# Formulation for XPS Spectral Change of oxides by Ar Ion Bombardment: Application of the Formulation to $Ta_2O_5$ System

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A formulation, which had been proposed to explain the change of XPS spectra for $TiO_2$ as a function of ion sputtering time, was modified in order to describe that for $Ta_2O_5$. It was confirmed that components of $Ta^{4+}$, $Ta^{2+}$, and $Ta^0$ as reduced states appeared in addition to the $Ta^{5+}$ state in Ta 4f XPS spectra for $Ta_2O_5$ during Ar ion sputtering with 2 kV acceleration voltage. This formulation based on reaction equations which contain four reduction processes (from $Ta^{5+}$ to $Ta^{4+}$, $Ta^{4+}$ to $Ta^{2+}$, $Ta^{2+}$ to $Ta^+$, and $Ta^+$ to $Ta^0$) and sputtering effects.

Using five fitting parameters (three reduction coefficients, sputtering yield, and information depth), the present formula was fitted to the experimental results. The fitting results agreed satisfactorily with the experimental results for $Ta_2O_5$. The formulation, which described the XPS spectral change of $TiO_2$ by ion bombardment, can be also applied to the change of XPS spectra for $Ta_2O_5$ as a function of ion sputtering time. This formulation can predict that the change of the chemical states in oxides by ion bombardment.

## 1. Introduction

Many transition metal oxides are used for various applications; electronic or magnetic devices, displays, catalysis, sensors, anti-corrosion coatings and so on. Ar ion sputtering changes chemical states and composition of such oxides [1-5]. For example, the oxides ($TiO_2$, $Ta_2O_5$, $Nb_2O_5$ etc.) are reduced by ion bombardment and extra components appear in feature of an original XPS spectrum. For XPS spectra of $Ta_2O_5$ after the Ar ion sputtering, Hofmann and Sanz reported that $Ta^{4+}$, $Ta^{2+}$, and $Ta^0$ as the reduced states appeared in addition to $Ta^{5+}$ as the initial state [5]. Therefore, it is difficult to determine the true chemical state during the depth profiling using the ion sputtering. On the other hand, we reported that fractions of the reduced state ($Ti^{2+}$ and $Ti^{3+}$) in $TiO_2$ after the Ar ion sputtering can be formulated as a function of sputtering time, although the formulation was limited to predict the spectral change of two reduced state [6,7].

We modified this formulation to explain the XPS spectral change of $Ta_2O_5$ in which the number of the reduced states after Ar ion bombardment is larger than that in $TiO_2$ [5, 8].
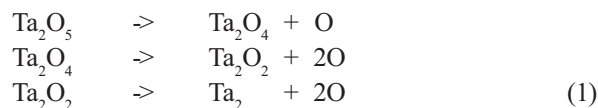
## 2. Model for reduction of oxides by ion bombardment as a function of sputtering time

Tanuma et. al proposed an equation for electron stimulated desorption (ESD) of $SiO_2$, considering the existence of the intermediate state (SiO) between the initial state ($SiO_2$)

and the final state (Si) [9].

Similarly to electron irradiation, valence numbers are reduced by ion bombardment and this reduction can also be expressed by the same reaction as (1) [6, 7]. Several intermediate states ($M_nO_{m-1}$, … $M_nO_{m-j}$, $M_nO_{m-j-1}$,… , $M_nO$) are produced in addition to the initial state ($M_nO_m$) by ion bombardment. Using two reduction reactions, we formulated the change for $TiO_2$ which contain two reduction state ($Ti^{3+}$, and $Ti^{2+}$).

Hofmann and Sanz reported that $Ta^{4+}$, and $Ta^{2+}$ as the intermediate states, $Ta^{5+}$ as the initial state, and $Ta^0$ as the final state [5]. Following their results, four states ($Ta^{5+}$, $Ta^{4+}$, $Ta^{2+}$, and $Ta^0$) should be considered and the reactions are written in eq.(1).

$$
\begin{array}{llll}
Ta_2O_5 & > & Ta_2O_4 & + \ O \\
Ta_2O_4 & > & Ta_2O_2 & + \ 2O \\
Ta_2O_2 & > & Ta_2 & + \ 2O
\end{array} \quad (1)
$$

$Ta_2O_5$, $Ta_2O_4$, $Ta_2O_2$, $Ta_2$ are clusters which characterize the molecules, and composed in the same numbers of metal atoms.

Here, we supposed that a uniform reduced layer beneath the surface is formed by ion bombardment, and that the oxide can be reduced to two different sub-oxides and one metal. The differential equation for the fractions of chemical

*Journal of Surface Analysis Vol.13 No. 1 (2006) pp. 14 - 18*
*Special Issue for Recent Development of Oxide Surface Analysis*
*S. Hashimoto et. al. Formulation for XPS Spectral Change of oxides by Ar Ion Bombardment: ...*

states in the uniform reduced layer is given by eq. (2). The removal of atoms by sputtering is also taken into consideration. In the equation, the rate of change of the fractions of the original state ($Ta_2O_5$) in the reduced layer is given by the sum of the losses of $Ta_2O_5$ caused by reduction and removal from the surface by the sputtering, and gain of the unreduced substrate under the reduced layer. The increasing rate of $Ta_2O_4$ is the sum of the reduction from $Ta_2O_5$ to $Ta_2O_4$, the reduction from $Ta_2O_4$ to $Ta_2O_2$, the sputtering of reduced $Ta_2O_4$ and the appearance of the substrate and so on.

$$\frac{dN_1}{dt} = -\sigma_1 \cdot \frac{i}{e \cdot N_{Tot}} \cdot N_1 - S \cdot \frac{i}{e \cdot N_{Tot}} \cdot N_1 + S \cdot \frac{i}{e \cdot N_{Tot}} \cdot N_1^0$$

$$\frac{dN_2}{dt} = \sigma_1 \cdot \frac{i}{e \cdot N_{Tot}} \cdot N_1 - \sigma_2 \cdot \frac{i}{e \cdot N_{Tot}} \cdot N_2$$
$$- S \cdot \frac{i}{e \cdot N_{Tot}} \cdot N_2 + S \cdot \frac{i}{e \cdot N_{Tot}} \cdot N_2^0$$

$$\frac{dN_3}{dt} = \sigma_2 \cdot \frac{i}{e \cdot N_{Tot}} \cdot N_2 - \sigma_3 \cdot \frac{i}{e \cdot N_{Tot}} \cdot N_3$$
$$- S \cdot \frac{i}{e \cdot N_{Tot}} \cdot N_3 + S \cdot \frac{i}{e \cdot N_{Tot}} \cdot N_3^0$$

$$\frac{dN_4}{dt} = \sigma_3 \cdot \frac{i}{e \cdot N_{Tot}} \cdot N_3 - S \cdot \frac{i}{e \cdot N_{Tot}} \cdot N_4 + S \cdot \frac{i}{e \cdot N_{Tot}} \cdot N_4^0 \qquad (2)$$

$N_1(t)$, $N_2(t)$, $N_3(t)$, and $N_4(t)$ are fractions of $Ta_2O_5$, $Ta_2O_4$, $Ta_2O_2$, and $Ta_2$ at time ($t$, dimension : sec). $\sigma_1$, $\sigma_2$, and $\sigma_3$ are the reduction coefficients from $Ta_2O_5$ to $Ta_2O_4$, that from $Ta_2O_4$ to $Ta_2O_2$, and that from $Ta_2O_2$ to $Ta_2$. $i$ is the current density of primary ions (dimension : A/m²), $S$ is the sputtering yield (dimensionless: ions/ions), $e$ is the elementary electric charge (dimension : C), and $N_1^0$, $N_2^0$, $N_3^0$, and $N_4^0$ are the fractions (dimensionless: molecules) of the original $Ta_2O_5$, $Ta_2O_4$, $Ta_2O_2$, and $Ta_2$. $N_2^0 = N_3^0 = N_4^0 = 0$, when $Ta_2O_5$ is the initial state. The total numbers of the four types of molecules ($Ta_2O_5$, $Ta_2O_4$, $Ta_2O_2$, and $Ta_2$) in the layer reduced by ion bombardment is defined as $N_{Tot}$. Here, the molecule is treated as one unit per one metallic atom. The sputtering yield is the number of the molecules in all states removed by one incident ion, and is considered to be the same for $Ta_2O_5$, $Ta_2O_4$, $Ta_2O_2$, and $Ta$. The reduction coefficients mean the number of the molecules reduced by one primary ion until the energy of the ion is fully lost in the oxide.

Using the initial condition, $N_1(0) = N_1^0$, $N_2(0) = N_2^0 = 0$, $N_3(0) = N_3^0 = 0$, and $N_4(0) = N_4^0 = 0$, and definition of $k_j = S + \sigma_j$, the fraction of each state is obtained as follows:

$$N_1 = A_{11} \cdot \exp(-k_1 \cdot i \cdot t) + A_{10}$$

$$N_2 = A_{21} \cdot \exp(-k_1 \cdot i \cdot t) + A_{22} \cdot \exp(-k_2 \cdot i \cdot t) + A_{20}$$

$$N_3 = A_{31} \cdot \exp(-k_1 \cdot i \cdot t) + A_{32} \cdot \exp(-k_2 \cdot i \cdot t)$$
$$+ A_{33} \cdot \exp(-k_3 \cdot i \cdot t) + A_{30}$$

$$N_4 = A_{41} \cdot \exp(-k_1 \cdot i \cdot t) + A_{42} \cdot \exp(-k_2 \cdot i \cdot t)$$
$$+ A_{43} \cdot \exp(-k_3 \cdot i \cdot t) + A_{44} \cdot \exp(-k_4 \cdot i \cdot t) + A_{40}$$

$$(3)$$

Here,

$$A_{10} = \frac{S}{k_1} \cdot N_1^0$$

$$A_{11} = \frac{\sigma_1}{k_1} \cdot N_1^0$$

$$A_{l,0} = \frac{\sigma_{l-1}}{k_l} \cdot A_{l-1,0} + \frac{S}{k_l} \cdot N_l^0$$

$$A_{l,l} = \sum_{n=0}^{l-1} \frac{\sigma_{l-1}}{k_l - k_n} \cdot A_{l-1,n} + \frac{\sigma_l}{k_l} \cdot N_l^0$$

$$A_{l,m} = \frac{\sigma_{l-1}}{k_m - k_l} \cdot A_{l-1,m} \qquad \text{(for l > m)} \qquad (4)$$

The intensity of photoelectrons from a metallic element in each state is expressed as eq. (5), when the uniform reduced layer is formed at the surface of the oxide. The intensity of photoelectrons from the unreduced state, $I^M_{unred}$, is proportional to the sum of the fraction of the unreduced state in the reduced layer, $N_{unred}$, and that of the unreduced state in the substrate, $N_{sub}$. The intensities of photoelectrons from the reduced states, $I^M_{red}$, are proportional to their fraction, $N_{red}$. The details of these equations are described in elsewhere [7].

$$I^M_{unred} = K \cdot \eta_M \cdot (N_{unred} + L \cdot N_{sub})$$

$$I^M_{red} = K \cdot \eta_M \cdot N_{red}$$

$$L = \frac{\lambda_{sub}}{\lambda_{red}} \cdot \frac{\exp(-\dfrac{d_{red}}{\lambda_{sub} \cdot \sin\theta})}{1 - \exp(-\dfrac{d_{red}}{\lambda_{red} \cdot \sin\theta})}$$

$$K \equiv K_C \cdot \lambda_{red} \cdot \sin\theta \cdot \left(1 - \exp(-\dfrac{d_{red}}{\lambda_{red} \cdot \sin\theta})\right)$$

$$(5)$$

*Journal of Surface Analysis Vol.13  No. 1 (2006)  pp. 14 - 18*
*Special Issue for Recent Development of Oxide Surface Analysis*
*S. Hashimoto  et. al.  Formulation for XPS Spectral Change of oxides by Ar Ion Bombardment: ...*

Here, $\eta_M$ is the relative sensitive factor of the metallic element (dimensionless), the attenuation lengths in the reduced layer and the substrate are $\lambda_{red}$ and $\lambda_{sub}$ (dimension: m), $\theta$ is the take-off angle from a sample surface (dimension: degree), the homogeneous reduced layer with the thickness is $d_{red}$ (dimension: nm), and $K_C$ is constant.

L (dimensionless) can be understood as the thickness of the unreduced substrate that contributes to the intensity, defining the thickness of the reduced layer as a unit. Therefore, L is positive or zero. Especially, L becomes zero when the information depth of the photoelectron is sufficiently smaller than the thickness of the reduced layer. This total thickness that contributes to the intensity of the photoelectrons from the unreduced state, becomes L+1. The total thickness is defined as effective information depth (dimensionless), $\Lambda \equiv L + 1$.

### 3. Experimental

An anodic oxidized $Ta_2O_5$ thin film on Tantalum plate was used as specimen for the XPS analysis during ion bombardment. The thickness of the $Ta_2O_5$ thin film was 100 nm. The $Ta_2O_5$ thin film was sputtered with Ar ions with acceleration voltage of 2 kV in a hemispherical XPS spectrometer (SSX 100, SSI). The incident angle of Ar ions to the sample surface was 35°.

Monochromatized Al Kα was irradiated to the sample. Ta 4f, O1s and C 1s XPS spectra were measured. Electrons were sprayed in order to compensate the charging. Energy scale of the XPS spectra was corrected using the binding energy of adventitious carbon (C 1s = 284.6 eV).

### 4. Results and discussion
#### 4.1 Change of Ta 4f XPS spectra by ion sputtering

Fig. 1 shows changes of the Ta 4f XPS spectra from $Ta_2O_5$ during Ar ion bombardment with the acceleration voltage of 2 kV as a function of sputtering time. The result is very close to the results reported by Hofmann et. al. [5]. They attributed the additional components to $Ta^{5+}$, $Ta^{4+}$, $Ta^{2+}$, and $Ta^0$ appear after ion sputtering. The spectrum at sputtering time of 200 min, which is fitted to four components of $Ta^{5+}$, $Ta^{4+}$, $Ta^{2+}$, and $Ta^0$ is shown in Fig.2. The depth profile of four states is showed in Fig. 3.

The intensity of the original state ($Ta^{5+}$) decreases just after initial stage of ion sputtering, and it saturates after a long sputtering time. The intensity of the $Ta^{4+}$ state becomes maximal, and it becomes constant after about 15 min. The intensity of the $Ta^{2+}$ state increase just after the $Ta^{4+}$ state increased, and it saturates. The intensity of the $Ta^0$ state increase after the other states increased, and it saturated.

#### 4.2 Comparison between experimental result and calculation

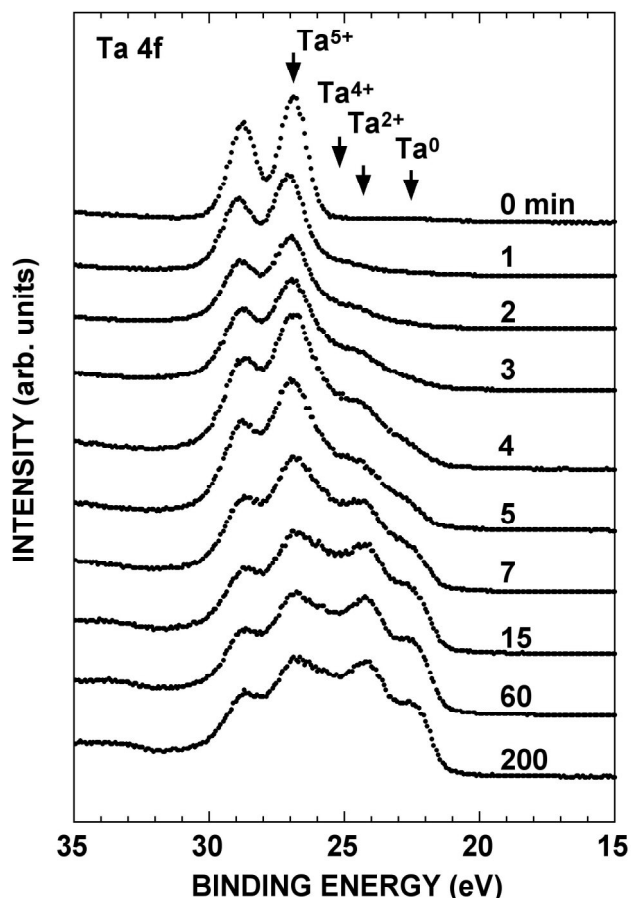Figure 4 shows the fraction of these four states ($Ta^{5+}$,



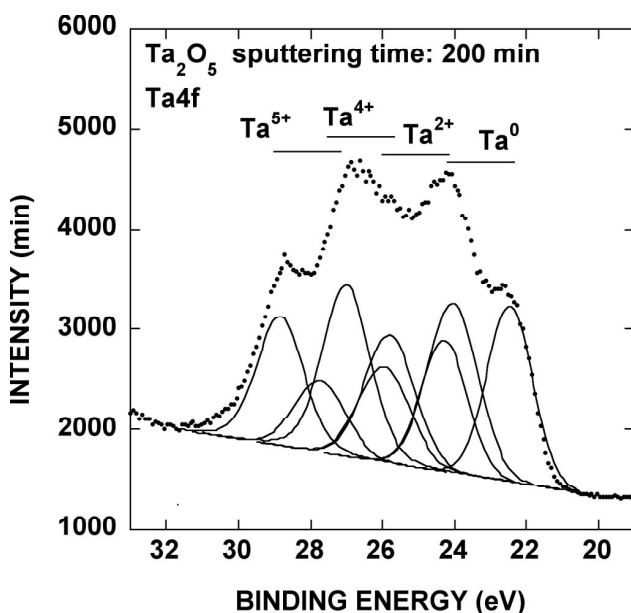Fig.1 Ta 4f XPS spectra of $Ta_2O_5$ as a function of Ar ion sputtering time. Acceleration voltage of Ar ion is 2 kV.



Fig.2 Peak fitted Ta 4f XPS spectra of $Ta_2O_5$. Sputtering time was 200 min. The spectrum was fitted, by supposing that 4 components ($Ta^{5+}$, $Ta^{4+}$, $Ta^{2+}$, and $Ta^0$) which is appeared after sputtering.

*Journal of Surface Analysis Vol.13 No. 1 (2006) pp. 14 - 18*
*Special Issue for Recent Development of Oxide Surface Analysis*
*S. Hashimoto et. al. Formulation for XPS Spectral Change of oxides by Ar Ion Bombardment: ...*

$Ta^{4+}$, $Ta^{2+}$, and $Ta^{0}$) as a function of sputtering. The circles represent this experimental result. The fraction is normalized as one.

Supposing that four states exist in the case of sputtering of $Ta_2O_5$, eq. (2) and (3) have four solutions ($N_1(0)= 1, N_2(0)= N_3(0)= N_4(0)= 0$ for 1: $Ta^{5+}$, 2: $Ta^{4+}$, 3: $Ta^{2+}$, 4: $Ta^{0}$), which contain three reduction coefficients ($\sigma_1$, $\sigma_2$, and $\sigma_3$).

Then, eqs.(5) become eqs. (6).

$$I^M_1 = K \cdot \eta_M \cdot (N_1(t) + (L - 1) \cdot N_1^{0})$$
$$I^M_i = K \cdot \eta_M \cdot N_i(t) \qquad \text{for } i = 2, 3, 4 \quad (6)$$

Here, effective reduction coefficients ( $\sigma_j^{eff} \equiv \dfrac{\sigma_j \cdot i}{N_{Tot} \cdot e}$ : $j$ =1, 2, 3) and an effective sputtering yield ( $S^{eff} \equiv \dfrac{S \cdot i}{N_{Tot} \cdot e}$ )

are used instead of the absolute reduction coefficients and the sputtering yield as the fitting parameters, because it is difficult to decide to the precise values of the current.

Fitting using the parameters of three effective coefficients, effective sputtering yield, and information depth were performed to the experimental results shown in Fig. 4. The calculated results are also displayed using lines.

Present formulation is based on reaction equations which contain three reduction processes (from $Ta^{5+}$ to $Ta^{4+}$, $Ta^{4+}$ to $Ta^{2+}$, and $Ta^{2+}$ to $Ta^{0}$) and sputtering effects. Using five fitting parameters (three reduction coefficients, sputtering yield, and information depth), the present formula was fitted to the experimental results. The fitting results agree satisfactorily with the experimental results.
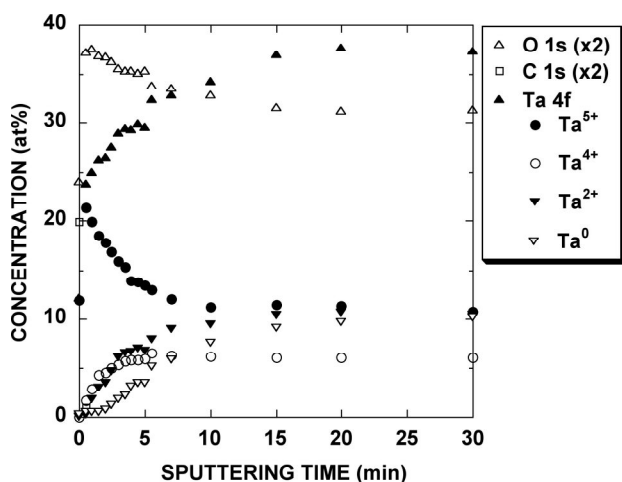
The obtained reduction coefficients were $\sigma_1^{eff} \equiv \dfrac{\sigma_1 \cdot i}{N_{Tot} \cdot e} =$ 0.37, $\sigma_2^{eff} \equiv \dfrac{\sigma_2 \cdot i}{N_{Tot} \cdot e} = 0.609$, $\sigma_3^{eff} = \dfrac{\sigma_2 \cdot i}{N_{Tot} \cdot e} = 0.251$,

respectively. It means that the reduction from $Ta^{4+}$ to $Ta^{2+}$ is faster than that from $Ta^{5+}$ to $Ta^{5+}$ or from $Ta^{2+}$ to $Ta^{0}$. Namely, the observed amount of $Ta^{4+}$ is relatively smaller than that of other states, after the change by ion bombardment are saturated. The reduction coefficients of $Ta_2O_5$ are the values in the same order, although $s_1$ (1.527) is ten times of $s_2$ (0.155) for $TiO_2$ [7]. It explains that relatively intense $Ta^{5+}$ state as the initial state are seen in the case of $Ta_2O_5$, although the reduced states ($Ti^{3+}$, and $Ti^{2+}$) are strong in the case of $TiO_2$. This results means that the formulation, which described the XPS spectral change of $TiO_2$ by ion bombardment, can be also applied to the change of $Ta_2O_5$. This formulation can determine the surface composition of an oxide changed by ion bombardment, if the bulk composition of the oxide, the correct reduction coefficients, and the sputtering yield are given. The surface composition after ion bombardment will be also predicted for an oxide which is composed by the different stoichiometric sub-oxides, because each change of such sub-oxide is calculated independently.

Furthermore, the present formulation will be able to expand to the compounds in which the larger numbers of reduced state appears as reported in ref. 8, by the modification of the equations (3).
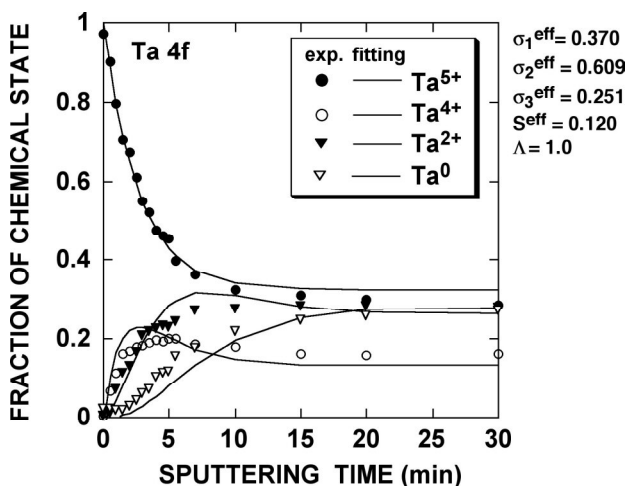


Fig.3 Surface concentration of Ta 4f, O 1s, and C 1s for $Ta_2O_5$ as a function of sputtering time. Four states ($Ta^{5+}$, $Ta^{4+}$, $Ta^{2+}$, and $Ta^{0}$) in Ta 4f after peak fitting are also displayed.

Fig. 4 Fraction of $Ta^{5+}$, $Ta^{4+}$, $Ta^{2+}$, and $Ta^{0}$ states in Ta 4f XPS spectra of $Ta_2O_5$ as a function of sputtering time. Circles represent experimental data and lines represent fitted results using present formulation.

*Journal of Surface Analysis Vol.13 No. 1 (2006) pp. 14 - 18*
*Special Issue for Recent Development of Oxide Surface Analysis*
*S. Hashimoto et. al. Formulation for XPS Spectral Change of oxides by Ar Ion Bombardment: ...*

## 5. Conclusion

It is difficult to determine the precise chemical state of the oxides by the change of XPS spectra after ion bombardment. A formulation, which had been proposed in order to explain the change of XPS spectra for $TiO_2$ as a function of ion sputtering time, was modified in order to explain that for $Ta_2O_5$.

The change of Ta XPS spectra for $Ta_2O_5$ was measured during Ar ion sputtering with 2 kV acceleration voltage of Ar ion bombardment. Components of $Ta^{4+}$, $Ta^{2+}$, and $Ta^0$ as reduced states have appeared in addition to the $Ta^{5+}$ state after ion bombardment of 2 kV.

Present formulation is based on reaction equations which contain three reduction processes (from $Ta^{5+}$ to $Ta^{4+}$, $Ta^{4+}$ to $Ta^{2+}$, and $Ta^{2+}$ to $Ta^0$) and sputtering effects. Using five fitting parameters (three reduction coefficients, sputtering yield, and information depth), the present formula was fitted to the experimental results. The fitting results agree satisfactorily with the experimental results.

This formulation, which described the XPS spectral change of $TiO_2$ by ion bombardment, can be also applied to the change of $Ta_2O_5$. This formulation can predict that surface composition of an oxide that is changed by ion bombardment, if the bulk composition of the oxide, the correct reduction coefficients, and the sputtering yield are given.

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