopy; Synchrotron radiation; Surface chemical reaction

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1. Introduction

Oxidation on Ti surfaces is not only interesting from a point of view of the oxidation mechanism for transition metals [1] but also of practical importance for extended applications [2]. It is well known that there are various kinds of Ti oxides with different oxidation states: Ti_2O, TiO, Ti_2O_3, Ti_3O_5, Ti_nO_{2n-1} (n=4, 5···10) and TiO_2 [3]. In order to investigate the oxidation kinetics on Ti surfaces, therefore, it is necessary to obtain information on the oxidation state of Ti atom as well as the oxygen uptake curve. The oxygen uptake curve at the initial stage of oxidation has been measured by O 1s photoelectron intensity [4, 5], O KLL Auger electron intensity [6, 7] and electron stimulated desorption of O^+ ions [8, 9]. For oxidation of polycrystalline Ti samples at room temperature (RT) [4, 7], the oxygen uptake curve showed a monotonous increase followed by a steady saturation, which is similar to that of Langmuir-Hinshelwood type adsorption [10]. This means that oxidation occurs in the limited surface region and the passivation effect of the resultant thin oxide is very significant for further oxidation. From curve-fitting analysis of Ti 2p photoelectron spectra obtained for oxidation at RT, it was observed that the abundance ratio between TiO, Ti_2O_3, Ti_3O_5 and TiO_2 is almost invariant in the whole O_2 dose range examined and the dominant oxidation state among them is not TiO_2 but TiO [11]. With elevating oxidation temperature from RT, the abundance ratio changes depending on O_2 dose and TiO_2 becomes dominant, but no oxides grow at high temperature above ~550°C [12]. Thus oxidation on Ti surfaces does not always proceed in a single phase of TiO_2 growth but results in various kinds of oxidation states depending O_2 pressure, O_2 dose and temperature.

In the case of oxidation on Ti single crystal surfaces, the oxygen uptake curve shows some breaks, at O_2 doses of which the oxygen uptake rate slows down substantially [5, 6]. Curve-fitting analysis of Ti 2p and O 1s photoelectron spectra revealed that the abundance ratio changes at the O_2 doses [5], suggesting that the oxygen uptake rate is concerned with the oxidation state. Such clear observation of the breaks in the oxygen uptake curve may be due to suppression of fast O_2 diffusion along grain boundaries, which is significant for polycrystalline Ti samples. In fact, the epitaxial growth of TiO_2 and the ordered structure of oxygen atoms in TiO_x (x<2) phase was confirmed by photoelectron diffraction of chemically-shifted O 1s and Ti 2p components for oxidation on the Ti(0001) surface at RT [5] and thus oxidation of the Ti single crystal does not progress in a manner of grain growth. In addition, low energy electron diffraction (LEED) observation showed a surface structural change from 1x1 to 2x2 at the initial stage for oxidation on the Ti(0001) surface at RT. Consequently it is clear that not only chemical analysis of the oxidation state but also observation of the surface structure and morphology are necessary for clarifying the oxidation mechanism on the Ti single crystal surface.

In this study, real-time Auger electron spectroscopy combined with reflection high-energy electron diffraction (RHEED-AES) was used to monitor the surface morphology in connection with the oxygen uptake curve during oxidation on the Ti(0001) single crystal surface. A periodic oscillation of the RHEED specular reflection spot intensity was observed for oxidation at 200°C and 5.0×10^{-8} Torr of O_2 pressure. The oxidation state corresponding to the surface morphological change was examined by high-resolution photoelectron spectroscopy of Ti 2p core level using synchrotron radiation at two photon energies (surface and bulk sensitive). Based on the O_2 dose dependence of the oxidation state and the surface morphology, the oxidation kinetics on the Ti(0001) surface at 200°C is discussed.

2. Experimental

The RHEED-AES experiments were performed using an ultrahigh vacuum apparatus with a base pressure of 5×10^{-11} Torr [13]. The incident energy and angle of a primary electron beam was 10 keV and ~1° along the [2-1-10] azimuth. The O KLL intensity $I_{\text{O-KLL}}$ was obtained by normalizing the peak intensity at a kinetic energy E_k of 512 eV by the background intensity at E_k=530 eV to eliminate the effects due to fluctuations in current and position of the primary electron beam. RHEED patterns were recorded with a CCD video camera system. The RHEED intensity profile of (0, 0) specular reflection spot $I_{(0,\,0)}$ was obtained from recorded patterns using commercial software.

High-resolution photoelectron spectroscopy using synchrotron radiation was performed using a surface chemical reaction analysis chamber (SUREAC 2000) at beamline BL23SU, SPring-8, Mikazuki-cho, Japan [14]. The base pressure of the chamber was 2.3×10^{-10} Torr. Each Ti 2p spectrum was obtained with an acquisition period of 135 s at two photon energies of 574.6 eV and 1549 eV. The corresponding E_k of the Ti $2p_{3/2}$ peak for Ti metal is 122 eV and 1096 eV, respectively, as shown later, so that the escape depth of Ti 2p photoelectrons for the present measurement geometry of surface normal detection is estimated as 7 Å (surface sensitive) and 23 Å (bulk sensitive), respectively [15]. Facilities for LEED observation and residual gas analysis were also available at SUREAC 2000.

The sample used for oxidation was a single crystal α-Ti(0001) surface with a size of 7x7x1 mm. The sample synthesis and surface preparation with chemical polishing were described in detail in Ref. 16. The mirror-polished Ti sample was mounted on a molybdenum holder and heated by radiative heating for photoelectron spectroscopy. In the RHEED-AES measurement, it was attached to a tantalum holder, which was used for direct resistive heading. The temperature of the sample was measured by a chromel-alumel thermocouple. The sample surface was cleaned by repeated cycles of annealing at 600°C and Ar^+ ion sputtering at 1 keV of acceleration voltage and a few μA of ion current. On the cleaned surface, there were no contaminants such as sulfur and chlorine except for a much small amount of oxygen as confirmed by AES and photoelectron spectroscopy, and a 1x1 structure was observed by LEED and RHEED as shown in Fig. 1(a). O_2 gas of 99.99% purity was introduced with a variable leak valve into the reaction chamber.

3. Results and discussion

Fig. 1(b) shows the O_2 dose dependence of $I_{\text{O-KLL}}$ and $I_{(0,0)}$ taken in situ as a function of O_2 pressure during oxidation on the Ti(0001) surface at 200°C. With increasing O_2 dose, the $I_{\text{O-KLL}}$ increases rapidly up to ~140 L and then slows down its rate. A profile of the oxygen uptake curve is independent of O_2 pressure and can be normalized by a quantity of O_2 dose as seen in Fig. 1(b). Thus the oxygen uptake kinetics is roughly divided into two O_2 dose regions (I) and (II) at ~140 L.

In region (I) below ~140 L, an oscillatory behavior in $I_{(0,0)}$ can be apparently observed. Upon O_2 introduction, the $I_{(0,0)}$ decreases rapidly and then increases steeply with a minimum at ~17 L. After showing a maximum at ~45 L, its gradual decrease continues up to ~140 L. In region (II) above ~140 L, it increases very slowly. The resultant minimum at ~140 L corresponds well to the break in $I_{\text{O-KLL}}$. The periodic oscillation in $I_{(0,0)}$ means that the surface morphology changes periodically between roughening and smoothing with progress of oxide growth. According to the surface morphological change, the region (I) is further divided into three regions (I-a), (I-b) and (I-c) at ~17 L and ~45 L, while such division is indistinctly recognized for $I_{\text{O-KLL}}$.

In order to clarify the reason for the periodic change in surface morphology, surface-sensitive photoelectron spectroscopy of Ti 2p was performed as shown in Fig. 2(a). Upon O_2 introduction, the doublet peak due to Ti metal decreases rapidly and eventually disappears at 83 L. This means that the oxide grown at 83 L is thicker than about three times of the escape depth, that is, ~21 Å. In other words, metallic Ti atoms located within ~21 Å from the surface are completely oxidized by exposing the Ti(0001) surface to O_2 gas of 83 L. In addition, the spectral feature for Ti metal is broadened with O_2 dose. The broadening is ascribed to the solid solution of adsorbed oxygen atom and the growth of Ti_2O and TiO [3, 5], because their chemical shifts in Ti 2p are smaller than ~1 eV and comparable to the peak width. Therefore the disappearance of the peak structure at ~122 eV means that not only metallic Ti atoms but also such oxides are oxidized. At 22L, a peak structure of TiO_2 can be observed definitely at 116.8 eV and with increasing O_2 dose above 22 L the TiO_2 peak appears dominantly more and more. Thus TiO_2 grows certainly in region (I) with showing the RHEED intensity oscillation.

In Fig. 3, comparison between Ti 2p photoelectron spectra taken at O_2 doses of 0 L, 50 L and 369 L is made to show up spectral features of other oxides than TiO_2. The chemical shift of Ti $2p_{3/2}$ for TiO, Ti_2O_3 and Ti_3O_5 was reported to be 1.2 eV, 2.8 eV and 3.9 eV, respectively [11]. Their peak positions are indicated with arrows in Fig. 3. The doublet peak of Ti metal is very sharp and the full width at half maximum (FWHM) of Ti $2p_{3/2}$ is 0.87 eV. The chemical shift of Ti $2p_{3/2}$ for TiO_2 is measured at 369 L to be 5.2 eV in accordance with the previous report for the TiO_2(110) single crystal [17]. The spin-orbit splitting for TiO_2 is 5.8 eV and slightly narrower than that for Ti metal, 6.2 eV. At 50 L, two broad structures are observed between Ti $2p_{3/2}$ peaks for Ti metal and TiO_2. The high-E_k structure is mainly ascribed to TiO with including Ti_2O and solid solution of oxygen [5]. Ti_2O_3 and Ti_3O_5 are concerned with the low-E_k structure. When the O_2 dose is increased to 369 L, the high-E_k structure disappears wholly, while the low-E_k structure still remains. From this comparison, it is understood that oxidation on the Ti(0001) surface continues step by step until a stoichiometry of TiO_2 is achieved.

The amount of Ti metal and oxides obtained from Fig. 2 is summarized as a function of O_2 dose in Fig. 4(a). After subtracting the linear background extrapolated from the high-E_k side, the amount of metallic Ti atom is estimated by the intensity at E_k=121.8 eV I_{Ti}. For TiO and TiO_2, the intensities at E_k=120.7 eV and 116.6 eV I_{TiO} and I_{TiO2} are approximately used, respectively. It is noted that the I_{TiO} is slightly affected by I_{Ti} and a contribution of the nonlinear background is not negligible for the case of I_{TiO2}. With increasing O_2 dose, the I_{Ti} decreases rapidly in region (I-a) and then slows down its rate in region (I-b). In region (I-c) above ~45 L, it is practically zero. Thus the O_2 dose dependence of I_{Ti} observed with high surface sensitivity shows characteristic changes corresponding well to the feature of RHEED intensity oscillation, suggesting that oxidation of metallic Ti atoms is accompanied with changes of the surface morphology, especially, roughening at the initial stage up to ~17 L.

On the other hand, the I_{TiO} decreases gradually with no significant breaks at ~17 L and ~45 L after showing an initial rapid increase. The initial increment upon O_2 introduction is due to an increase of TiO overcoming the influence of a decrease in I_{Ti}. As seen from the behavior of I_{Ti}, its contribution to I_{TiO} is negligibly small above ~17 L and therefore the gradual decrease in I_{TiO} originates mainly from further oxidation of TiO. Here it is noticed that the I_{TiO} approaches to zero at about 140 L, where the transition from region (I-c) to (II) occurs. This agreement suggests that a change of the oxidation kinetics for TiO present on the surface is associated with the transition of the surface morphological change from region (I-c) to (II). With regard to the growth of TiO_2, an initial linear increase of I_{TiO2} changes with decreasing its rate to a very gradual increase at the boundary between regions (I-b) and (I-c). There is no discernible break of I_{TiO2} at ~140 L. Consequently it is summarized that the surface morphological changes in regions (I-a), (I-b), and (I-c) are concerned with the oxidation kinetics for Ti metal, TiO_2 and TiO, respectively.

Owing to the high surface sensitivity in Fig. 2(a), it is difficult to trace the oxidation kinetic of metallic Ti atom at the interface deeper than ~21 Å. The O_2 dose dependence of Ti 2p photoelectron spectra taken under the bulk sensitive condition at 1549 eV is shown in Fig. 2(b). After O_2 introduction, the doublet peak of Ti metal decreases gradually and still remains with a large intensity at 305 L. On the other hand, the intensity at the peak position of Ti $2p_{1/2}$ for TiO_2, E_k=1085.5 eV, grows very gradually and is rather weak in comparison to that of Ti $2p_{3/2}$ for Ti metal even at 305 L. From the bulk-sensitive observation, it turns out that the interface between oxides and Ti substrate is located at the shallower depth than ~69 Å and growth of TiO_2 is limited beneath the surface.

In Fig. 4(b), the O_2 dose dependence of I_{Ti} obtained at E_k=1096.5 eV in Fig. 2(b) is shown to trace the oxidation of metallic Ti atom at the deep interface. For the data in region (II), a solid line is indicated as guide for eye. The I_{Ti} decreases in a manner of exponential decay with no significant breaks at the boundaries between regions (I-a), (I-b) and (I-c). This suggests that oxidation of metallic Ti atoms proceeds without having a strong correlation with the transitions of the surface morphological change at ~17 L and ~45 L. However, it reaches the solid line just at ~140 L, indicating that a change of the oxidation kinetics for Ti metal is closely associated with the difference in the surface morphological change between regions (I-c) and (II). In region (II), metallic Ti atoms are oxidized quite gradually as seen by a small decline of the solid line. Such gradual oxidation occurring above ~140 L is also observed at the subsurface as shown in Fig. 2(a), where the broad structure of Ti_2O_3 and Ti_3O_5 decreases in intensity and the peak due to TiO_2 is sharpened more and more. Thus oxidation takes place concurrently in the whole depth region from the surface to the interface.

Based on the above experimental results, we consider the oxidation kinetics on the Ti(0001) surface in connection with the surface morphological change. In region (I-a) below ~17 L, oxidation of metallic Ti atoms into Ti_2O and TiO with including solid solution of oxygen atoms occurs dominantly in the surface layer. Some of adsorbed oxygen atoms remain on the surface and the others diffuse into the subsurface. Photoelectron diffraction study revealed that the diffused oxygen atoms occupy the lattice sites to form an ordered structure, while the oxygen atoms present on the surface are randomly located [5]. The random distribution of oxygen atoms seems to be a reason for roughening the surface morphology in region (I-a). Probably the oxidation of metallic Ti atoms on the surface is completed at ~17 L and then further oxidation of Ti_2O and TiO into Ti_2O_3, Ti_3O_5 and TiO_2 occurs on the surface as indicated by the decrease of I_{TiO} in Fig. 4(a). If the oxide such as Ti_2O_3, Ti_3O_5 and TiO_2 grows at 200°C with an ordered structure as reported at RT in Ref. 5, the surface morphology could be smoothed, leading to a recovery of $I_{(0,0)}$ in region (I-b). As observed in Fig.4(a), the growth of TiO_2 slows down its rate at ~45 L, although O_2 adsorption continues without a saturation as observed by $I_{O\text{-}KLL}$ in Fig. 1 and metallic Ti atoms are frequently oxidized at the deeper interface as seen in Fig. 4(b). This suggests that after almost completion of TiO_2 growth in the surface layer oxides grow under the surface TiO_2 layer. It is likely that the resultant growth of oxides make the surface morphology roughened in spite of their location at the subsurface. When the oxides reaches a certain thickness and/or a certain stoichiometry, diffusion of adsorbed oxygen atoms is considerably suppressed, leading to self-limitation of oxidation at ~140 L as seen in Figs. 1 and 4(b). During self-limiting oxidation in region (II), very gradual oxidation is possible to change Ti_2O_3 and Ti_3O_5 into TiO_2 in the surface layer as seen in Fig. 2(a). As a result, the surface morphology is slightly recovered as observed in Fig. 1.

4. Conclusion

The oxidation kinetics on the Ti(0001) surface at 200°C and 5.0×10^{-8} Torr of O_2 pressure was investigated by real-time AES combined with RHEED and real-time photoelectron spectroscopy using synchrotron radiation. From the periodic oscillatory behavior of RHEED specular reflection spot intensity, the oxidation kinetics is divided into four regions at O_2 doses of ~17 L, ~45 L and ~140 L. Below ~17 L, growth of Ti_2O and TiO dominates with roughening the surface morphology. At O_2 doses between ~17 L and ~45 L, further oxidation of them into Ti_2O_3, Ti_3O_5 and TiO_2 results in recovering the surface morphology, maybe because of disappearance of randomly distributed oxygen atoms present on the surface. Above ~45 L, metallic Ti atoms are still oxidized at the deeper interface and TiO_2 grows very gradually beneath the surface. Such growth of oxides at the interface degrades significantly the surface morphology. After ~140L, the oxidation rate is considerably reduced due to the passivation effect of grown oxides. During O_2 exposure above ~140 L, growth of TiO_2 continues very gradually with smoothing the surface morphology.

Acknowledgements

The synchrotron radiation experiments were performed at the SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JAERI) (Proposal Nos. 2001B0044-NS-np, 2002A0167-CS1-np and 2003B0634-CS1-np).

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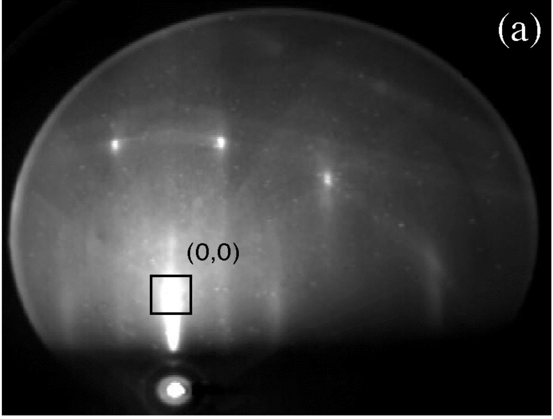
Figure captions

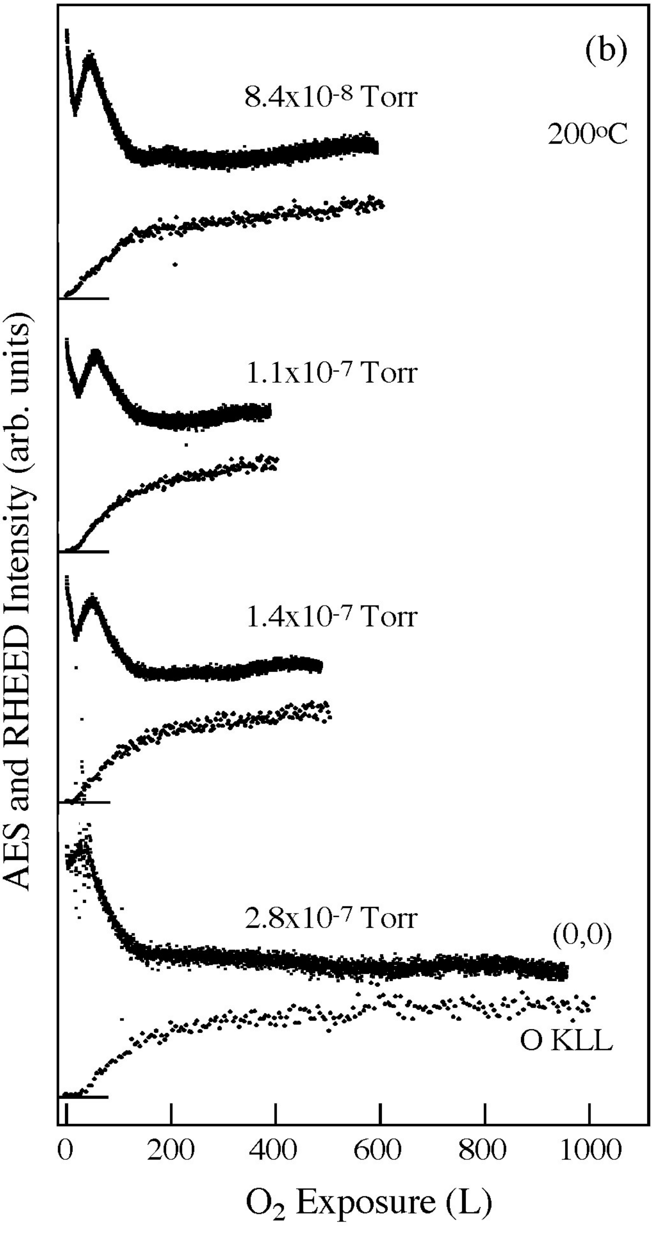
Fig. 1. (a) RHEED pattern of the clean Ti(0001)1x1 surface and (b) time evolution of RHEED specular reflection spot intensity taken in situ as a function of O_2 pressure during oxidation on the Ti(0001) surface at 200°C, compared with that of O KLL Auger electron intensity.

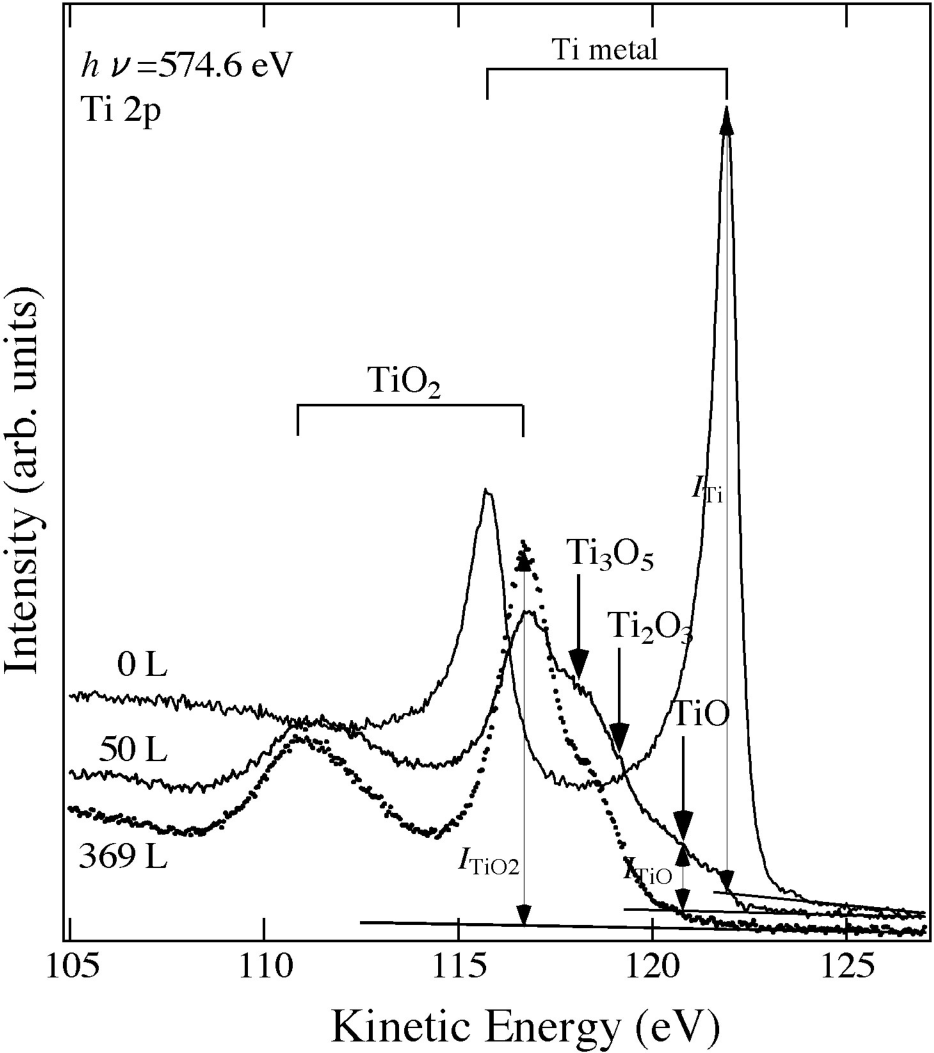
Fig. 2. O_2 dose dependence of Ti 2p photoelectron spectrum taken in situ during oxidation on the Ti(0001) surface at 200°C and 5.0×10^{-8} Torr of O_2 pressure. The photon energy was (a) 574.6 eV and (b) 1549 eV.

Fig. 3. Ti 2p photoelectron spectra taken at O_2 doses of 50 L and 369 L, compared with that for the clean Ti(0001) surface. The Ti $2p_{3/2}$ peak position for TiO, Ti_2O_3 and Ti_3O_5 are indicated with arrows. The spin-orbit splitting doublet for Ti metal and TiO_2 are also indicated with bars.

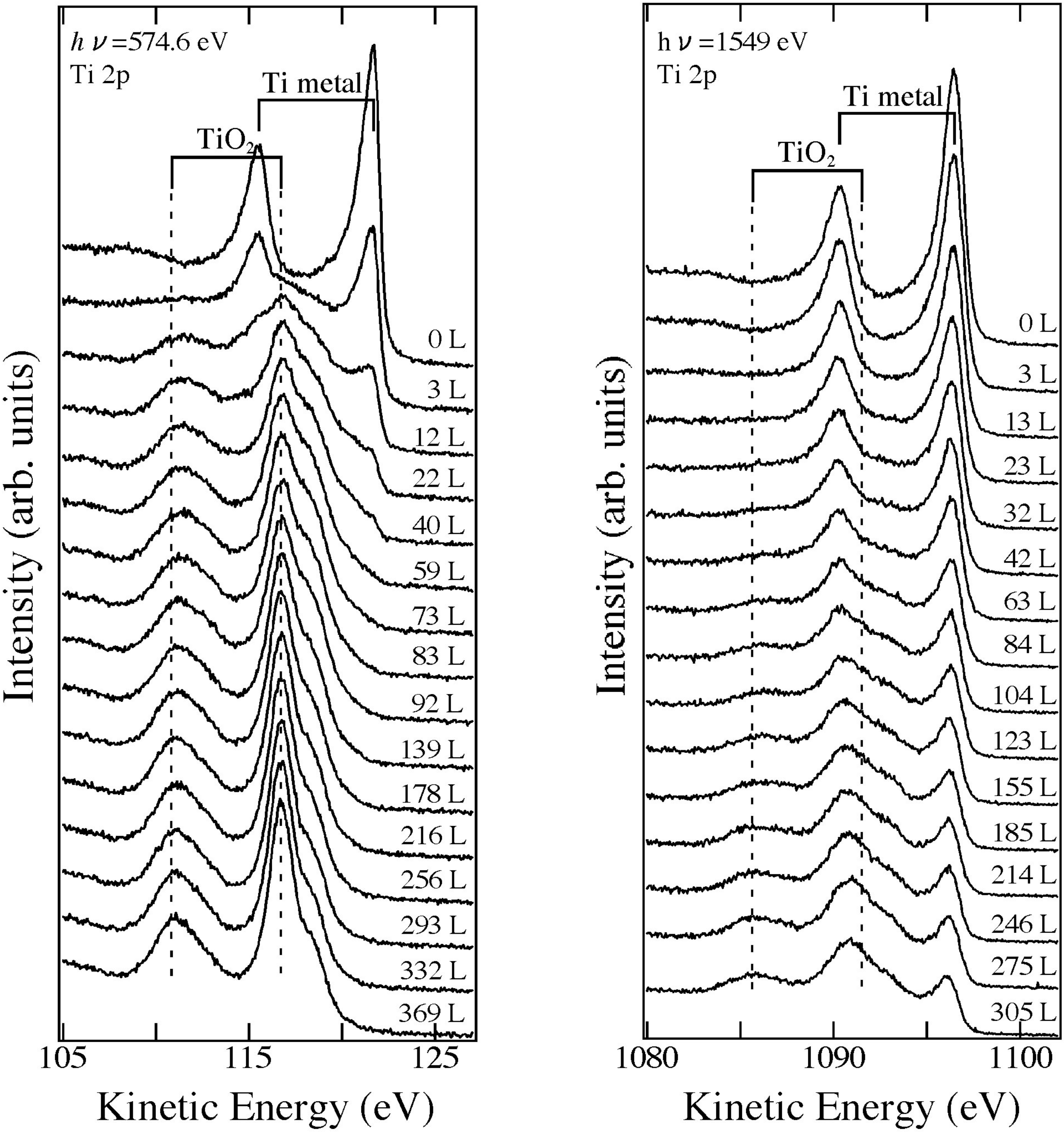
Fig. 4. (a) O_2 dose dependence of I_{Ti} (open circles), I_{TiO} (solid rhombuses) and I_{TiO2} (solid circles) obtained from Fig. 2(a). (b) O_2 dose dependence of I_{Ti} obtained from Fig. 2(b).


(a)
(0,0)


(b)
200°C
8.4x10-8 Torr
1.1x10-7 Torr
1.4x10-7 Torr
2.8x10-7 Torr
(0,0)
O KLL
AES and RHEED Intensity (arb. units)
0
200
400
600
800
1000
O2 Exposure (L)

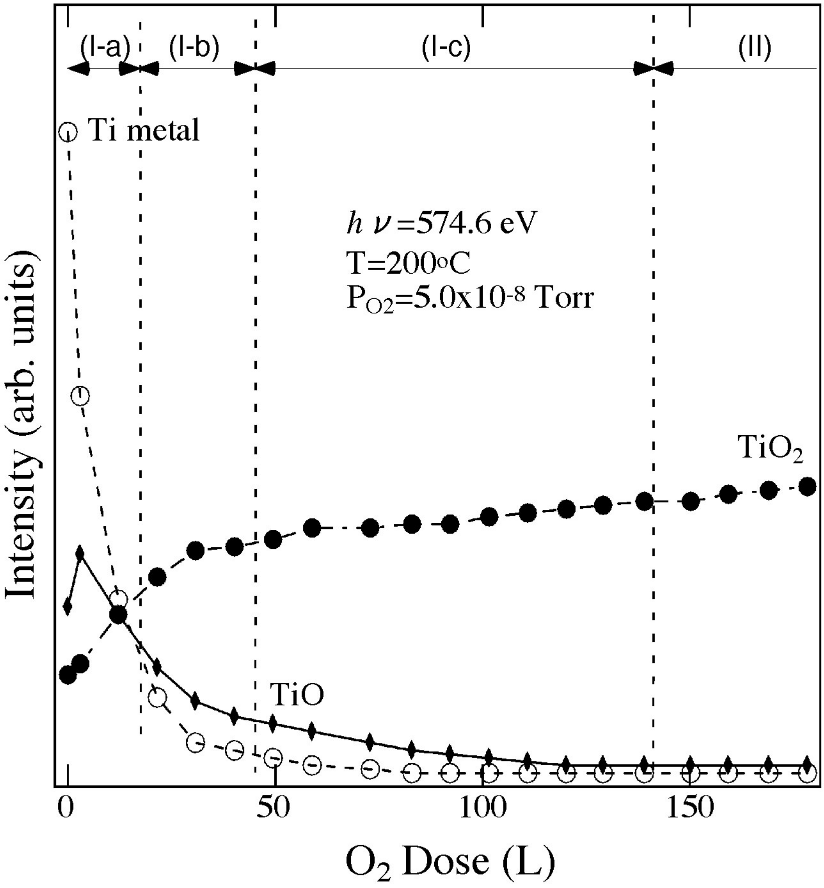


$h\nu$=574.6 eV
Ti 2p
Ti metal
TiO_2
Ti_3O_5
Ti_2O_3
TiO
I_{Ti}
I_{TiO2}
I_{TiO}
0 L
50 L
369 L
Intensity (arb. units)
Kinetic Energy (eV)
105
110
115
120
125

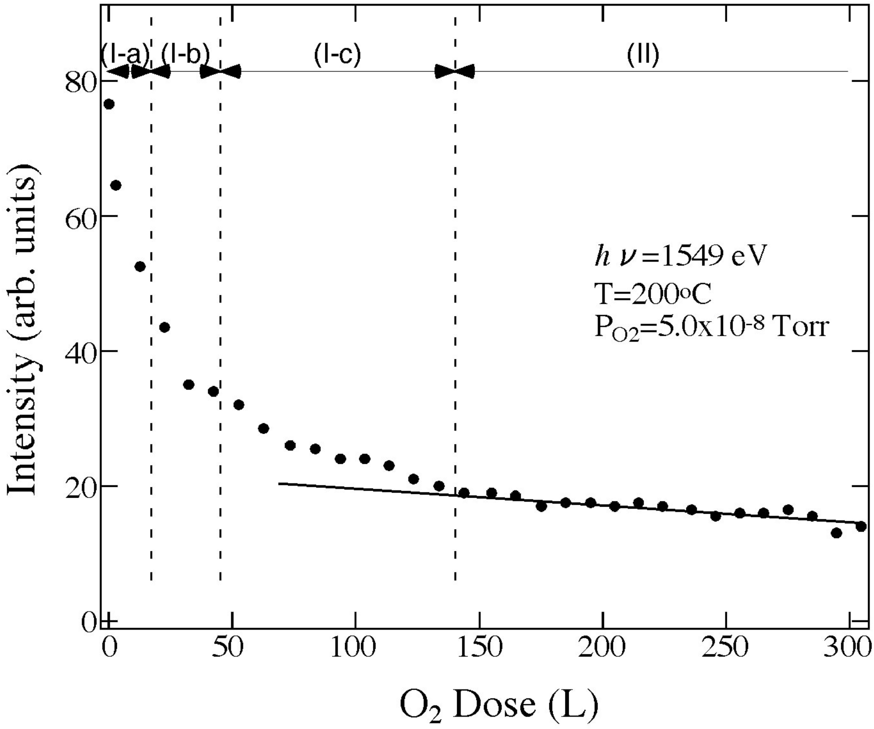

h ν =574.6 eV
Ti 2p
Ti metal
TiO$_2$
0 L
3 L
12 L
22 L
40 L
59 L
73 L
83 L
92 L
139 L
178 L
216 L
256 L
293 L
332 L
369 L
Intensity (arb. units)
105
115
125
Kinetic Energy (eV)
h ν =1549 eV
Ti 2p
Ti metal
TiO$_2$
0 L
3 L
13 L
23 L
32 L
42 L
63 L
84 L
104 L
123 L
155 L
185 L
214 L
246 L
275 L
305 L
Intensity (arb. units)
1080
1090
1100
Kinetic Energy (eV)

(a)

(b)


(I-a)
(I-b)
(I-c)
(II)
Ti metal
$h\nu$=574.6 eV
T=200°C
P_{O2}=5.0x10^{-8} Torr
TiO$_2$
TiO
Intensity (arb. units)
0
50
100
150
O$_2$ Dose (L)

(a)


(I-a)
(I-b)
(I-c)
(II)
80
60
40
20
0
$h\nu$=1549 eV
T=200°C
P_{O2}=5.0x10^{-8} Torr
Intensity (arb. units)
0
50
100
150
200
250
300
O$_2$ Dose (L)

(b)