CHANGES OF X-RAY PHOTOELECTRON SPECTRA BY ION SPUTTERING

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Abstract Round-robin experiments have revealed that the O1s XPS line gives a better correction of the binding energy shift by the charge up than the C1s XPS line does. Moreover, an oxide can be unchanged or damaged or reduced by ion sputtering and the change can be predicted by the ionisity and the free formation enthalpy.

Key word x-ray photoelectron spectroscopy (XPS), binding energy, charge up, ion sputtering, oxide

INTRODUCTION

It has been reported that the correction using C1s, which originates from the contamination of carbon, does not always give a correct binding energy [1]. Chemical states of several compounds are altered by ion bombardment used for depth profiling in XPS (X-ray Photoelectron Spectroscopy) [2]. Round-robin experiments have been performed in order to establish the correction of the binding energy of XPS spectra for oxides by charging resulting from radiation of x-rays or Ar ion sputtering and to determine the criteria for the change of chemical state by Ar ion sputtering.

EXPERIMENTAL

The XPS spectrometers used in the round-robin measurements by the seven laboratories are shown in TABLE 1. Plates of Al₂O₃, SiO₂, MgO and TiO₂ and powder of NiO were used as specimens. Al2p (Si2p, Mg1s, Ti2p and Ni2p), C1s and O1s spectra for Al₂O₃ (SiO₂, MgO, TiO₂ and NiO) were measured while Ar ion sputtering were performed until the binding energy and intensity of every line became stable.

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TABLE 1 XPS spectrometers used for the round-robin experiments

Lab.	Model	Analyzer	Source
B	VG-ESCA3 Mark II	Hemispherical	Al K α
C	Kratos Model ES-300	Hemispherical	Al K α
D	VG-ESCA Lab 5	Hemispherical	Al K α
E	VG-ESCA3 Mark II	Hemispherical	Al K α
F	PHI-550E	CMA	Mg K α
I	PHI-5300	Hemispherical	Al K α
K	PHI-5400MC	Hemispherical	Al K α

RESULTS AND DISCUSSION

Correction of binding energy Binding energy shift of the Al2p (Si2p or Mg1s) line by charge up which is caused by radiation of x-ray and ion sputtering shifts to a high binding energy in Al₂O₃ (SiO₂ or MgO). The amount of shift is different among the laboratories and samples; it is clear that the differences between the O1s and Al2p lines are much smaller than those between the C1s and Al2p lines. Fig. 2 shows the binding energy differences between O1s and Al2p lines of Al₂O₃ which are measured at the seven laboratories. The scatter of the binding energy differences between the O1s and Al2p lines is less than 1 eV among the laboratories. The scatter of the binding energy differences between the O1s and Si2p (Mg1s) lines of SiO₂ (MgO) was also as small as those between the C1s and Si2p (Mg1s) lines. The round-robin measurements reveal that the correction using the binding energy of the O1s line give a better correction for the binding energy shift of Al₂O₃ (SiO₂ or MgO) than that using the binding energy of the C1s line which is commonly used.

Change of the chemical state by ion sputtering Fig. 3 shows the change of Ti2p XPS spectra of TiO₂ as a function of Ar ion sputtering time. After Ar ion sputtering, components of Ti³⁺ and Ti²⁺ appear besides that of Ti⁴⁺ in the Ti2p line. A component of Ni⁰ appeared besides that of Ni²⁺ in the Ni2p line of NiO. The additional components of TiO₂ and NiO by Ar ion sputtering is due to the reduction of the oxides, which agrees with the previous results [4][5].

Fig. 1 Relationship between binding energy difference between C1s and Al2p lines of Al₂O₃ plate and that between for O1s and Al2p lines. (Lab. : O; C, ●; D, △; E, ▲; F, ■; I)

Fig. 2 Binding energy difference between O1s and Al2p lines of Al₂O₃ plate at each laboratory.

Fig. 4 shows FWHM (Full Width Half Maximum) of the Al2p line of Al₂O₃, Si2p line of SiO₂ and Mg1s line of MgO before and after Ar ion sputtering. The FWHM of the Al2p line and the Si2p line increase by Ar ion sputtering, although new components are not observed in

Al_2O_3 and SiO_2 . The increase of FWHM results from the damage induced at the surface by ion sputtering [6]. On the other hand, no changes are seen in XPS spectra of MgO by ion sputtering.

The change of the chemical state for the oxides by ion sputtering is classified to three categories. The chemical state is not changed in the oxides of the first category as exemplified by MgO , the damage is induced in the oxides of the second category as Al_2O_3 and SiO_2 and the oxides in the third category such as TiO_2 and NiO are reduced. Kelly et al. proposed a criteria for the change of the chemical state by ion sputtering that the oxides are reduced when the free formation enthalpy of an oxide is smaller than that of the thermally reduced oxide [7]. Moreover, a tendency is seen that the oxides having the ionic character such as MgO are not changed by ion sputtering.

Comparing the published data for the oxides [2] with our data, the changes of the chemical state for the oxides by ion sputtering can be classified by the free formation enthalpy and the ionicity.

Fig. 3 Change of $\text{Ti}2p$ XPS spectra for TiO_2 as a function of Ar ion sputtering time.

Fig. 4 FWHM of (a) $\text{Al}2p$ line of Al_2O_3 , (b) $\text{Si}2p$ line of SiO_2 and (c) $\text{Mg}1s$ line of MgO before and after Ar ion sputtering. (Lab.: $\square$; B, $\circ$; C, $\bullet$; D, Δ ; E, $\blacksquare$; I, $+$; K)

The diagram is shown in Fig. 5. We apply the Kelley's criteria for the oxides that are reduced. Ha^i and Ha^r are the free formation enthalpy of the starting oxides and reduced oxides, respectively. We used the ionicity (I) that Pauling defined [8] as the parameter of the bond character. The diagram predicts how the chemical state of the oxides can be changed by ion sputtering; the oxides in the region A ($\text{Ha}^i < \text{Ha}^r$ and $I > 0.5$) are unchanged, the oxides in the region B ($\text{Ha}^r < \text{Ha}^i$ and $I < 0.5$) are damaged and the oxides in the region C ($\text{Ha}^i > \text{Ha}^r$) are reduced.

SUMMARY

The round robin experiments by the seven laboratories have been performed in order to correct the shift of the binding energy of XPS spectra for Al_2O_3 , SiO_2 , MgO , TiO_2 and NiO and to establish the criteria of the change of the chemical state for the oxides by ion sputtering. We have revealed that the $\text{O}1\text{s}$ XPS line gives a better correction of the binding energy shift by the charge up than the $\text{C}1\text{s}$ XPS line does. Moreover, a oxide can be unchanged or damaged or reduced by ion sputtering and the change can be predicted by the ionicity and the free formation enthalpy

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Fig. 5 Surface alteration of various oxides [2] by Ar ion sputtering, which is classified by free formation enthalpy and ionicity defined by Pauling. (region A; unchanged region, B; damage induced region, C; reduced region)

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