TIME-RESOLVED PHOTOELECTRON SPECTROSCOPY OF OXIDATION ON THE Ti(0001) SURFACE

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Abstract

High-resolution photoelectron spectroscopy using synchrotron radiation was applied for monitoring in real time the oxidation kinetics on the Ti(0001) surface at 405ºC with dry O_2 gas. The time evolution of O 1s photoelectron intensity showed a linear uptake curve up to ~90 L followed by a sudden saturation up to ~160 L and then a restart of the linear increase, indicating that O_2 adsorption obeys a zero-order reaction scheme before and after the saturation. Corresponding to the first linear uptake and saturation, the surface core level shift (SCLS) component of Ti 2p decreased predominantly and disappeared completely, and appeared again after the saturation and remained persistently during TiO_2 growth. Thus the zero-order reaction of O_2 adsorption on the Ti(0001) surface at 405ºC is concerned with the metallic Ti layer on the outermost surface.

Keywords: Photoelectron spectroscopy, Synchrotron radiation, Titanium, Oxidation
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1. Introduction

Titanium (Ti) is utilized in extensive applications such as space shuttle, aircraft, automobile, medicine and computer, because of its superior properties of light weight, strong, anticorrosive and heat-resistance. However, Ti surfaces are so reactive as to form easily compounds with any molecule except for rare gases. Passivation of the Ti surface with oxides and nitrides or modification of it with ion implantation is therefore of practical importance. For realizing passivation of the Ti surface with oxides, the initial oxidation kinetics of polycrystalline Ti films has been investigated by X-ray photoelectron spectroscopy (XPS) [1-3], Auger electron spectroscopy (AES) [4-6] and ultraviolet photoelectron spectroscopy (UPS) [7]. These studies clarified that a mixture of different oxidation states of Ti (0, +1, +2, +3, +4) are present during the whole course of O_2 exposure, while TiO_2 grows preferentially, and oxygen accumulates beneath the surface at room temperature.

For the single crystal Ti(0001) surface, detailed studies on the initial oxidation kinetics were performed with respect to the lattice site of adsorbed oxygen by X-ray photoelectron diffraction (XPD) [8], the oxygen adsorption state by photon-stimulated desorption (PSD) [9], the oxygen uptake curve by AES [10] and the electronic structure by electron energy loss spectroscopy (EELS) and UPS [11]. The uptake curve of O KVV Auger electron intensity showed three significant breaks at which the increase rate slows down, indicating that the reaction kinetics for O_2 adsorption and oxide growth changes depending on O_2 dose. It was observed by XPS [8] and AES [10] that such changes are associated with progress of the oxidation state from TiO to Ti_2O_3 and TiO_2. However, identification of the oxidation state was not clear for lack of the energy resolution in XPS and AES. Although most of the previous studies have been performed at room temperature, further interesting results were reported for oxidation at high temperature. In the case of polycrystalline Ti, it was observed that upon increasing the O_2 dose the work function shows a larger decrease at higher temperature above 100°C followed by an increase and a subsequent plateau [12], suggesting that adsorbed oxygen atoms diffuse below the surface at the initial stage with a decrease of work function. Vaquila et al. [13] reported that no oxygen is detected at the surface over 400°C, indicating existence of a metallic Ti layer on the outermost surface during oxidation. Thus the diffusion of oxygen into bulk Ti is considerably enhanced when elevating temperature above 400°C. In situ observation is therefore necessary for clarifying the oxidation kinetics on Ti surfaces at high temperature.

In the present study, high-resolution photoelectron spectroscopy using synchrotron radiation was applied for monitoring in real time the chemically shifted components of O 1s and Ti 2p core levels during initial oxidation on the Ti(0001)1x1 surface at 405°C. For the Ti 2p photoelectron spectrum, the surface core level shift (SCLS) component was observed, making it possible to discern the surface metallic Ti layer from bulk Ti. The uptake curve of O 1s photoelectron intensity showed a plateau followed by an almost linear increase and then a restart of the linear increase, meaning that O_2 adsorption is a zero-order reaction. The O_2 adsorption kinetics during TiO_2 growth is discussed in terms of the metallic Ti layer on the outermost surface.

2. Experimental

Photoelectron spectroscopy experiments using synchrotron radiation were performed with the surface reaction analysis chamber at beamline BL23SU, SPring-8, Mikazuki-cho, Japan [14, 15]. The base pressure of the chamber was 3×10^{-8} Pa. The O 1s and Ti 2p photoelectron spectrum were obtained by the duration of 80 s and 135 s, respectively, at the photon energy of 736 eV. The kinetic energy thus was ~205 eV and ~280 eV, respectively, so the escape depth of photoelectrons for the measurement geometry of surface normal detection is ~8 Å.

The sample used was a single crystal Ti(0001) surface with a size of 5x5x1 mm. After mechano-chemical polishing (MCP) [16], it was loaded into the chamber. The Ti crystal mounted on a sample holder made of molybdenum was annealed by radiative heating and its temperature was measured by a chromel-alumel thermocouple. The sample surface was cleaned by repeated cycles of annealing at 600°C in ultrahigh vacuum of ~10^{-8} Pa. For the cleaned surface, a clear 1x1 structure was observed by reflection high-energy electron diffraction (RHEED) and a quite small amount of chlorine, sulfur and oxygen was detectable by photoelectron spectroscopy. Dry O_2 gas of 99.99% purity was introduced with a variable leak valve into the chamber.

3. Results and discussion

Fig. 1 shows the O_2 dose dependence of O 1s photoelectron intensity I_{O-1s} taken in situ during oxidation at 405°C and 6.7×10^{-6} Pa of O_2 pressure. The I_{O-1s} is obtained by integrating the whole O 1s spectrum with including all chemically shifted components. Upon O_2 introduction, the I_{O-1s} increases almost linearly up to ~90 L and then saturates suddenly. Such a behavior of the oxygen uptake curve is similar to that for H_2O adsorption on the Si(001)2x1 surface [17], where the H_2O uptake rate is independent of the amount of adsorbed oxygen and hydrogen and suddenly changes to zero at the same time of disappearance of dimer dangling bonds. Thus the H_2O uptake rate is independent of the adsorbate coverage, so H_2O adsorption on the Si(001)2x1 surface is called a zero-order reaction. Similarly it is understood that O_2 adsorption on the Ti(0001) surface obeys a zero-order reaction scheme at the initial stage up to ~90 L.

It is noteworthy that the I_{O-1s} restarts to increase almost linearly at ~160 L after the saturation. A slight slowing down of the increase rate seems to be due to the inelastic scattering of O 1s photoelectrons because of thick oxides. Thus the zero-order reaction of O_2 adsorption is possible even after the saturation to progress up to at least ~330 L examined. This means that the clean surface area with high reactivity appears again after forming a completely oxidized surface and exists persistently during oxide growth.

From the oxygen uptake curve in Fig. 1, O_2 adsorption on the Ti(0001) surface can be divided into three regions of O_2 dose D_{O2}: (A) D_{O2}<90 L for the zero-order reaction region, (B) 90 L< D_{O2}<160 L for the saturation region and (C) 160 L< D_{O2} for the zero-order reaction region.

Fig. 2 shows the O_2 dose dependence of Ti 2p photoelectron spectrum taken in situ during oxidation at 405°C and 6.7×10^{-6} Pa of O_2 pressure. When increasing D_{O2} in region (A), the peak position shifts slightly toward the high binding energy E_B side with a significant

decrease of the peak intensity. No chemically shifted components due to oxides are observed definitely as a shoulder or a peak structure and the peak width increases gradually in accordance with an increase of I_{O-1s}. These indicate that the oxidation state is restricted to TiO and Ti_2O_3 with mall chemical shifts and growth of TiO_2 with a large chemical shift is not predominant [2, 8].

In region (B), the doublet peak due to metallic Ti decreases substantially and in turn two broad peaks appear increasingly at the peak position of TiO_2 [18] irrespective of the saturation of I_{O-1s}. This suggests that the saturation of I_{O-1s} does not mean completion of the oxidation reaction but is associated with a change of the oxidation state. At the end of region (B), the spectral feature of metallic Ti is rather broad with a comparable intensity to that of TiO_2. When the D_{O2} changes from region (B) to region (C), the broadened peak of metallic Ti becomes sharper with increasing D_{O2} up to ~240 L. From this exposure onwards, the position, intensity and width of the metallic Ti peak are maintained unchanged. Especially it is noted that the E_B of the metallic Ti peak is very close to that for the cleaned surface. On the other hand, the broad peaks of TiO_2 increase steadily in accordance with an increase of I_{O-1s} and are a dominant spectral feature at 333 L. This is a clear evidence of the existence of a metallic Ti layer on the outermost surface during TiO_2 growth.

In order to represent more clearly the changes in Ti 2p due to O_2 adsorption in region (A), a difference spectrum between the spectra taken at 0 L and 14.7 L is shown in Fig. 3. The peak position of Ti $2p_{3/2}$ for the cleaned surface at 0 L is indicated as a broken line. At 14.7 L, the peak position shifts slightly to higher E_B. Such a small change can be observed definitely as an asymmetric profile in the difference spectrum, which shows a very small and a large change at the high and low E_B side, respectively. This proves clearly that the Ti $2p_{3/2}$ peak is preferentially reduced at the low-E_B side by O_2 adsorption. Namely the Ti $2p_{3/2}$ peak consists of at least two components. According to the preferential change upon O_2 adsorption, the low- and high-E_B component is ascribed to the metallic Ti layer on the outermost surface and bulk Ti, respectively. This assignment means a surface core level shift (SCLS) of Ti 2p toward the lower E_B on the Ti(0001)1x1 surface. Feibelman et al. [19] predicted theoretically that the SCLS of Ti 2p for the Ti(0001) surface is 0.25 eV toward higher E_B in disagreement with the present observation. Nevertheless it is of practical importance to trace straightforwardly the existence of a metallic Ti layer on the surface using the low-E_B component during O_2 adsorption. In fact, it can be clearly concluded that there still remains metallic Ti on the surface during growth of a thick TiO_2 layer, since a small but pronounced peak of Ti $2p_{3/2}$ appears even at 333 L as shown in Fig. 3.

Next the behavior of the metallic Ti layer on the surface during oxidation is considered using the peak intensity and width of Ti $2p_{3/2}$ versus D_{O2} given in Fig. 4. The peak intensity is measured after the background subtraction at E_B=453.9 eV for the broken line in Fig. 3 and the peak width is a full width at half maximum (FWHM). The peak intensity decreases linearly up to 25.4 L as guided with a broken line and then decreases more rapidly. It approaches a saturation level at 158 L with no changes up to 333 L. Namely the D_{O2} dependence of the peak intensity shows beaks at 25.4 L and 158 L as indicated with arrows A and B. The D_{O2} of break B is equal to where the I_{O-1s} restarts to increase linearly. Thus in

region (C), the zero-order reaction of O_2 adsorption proceeds with keeping the surface coverage of metallic Ti constant. At the D_{O2} of break A, it was observed from peak-fitting analysis of O 1s spectrum that the chemically shifted component due to TiO_2 starts to increase (not shown here). The agreement with the TiO_2 growth suggests that the bulk Ti is oxidized in addition to the surface metallic Ti, leading to a rapid decrease of the peak intensity. At the D_{O2} between arrows A and B, no significant change is observed for the decay curve of the peak intensity, indicating that the bulk Ti continues to be oxidized during the saturation of the oxygen uptake curve. This seems to be concerned with deoxidization near the surface, since the metallic Ti layer appears on the surface at the start of region (C).

The peak width also shows an interesting behavior against D_{O2}. Once O_2 gas is introduced, the peak width decreases and then increases monotonously. At the D_{O2} of break B, it starts suddenly to decrease with D_{O2} and saturates after ~240 L. The initial rapid decrease is ascribed to the preferential reduction of the SCLS component. With increasing D_{O2}, the SCLS component decreases further and possibly disappears at ~90 L where the oxygen uptake curve saturates. Oxidation of the surface and bulk Ti leads to an increase of TiO, Ti_2O_3 and TiO_2. Among them, the peak position of TiO is close to that of metallic Ti, the chemical shift of which is 1.2 eV comparable to the peak width [2], so giving rise to broadening the peak width of Ti $2p_{3/2}$. As a competition between the narrowing due to SCLS reduction and the broadening due to TiO, the initial narrowing of the peak width is changed into the broadening with increasing D_{O2}. Just in region (C), the peak width is narrowed rapidly in coincidence with the restart of rapid O_2 adsorption. The reason is that TiO beneath the surface is further oxidized into Ti_2O_3 and TiO_2 with a large chemical shift of 2.8 eV and 5.2 eV, respectively, [2, 18] and therefore the contribution of TiO to the peak width of Ti $2p_{3/2}$ diminishes. The almost constant value of the peak width during the saturation is narrower than that for the cleaned surface, 0.94 eV, as indicated with a broken line. In this case, the narrow width of 0.7~0.8 eV is due to a decrease of the contribution of bulk Ti. Because of thick oxide, the metallic Ti present under the oxide can hardly be observed. A very small amount of bulk Ti existing between the surface metallic Ti layer and the oxide may be concerned with the spectral feature. Thus the D_{O2} dependence of both the peak intensity and width of Ti $2p_{3/2}$ is interpreted well in terms of the persistent existence of the surface metallic Ti layer during TiO_2 growth.

4. Conclusion

The initial oxidation kinetics on the Ti(0001) surface at 405℃ was investigated by real-time photoelectron spectroscopy using synchrotron radiation. With increasing O_2 dose, the oxygen uptake curve obtained by O 1s photoelectron intensity showed a linear increase followed by a saturation, indicating that O_2 adsorption on the Ti(0001) surface at 405℃ is a zero-order reaction. In contrast with the case of H_2O adsorption on Si surfaces at room temperature, which is also a zero-order reaction, the O_2 adsorption on the Ti(0001) restarts with a zero-order reaction scheme after the saturation. The spectral changes of Ti 2p during oxidation clarified that there is a surface core level shift (SCLS) component at the low E_B side for the Ti(0001)1x1 surface. Therefore we can discriminate the metallic Ti on the outermost surface from the bulk Ti. Upon O_2 gas introduction, the surface metallic Ti is predominantly

oxidized as demonstrated by a preferential decrease of the SCLS component and bulk Ti is additionally oxidized after 25 L, where TiO_2 starts to grow. It was found that the restart of O_2 adsorption after the saturation is associated with appearance of a metallic Ti layer on the surface and subsequently a surface Ti layer exists persistently during TiO_2 growth. Consequently the zero-order reaction of O_2 adsorption on the Ti(0001) surface is ascribed to metallic Ti existing on the surface of Ti oxides.

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Figure captions

Fig. 1.   O 1s photoelectron intensity versus O_2 dose taken in situ during oxidation on the Ti(0001) surface at 405°C and 6.7×10^{-6} Pa of O_2 pressure. The photon energy was 736 eV. The period of saturation in the uptake curve is indicated as an arrow.

Fig. 2.   Ti 2p photoelectron spectrum versus O_2 dose taken in situ during oxidation on the Ti(0001) surface at 405°C and 6.7×10^{-6} Pa of O_2 pressure. The photon energy was 736 eV. The peak positions of Ti 2p for metal and TiO_2 are indicated as bars.

Fig. 3.   Ti 2p photoelectron spectra obtained at 0 L (cleaned) and 14.7 L (oxidized), a difference spectrum between them, and Ti 2p photoelectron spectrum at 333 L. The peak position of Ti $2p_{3/2}$ for the cleaned surface is indicated as a broken line.

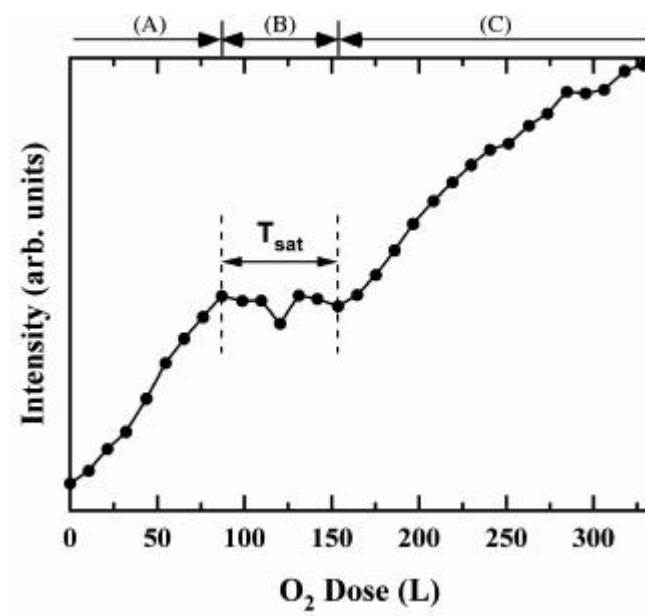Fig. 4. O_2 dose dependence of (a) the peak intensity and (b) full width at half maximum (FWHM) of Ti $2p_{3/2}$ for Ti metal obtained from Fig. 2.
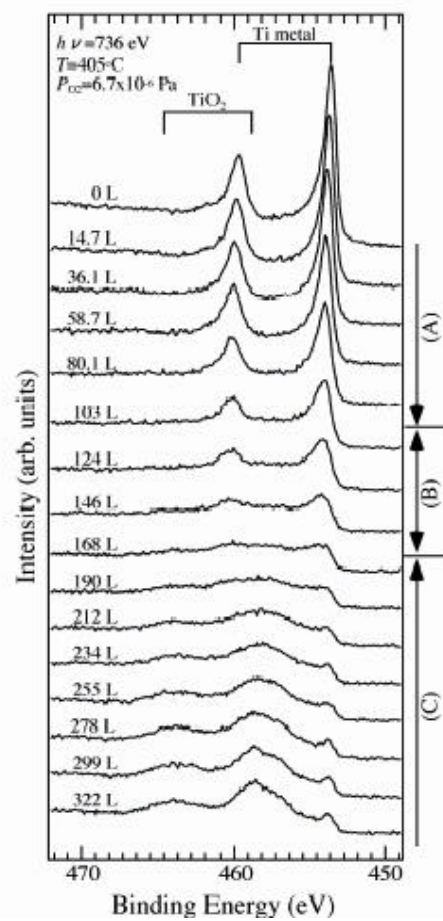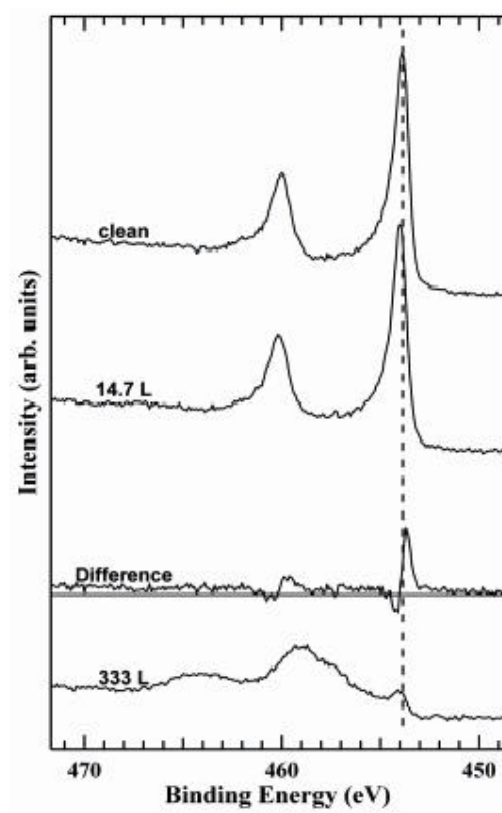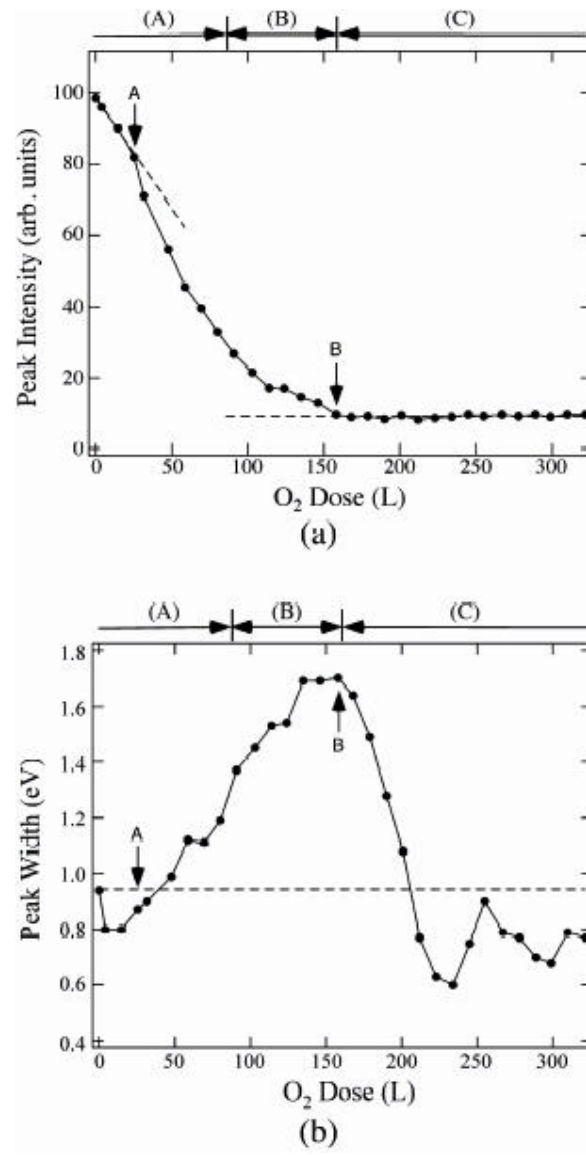
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