

## Changes of XPS Spectra from Oxides by Ion Bombardment

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When materials are analyzed by XPS or AES sputter depth profiling, it becomes difficult to determine precise chemical states of the materials which are damaged by ion bombardment. The damages of oxides by ion bombardment, which are reflected in XPS or AES spectra, are reviewed. Firstly, the classification of the changes was described. Additional peaks appear as a result of the reduction for the one type of the oxides, the spectra are broadened for the second one, and the third type oxides are unchanged. It is pointed out that these changes are related to the enthalpy and bond-type. Secondly, the intensities of photoelectrons and Auger electrons from the reduced state were reviewed. The time dependence of the intensities, in which the intensities from the reduced states and original state were saturated after long sputtering, was formulated using reduction cross sections by the ion bombardment and sputtering yield.

### INTRODUCTION

Ion sputtering is widely used for depth profiling of samples, or cleaning of samples. Ion bombardment causes change of surface concentration by preferential sputtering for alloys[1] and chemical state of some compounds are changed[2 - 18]. The shape of the XPS spectra (X-ray Photoelectron Spectroscopy) or AES spectra (Auger Electron Spectroscopy) are changed by the ion bombardment. Especially, thin films and coatings of the oxides (TiO<sub>2</sub>, NiO, WO<sub>3</sub>, PbO, CrO<sub>3</sub>, etc.) which additional peaks appears in the XPS spectra are used for various applications, such as catalyst, displays, sensors, anti-corrosion coatings and so on. It becomes difficult to determine the chemical state from the feature obtained by the sputter depth profiling of the oxides, because the obtained spectra are not recognized whether it is resulted from the original state or

the reduced state.

A lot of experiments have been performed for the surface change by ion bombardment for various compounds. In this article, the changes of the oxides by the ion bombardment were reviewed, considering the change in the XPS spectra.

### CHANGE OF OXIDES BY ION BOMBARDMENT IN XPS SPECTRA

The changes of the oxides by the ion bombardment were classified to 3 categories[2, 3], in which the changes appeared as the change of the XPS spectra[2 - 18]. The three types are (I) oxides that the additional XPS peaks appears by the reduction : NiO, WO<sub>3</sub>, PbO, CuO etc. (II) oxides that the FWHMs (Full width at half maximum) of the spectra are broadening and the surface becomes amor-

Table 1. Changes of oxides by ion bombardment which are classified by XPS spectral change or other techniques[2 - 18].

Change	Oxides
Additional peaks appears (reduction)	Ag <sub>2</sub> O, Au <sub>2</sub> O <sub>3</sub> , CdO, Co <sub>2</sub> O <sub>3</sub> , Co <sub>3</sub> O <sub>4</sub> , IrO <sub>2</sub> , MnO <sub>2</sub> , MoO <sub>3</sub> , Nb <sub>2</sub> O <sub>3</sub> , NbO <sub>2</sub> , Nb <sub>2</sub> O <sub>5</sub> , RuO <sub>2</sub> , Ta <sub>2</sub> O <sub>3</sub> , Ta <sub>2</sub> O <sub>5</sub> , U <sub>3</sub> O <sub>8</sub> , V <sub>2</sub> O <sub>5</sub> , TiO <sub>2</sub> , Ti <sub>2</sub> O <sub>3</sub> , NiO, WO <sub>3</sub> , PbO, PbO <sub>2</sub> , CuO, Cu <sub>2</sub> O, CrO <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub> , Fe <sub>3</sub> O <sub>4</sub>
FWHM broadening (becoming amorphous)	SiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , GeO <sub>2</sub> , Y <sub>2</sub> O <sub>3</sub> , Cr <sub>2</sub> O <sub>3</sub> , MoO <sub>2</sub> , Bi <sub>2</sub> O <sub>3</sub> , SnO <sub>2</sub>
No change	CaO, MgO, BeO, ZnO, CoO, MnO, SnO, ThO <sub>2</sub> , ZrO <sub>2</sub> , HfO <sub>2</sub> , UO <sub>2</sub>

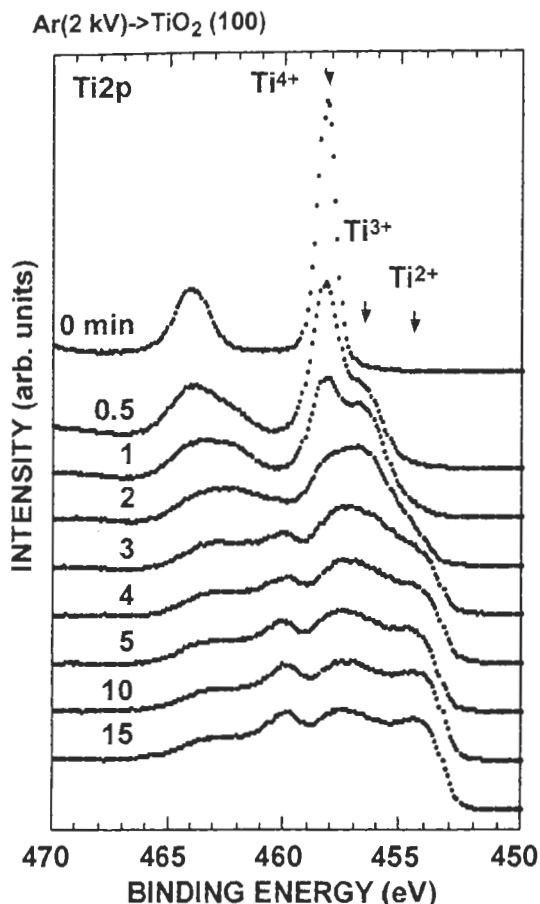


Fig. 1. Ti 2p XPS spectra of  $\text{TiO}_2$  single crystal as a function of sputtering time. Acceleration voltage of Ar ion is 2 kV [8].

phous:  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  etc. (III) oxides that no spectral change appears:  $\text{CaO}$ ,  $\text{MgO}$  etc. The summary of the previous results is listed in Table I [2 - 18].

#### Oxides that additional XPS peaks appear by reduction

It is reported that the additional components appear in addition to the original 4+ state of  $\text{TiO}_2$  after the Ar ion sputtering [2, 8 - 11]. Ti 2p XPS spectra of the  $\text{TiO}_2$  single crystal measured during Ar ion bombardment with 2 kV acceleration voltage as a function of the sputtering time are shown in Fig. 1 [8]. Only  $\text{Ti}^{4+}$  component is observed in the Ti 2p XPS spectrum of as received  $\text{TiO}_2$ . Although additional components of 3+ and 2+ state appear, the smaller state than 2+ is not observed.

$\text{TiO}_2$ ,  $\text{Ti}_2\text{O}_3$ ,  $\text{Ti}_3\text{O}_5$ ,  $\text{TiO}$ ,  $\text{Ti}_2\text{O}$ ,  $\text{Ti}_3\text{O}$  and other phases ( $\text{Ti}_4\text{O}_5$ ,  $\text{Ti}_4\text{O}_7$ ,  $\text{Ti}_5\text{O}_9$ ) are reported in Ti-O system [19, 20]. Most of the oxides are coordinated from  $\text{TiO}_6$  octahedrons or  $\text{TiO}_4$  tetrahedrons, and the coordination of the oxide is

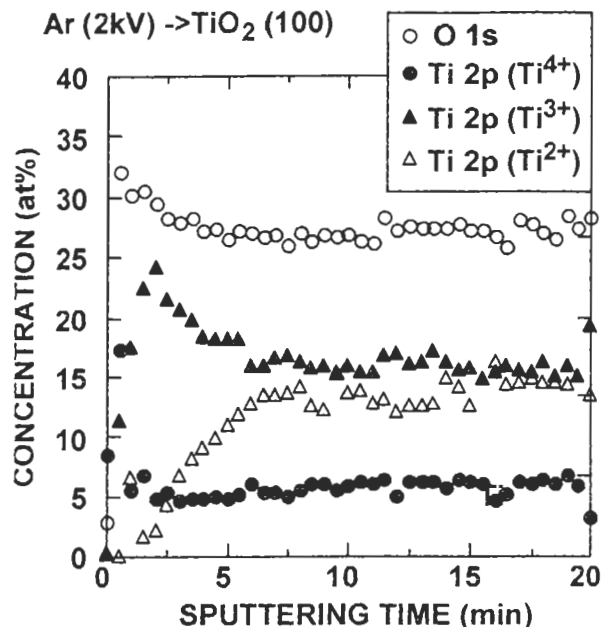


Fig. 2. Surface concentration of  $\text{TiO}_2$  single crystal as a function of sputtering time. Ti 2p XPS spectrum is separated to three components ( $\text{Ti}^{4+}$ ,  $\text{Ti}^{3+}$  and  $\text{Ti}^{2+}$ ). Acceleration voltage of Ar ion is 2 kV [8].

similar to the others. The crystal structures in the Ti-O system may suggest that two chemical states which appeared by the sputtering are not always  $\text{Ti}_2\text{O}_3$  or  $\text{TiO}$ , although we assigned them as 3+ and 2+.

The change of concentration of  $\text{TiO}_2$  as a function the sputtering time is shown in Fig. 2 [8]. The Ti  $2p_{3/2}$  spectrum was separated to three components ( $\text{Ti}^{4+}$ ,  $\text{Ti}^{3+}$ ,  $\text{Ti}^{2+}$ ) by peak fitting. The figure shows that the reduction to the  $\text{Ti}^{3+}$  state from the  $\text{Ti}^{4+}$  state has already occurred at the initial stage of the sputtering. After the component of  $\text{Ti}^{3+}$  becomes maximal, it gradually decreases and it remains constant. The  $\text{Ti}^{2+}$  state appears when the component of  $\text{Ti}^{3+}$  begins to decrease and the states reach constant. Similar depth profiling were obtained by Hofmann et. al [10]. The total intensity of Ti increases and that of O decreases as a function of the sputtering time.

Moreover, Mathieu et al. measured the intensities of Ti and O in  $\text{TiO}_2$  using the AES as a function of the sputtering time [21]. They reported that the intensity of Ti increases and that of O decreases and that the intensities become constant. The intensity ratio of O and Ti (O/Ti) for the oxide, in which the intensities become constant after the sufficient sputtering, increases in the order of  $\text{TiO}_2$ ,  $\text{Ti}_2\text{O}_3$ ,  $\text{TiO}$ . A method to predict the change of the concentration by the ion bombardment was reported [22,

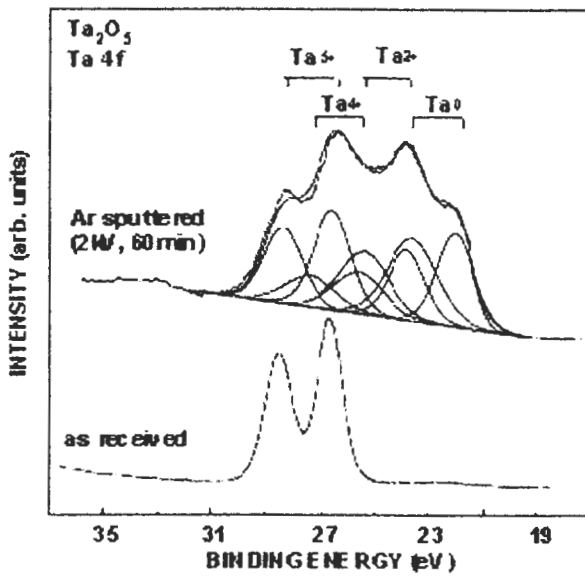


Fig. 3. Ta 4f XPS spectrum of Ta<sub>2</sub>O<sub>5</sub> powder before and after Ar sputtering. Acceleration voltage of Ar ion is 2 kV.

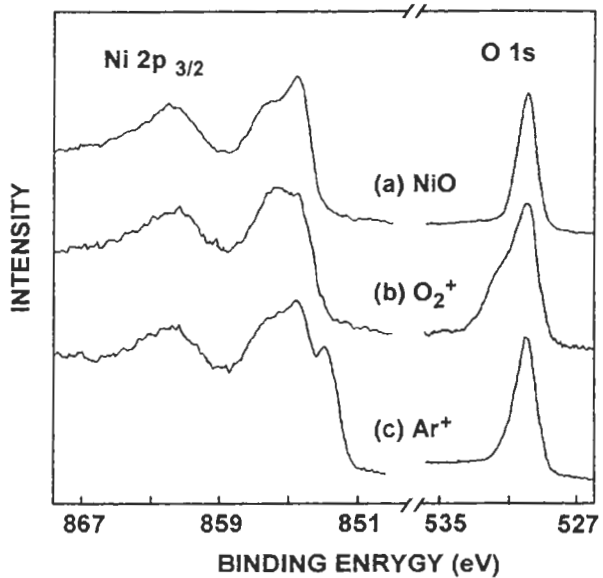


Fig. 5. Ni 2p and O 1s XPS spectra of NiO prepared by thermal oxidation of Ni. Acceleration voltage of Ar ion and O<sub>2</sub><sup>+</sup> is 400 V. [12]

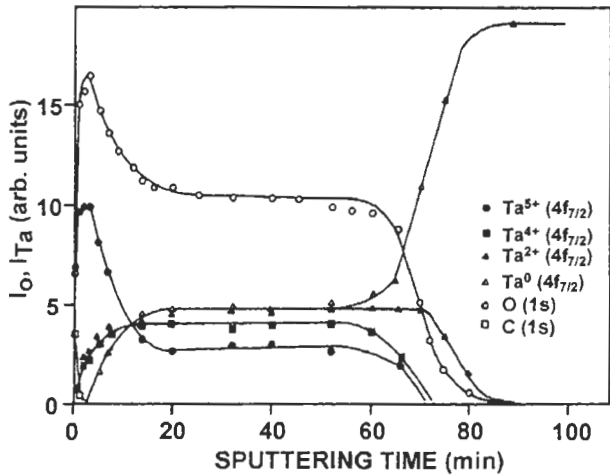


Fig. 4. Depth profile of each state of Ta, C, and O for anodic oxidized Ta<sub>2</sub>O<sub>5</sub> on Ta [11]. Acceleration voltage of Ar ion is 2 kV.

23], which is reviewed in the later chapter.

As seen in Table 1, some oxides such as Ta<sub>2</sub>O<sub>5</sub>, Nb<sub>2</sub>O<sub>5</sub>, CuO, or NiO which have several valence states like TiO<sub>2</sub>, are reduced by the ion bombardment. Figure 3 shows the change of XPS spectra by the ion sputtering of the Ta<sub>2</sub>O<sub>5</sub> powder, which was pressed to a pellet. The peak fitting for the Ta 4f XPS spectra of the sputtered Ta<sub>2</sub>O<sub>5</sub> powder expressed that Ta<sup>4+</sup>, Ta<sup>2+</sup> and Ta<sup>0</sup> as the reduced states are seen in addition to Ta<sup>5+</sup> as the original state.

Figure 4 shows the depth profile of each state for the anodic oxidized Ta<sub>2</sub>O<sub>5</sub> on Ta [11]. After Ta<sup>5+</sup> as Ta<sub>2</sub>O<sub>5</sub> is de-

creased and Ta<sup>4+</sup>, Ta<sup>2+</sup> and Ta<sup>0</sup> as the reduced states, the intensities become constant are increased as seen in the case of TiO<sub>2</sub>. Similar change is seen for Nb<sub>2</sub>O<sub>5</sub> [10, 11].

CuO is reduced and the 1+ state appears in addition to the 2+ state [13]. The results for NiO which were prepared by the thermal oxidation of Ni are shown in Fig. 5 [12]. A metallic state as the reduced state appears as the results of the Ar<sup>+</sup> ion bombardment, although the spectrum is almost same after O<sub>2</sub><sup>+</sup> ion bombardment [12].

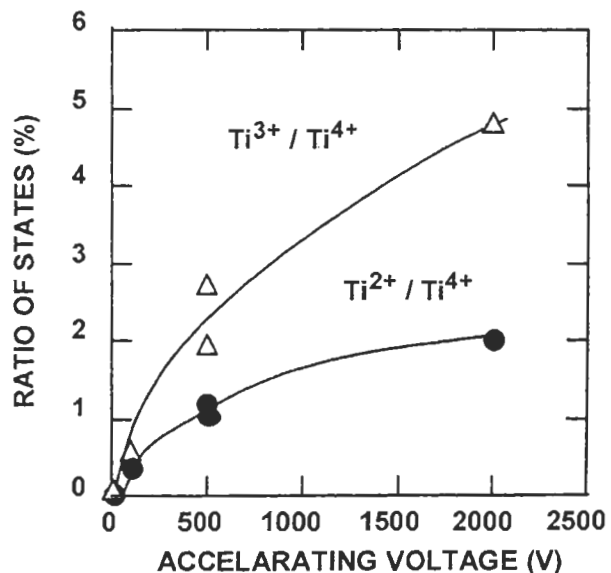


Fig. 6. Intensities of Ti<sup>3+</sup> and Ti<sup>2+</sup> state of sputtered TiO<sub>2</sub>, that surface reached a steady state, as a function of acceleration voltage. Intensities of states are normalized by that of Ti<sup>4+</sup> [8].

The intensity from 2+ state was increased in  $Fe_3O_4$  after the ion bombardment. In iron and another element system oxide with the spinel type structure, a site of iron ion is substituted by the element. Suzuki et. al. measured the XPS spectra from the sputtered single crystal of  $Fe_2NiO_4$  and  $Fe_2ZnO_4$ [15]. For  $Fe_2NiO_4$ , the metallic Ni were observed in addition to the  $Ni^{2+}$  state and the  $Fe^{2+}$  state as reduced state were observed. On the other hand, the change for the chemical state of Fe from 3+ to 2+ is observed but Zn is stable for  $Fe_2ZnO_4$ .

Figure 6 shows the relationship between the intensities of the reduced state from  $TiO_2$  and the acceleration voltage[8]. The intensities of the reduced states are normalized by that of the  $Ti^{4+}$  state. The  $Ti^{3+}$  state increases with elevating acceleration voltage. The  $Ti^{2+}$  state is not observed at 10 V and the amount of the  $Ti^{2+}$  state increases with increasing acceleration voltage. This result suggests that a critical energy in the range between 10 and 100 V exists for the reduction from the  $Ti^{3+}$  state to the  $Ti^{2+}$  state.

**Oxides which FWHMs of spectra are broadening**

FWHM are changed for oxides such as  $SiO_2$  or  $Al_2O_3$ , although the additional peaks, which are observed in  $TiO_2$ ,  $Ta_2O_5$ ,  $CuO$ , or  $NiO$ , was not observed. Ajioka and Ushino measured the thermally oxidized  $SiO_2$  on Si wafer using XPS with ion implantation of  $As^+$ . Figure 7 shows the change of Si 2p XPS spectrum before and after the ion bombardment of  $As^+$  with 70 kV[17]. Although the binding energy of the peak is same, the FWHM becomes large after the ion sputtering.

A results of the change of FWHM for Si 2p XPS spectra from  $SiO_2$  plate is shown in Fig. 8, which were performed in the round robin experiments in Iron and Steel

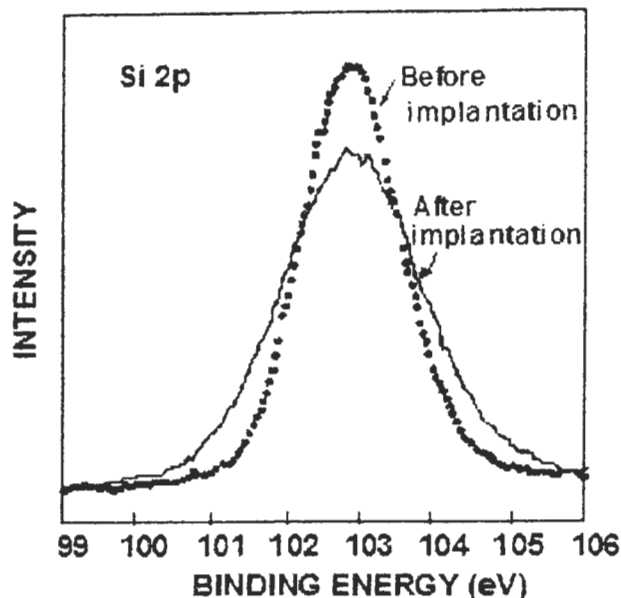


Fig. 7. Si 2p XPS spectra of thermally oxidized  $SiO_2$  on Si wafer as a function of sputtering time. Acceleration voltage of  $As^+$  ion is 70 kV[17].

Institute of Japan[2]. The FWHM of the XPS spectra almost increased in all of the laboratories. Hofmann and Thomas obtained the similar results in the case of  $He^+$ ,  $Ar^+$ , and  $Xe^+$  ion implantation to the thermally oxidized  $SiO_2$  on Si wafer[16]. The FWHM increased in the range of 0.5 to 2 kV, the increase by  $He^+$  sputtering was larger than that by  $Ar^+$  or  $Xe^+$ , and the increase depended on the acceleration voltage. The successive  $Xe^+$  ion sputtering decreased the FWHM after the sputtering of  $He^+$  and the further  $He^+$  bombardment increased the FWHM[16]. They thought that the change of the chemical state was occurred in the ion range of the samples and that increase of the FWHM by the ion sputtering was due to the disordering of the angle change of Si-O.

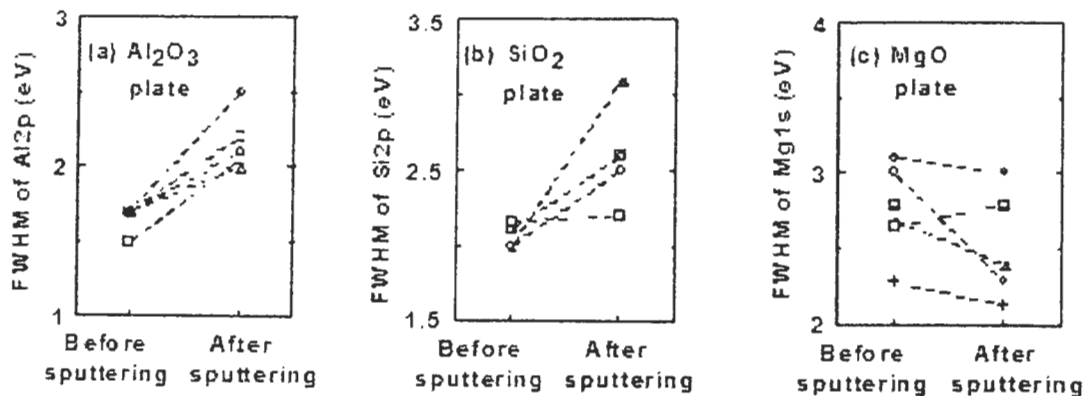


Fig. 8. FWHM of XPS spectra before and after Ar ion sputtering [2]. (a) Si2p for  $SiO_2$  plate, (b) Al2p for  $Al_2O_3$  plate, and (c) Mg1s for MgO plate.

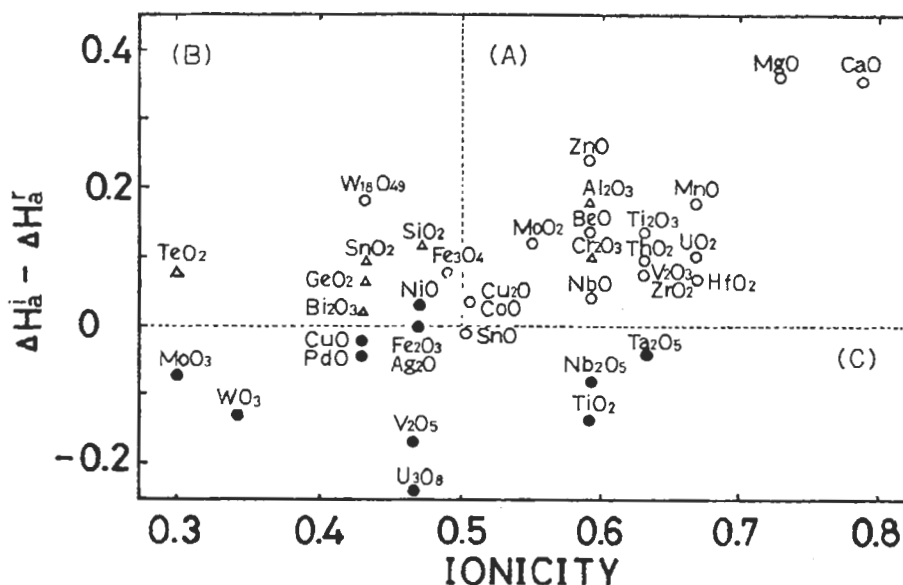


Fig. 9. Surface change for various oxides by Ar ion sputtering, which is classified by atomization heat and ionicity. (A): stable region, (B): FWHM broadening / becoming amorphous region, (C): additional peaks appearing / reduced region)[2, 3]

The round robin tests for the Al<sub>2</sub>O<sub>3</sub> plate were performed and the FWHM of Al 2p XPS spectra of Al<sub>2</sub>O<sub>3</sub> plate increased by Ar<sup>+</sup> ion sputtering[2]. The results are also shown in Fig. 8(b).

Diffraction techniques or RBS (Rutherford Backscattering Spectroscopy) showed that the oxide single crystals such as SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, GeO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>, MoO<sub>2</sub>, SnO<sub>2</sub>, TiO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>, etc. becomes amorphous or polycrystalline after the ion sputtering, but that the other oxides such as CaO, MgO, BeO, ZnO are not changed[4, 23-27].

#### Oxides which the spectra are unchanged

XPS spectrum for some oxide such as MgO, BeO, CaO does not change after the ion bombardment. Figure 8(c) shows the FWHM of Mg 1s XPS peak for MgO before and after the ion bombardment by Ar<sup>+</sup> ions[2].

#### Summary of spectral change by ion bombardment

Kelly et al. reported a criterion on the reduction of the oxides by the ion bombardment using the atomization heat[6]. The oxide of which the atomization heat is smaller than that of the reduced product, namely the change of the atomization heat is positive, can be reduced by the ion bombardment. Kim et al. estimated the free formation enthalpy of the oxides and gave a criterion that the oxide with less than 60 kcal/mole of the free formation energy is reduced by ion sputtering[5].

Moreover, as a criterion of the becoming amorphous, the oxides were classified from the bond type which is defined using ionicity by Pauling[27]. The oxides with high ionicity such as CaO, which are ionic compounds, keep the crystal structure, but the oxides with low ionicity become amorphous by the ion bombardment[2, 4]. Some oxides becoming amorphous are reduced and the additional peaks appear in XPS spectrum, and others are the oxides which keep the chemical state but the FWHM becomes large.

Summarizing these results on the XPS results and the criterion, the oxides are classified to three groups as seen in the Fig. 9[2] using the change of the atomization heat and ionicity[28]. They are (A) oxides that are not changed, (B) oxides that are damaged (but not reduced), and (C) oxides that are reduced. Namely, the oxides having positive atomization heat change and large ionicity are unchanged. The oxides having positive atomization heat change and small ionicity are damaged. The oxides having negative atomization heat change are reduced.

Ion bombardment with the energy of several keV causes collision cascade within a depth of about 10 nm of the surface of sample[29]. The recoiled atoms in the collision cascade would be stabilized as an oxide having the lowest free formation enthalpy. Then the oxides with the positive change of the free formation enthalpy do not change, but the oxides with a negative change are reduced.

Table 2. Average projected range ( $R_p$ ) and straggling ( $\Delta R_p$ ) of Ar implanted into  $TiO_2$  as a function of acceleration voltage[8].

Acceleration voltage	10 V	100 V	500 V	2 kV
Projected range : $R_p$ (nm)	0.28	0.57	1.17	2.6
Straggling : $\Delta R_p$ (nm)	0.05	0.20	0.52	1.2

**INTENSITIES OF PHOTOELECTRONS FROM REDUCED LAYER**

**Distribution of reduced layer by ion bombardment**

The amount of the reduced state for the oxides becomes constant after the sufficient ion sputtering as seen in  $TiO_2$  and  $Ta_2O_5$ , etc[8, 10, 11, 21]. It is considered that the radiation damage is localized near surface[16]. Moreover, the TEM (Transmission Electron Microscopy) observation revealed that the ion implantation with more than several ten keV causes the structural change and that the damage layer localized near surface[30]. The angle resolved XPS for  $TiO_2$  showed that the damage is localized near surface[9, 31]

The profile of the implanted ions with more than several ten keV becomes Gaussian distribution from LSS theory[32]. The damage by the ion bombardment are located in the shallower depth than the ion range ( $R_p$ ). Although the LSS theory can not always be applied to the sputtering in the several keV range, the approximated distribution can be estimated using the software of the Monte Carlo simulation which is based on the TRIM code[33]. The more precise profile is calculated using the molecular dynamics simulation[34].

The calculated ion range and straggling ( $\Delta R_p$ ) of 10 - 2keV Ar implanted to  $TiO_2$  using LSS theory are tabulated in Table 2. Assuming that the reduced range is same as the implanted depth and that the range is sum of the ion range and the straggling, the reduced range is about 3-4 nm. The thickness is close to the value (2.6 nm) of inelastic mean free path[35]. This means that the reduced layer suffered from the spectra of AES or XPS but that the substrate beneath the reduced layer also contribute to the spectra.

**FORMULATION OF CONCENTRATION OF REDUCED STATE AS A FUNCTION OF ION DOSE**

It is reported that the ratio of the Ti and O AES intensities can give relative stoichiometric information, because the surface composition of various Ti sub-oxides reaches an individual value as a result of the reduction by the sput-

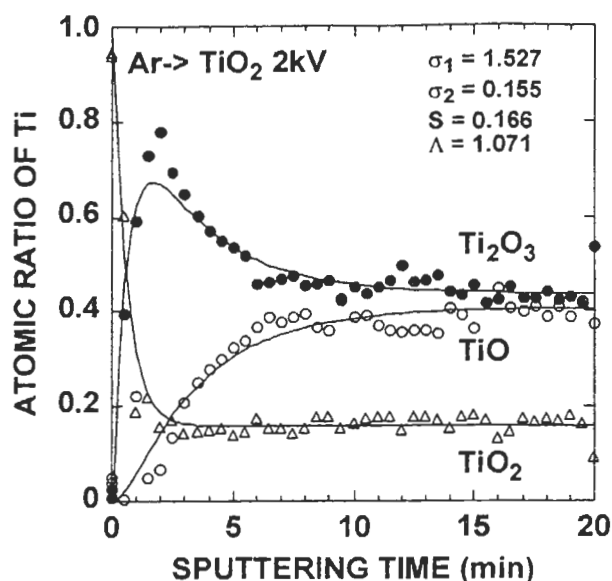


Fig. 10. XPS depth profile of  $Ti^{4+}$ ,  $Ti^{3+}$  and  $Ti^{2+}$  states for  $TiO_2$  single. Circles and triangles represent experimental data and lines are fitted results.[22]

tering[21, 23].

On the other hand, ESD (Electron Simulated Desorption) of  $SiO_2$ [36, 37], or duration of polymer by x-ray irradiation [38] were calculated using two successive reduction process with constant reaction cross section. Considering sputtering effects, the reduction by the ion bombardment is formulated using the similar reduction reaction[22, 23]. The concentration ( $N_j$ ,  $j=1,2,3$ ) of the reduced oxide ( $M1 \rightarrow M2$ ,  $M2 \rightarrow M3$ ) by the ion sputtering can be expressed as the reduction equation of eq. (1) using the reduction coefficient per one ion ( $\sigma_1$ : for  $M_1 \rightarrow M_2$ ,  $\sigma_2$ : for  $M_2 \rightarrow M_3$ ), sputtering yield ( $S$ ) for the ion bombardment of current density of  $i$ . In eq.(1), the change by the sputtering is the sum of the generation of the reduced state, sputter removal of the surface and the appearance of the substrate.  $N_j^0$  is the initial concentration of each state, and  $N_{Tot}$  is the number of the numbers of Ti in the reduced layer.

$$\begin{aligned} \frac{dN_1(t)}{dt} &= \frac{\sigma_1 \cdot i}{N_{Tot} \cdot e} \cdot N_1(t) - \frac{S \cdot i}{N_{Tot} \cdot e} \cdot N_1(t) + \frac{S \cdot i}{N_{Tot} \cdot e} \cdot N_1^0 \\ \frac{dN_2(t)}{dt} &= \frac{\sigma_1 \cdot i}{N_{Tot} \cdot e} \cdot N_1(t) - \frac{\sigma_2 \cdot i}{N_{Tot} \cdot e} \cdot N_2(t) - \frac{S \cdot i}{N_{Tot} \cdot e} \cdot N_2(t) + \frac{S \cdot i}{N_{Tot} \cdot e} \cdot N_2^0 \quad (1) \\ \frac{dN_3(t)}{dt} &= \frac{\sigma_2 \cdot i}{N_{Tot} \cdot e} \cdot N_2(t) - \frac{S \cdot i}{N_{Tot} \cdot e} \cdot N_3(t) + \frac{S \cdot i}{N_{Tot} \cdot e} \cdot N_3^0 \end{aligned}$$

Supposing that substrate is pure oxide ( $N_1^0 = 1$ ,  $N_2^0 = N_3^0 = 0$ ) the information depth ( $\Lambda$ ) is also considered as the

thickness of the reduced layer is one unit and  $K$  is proportional constant, Intensities of each state is expressed by eq. (2).

$$I_1(t) = K \cdot \left( \frac{\sigma_1}{k_1} \cdot \exp(-k_1 \cdot t) + \frac{S}{k_1} \right) + K \cdot (\Lambda - 1)$$

$$I_2(t) = K \cdot \left( \frac{\sigma_1^2}{k_1 \cdot (\sigma_2 - \sigma_1)} \cdot \exp(k_1 \cdot t) + \frac{\sigma_1 \cdot \sigma_2}{k_2 \cdot (\sigma_2 - \sigma_1)} \cdot \exp(-k_2 \cdot t) + \frac{\sigma_1 \cdot S}{k_1 \cdot k_2} \right)$$

$$I_3(t) = K \cdot \left( \frac{\sigma_1 \cdot \sigma_2}{k_1 \cdot (\sigma_1 - \sigma_2)} \cdot \exp(k_1 \cdot t) + \frac{\sigma_1 \cdot \sigma_2}{k_2 \cdot (\sigma_2 - \sigma_1)} \cdot \exp(-k_2 \cdot t) + \frac{\sigma_1 \cdot \sigma_2}{k_1 \cdot k_2} \right) \quad (2)$$

Here,  $k_j = \sigma_j + S$ ,  $N_1^0$  is the initial concentration of  $Ti^{+}$  state.

The fitting for the experimental results of Fig. 3 are shown in Fig 10. The figure is an example of  $TiO_2$  single crystal sputtered by 2 kV  $Ar^+$ . The fitting results displayed by the lines agree with the experimental data.

## SUMMARY

$Ar$  ion sputtering sometimes causes the surface damage and it becomes difficult to characterize the compounds using XPS or AES. This review shows the spectral change of oxide.

Firstly, XPS spectra of the oxides were reviewed. Three types of the change are observed, (1) reduced and additional peaks in XPS ;  $TiO_2$ ,  $Ta_2O_5$ ,  $Nb_2O_5$ ,  $NiO$ ,  $CuO$  etc., (2) amorphousization or the broadening of FWHM :  $SiO_2$ ,  $Al_2O_3$ , etc. (3) no changed :  $CaO$ ,  $MgO$ ,  $ZnO$  etc. The change by ion sputtering are summarized by the atomization heat and ionicity.

Secondly, the intensities of the XPS and AES peaks of the reduced state are reviewed and the intensities can be formulated by the reaction differential equation using the reduction coefficient and sputtering yield.

Therefore, it is very difficult for the important oxides for the actual applications to estimate the real chemical structure by the interference caused by the ion sputtering. However, the further trials will make a progress to determine the true structures, although the interference does not completely hide information of the original state.

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