Alternation of Ti 2p XPS Spectrum for TiO_2 by Ar Ion Bombardment

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Angle resolved XPS measurements were performed for a reduced TiO_2 single crystal after Ar ion sputtering with 500 V in order to examine the depth profile of the reduced states. Comparing this angle resolved XPS measurement with the calculation, the component of Ti^{2+} has a gaussian like depth distribution. The component of Ti^{3+} is a localized near surface and smoothly distributed inner layer. Ar ion bombardment with low angle incidence was performed in order to decrease the thickness of the reduced layer. The intensities of the reduced states decreased with lowering incident angle of Ar ion. Moreover, ion bombardment with the low angle incidence has revealed that most of the reduced states are decreased and the intensities of the undamaged Ti^{4+} components are increased. These results prove that suitable conditions for the Ar ion sputtering will give a correct depth profile of the chemical states for the compounds which are altered by the ion bombardment.

1. Introduction

Ar ion sputtering alters chemical states and composition of some compounds [1-5]. For example, the oxides (TiO_2, NiO, Ta_2O_5, CuO etc.) are reduced by ion bombardment and extra components appear in feature of an original XPS spectrum. Many transition metal oxides reduced by the ion bombardment are used for a lot of applications; electronic or magnetic devices, displays, catalysts, sensors, anti-corrosion coatings and so on. The alternation hinders the determination of chemical state in the depth profiling.

We reported that amounts of the reduced state (Ti^{2+} and Ti^{3+}) in TiO_2 by the Ar ion sputtering decreased with lowering acceleration voltage [6]. Moreover, preferential sputtering for the implanted ion with lower incidence angle is milder than that with higher incidence angle [7]. However, the details of the ion bombardment with low energy or low angle incidence are not known.

Therefore, angle resolved XPS measurements were performed for a TiO_2 single crystal after Ar ion sputtering in order to examine the depth profile of the reduced state. Ar ion bombardment with low incidence angle was performed in order to decrease the thickness of the reduced layer.

2. Experimental

A TiO_2 (100) single crystal (Furuuchi Chemical Corp.) was used as a specimen for the XPS analysis during ion bombardment. The TiO_2 single crystals were sputtered with Ar ions with acceleration voltages of 500 V, 1 kV and 2 kV, and the spectra were obtained using two hemispherical XPS spectrometers.

XPS spectra were measured with monochromatized Al Kα irradiation. Ti 2p, 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) or oxygen of TiO_2 (O 1s = 529.9 eV [8]) in the case of no adventitious carbon [2].

Angle resolved measurement was performed for TiO_2 sputtered by Ar ions of 500 V with 36° incidence using a PHI-5800 (PHI) spectrometer. Ar ions were 5° bent in order to avoid the sputtering by fast neutral atoms or multiply charged ions. Take-off angle of photoelectrons from the sample surface was changed between 6 and 80°. Sputtering of 1 kV acceleration voltage with low angle incidence was carried out in an SSX-100 (SSI) spectrometer. The incident angle of Ar ions to the sample was 10 and 35°. The sputtering with the low-angle incidence was performed for both of the as-received TiO_2 and reduced TiO_2 by sputtering with 2 kV.

Projected ranges of Ar ions were calculated using Monte Calro simulation using TRIM binary collision code [9] (SRIM-1996 a freeware by IBM).

3. Results and discussion

3.1 Alternation of Ti 2p XPS spectra by ion sputtering

Fig. 1 shows changes of the Ti 2p XPS spectra from TiO_2 during Ar ion bombardment

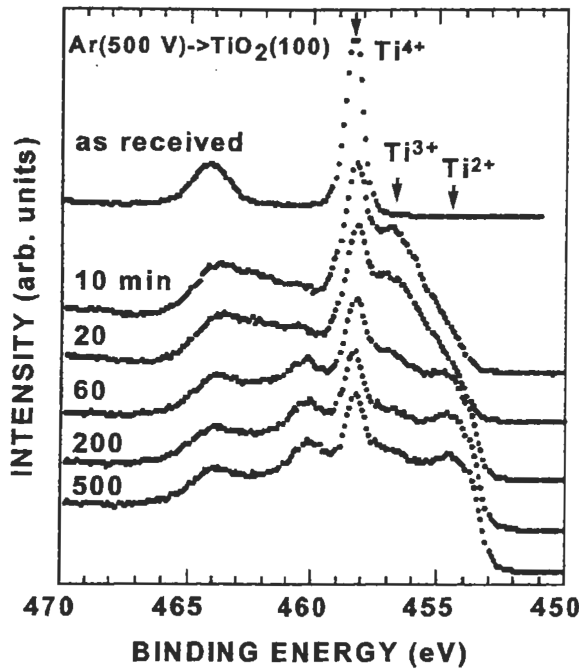

Fig. 1 Ti 2p XPS spectra of TiO_2 single crystal as a function of Ar ion sputtering time. Acceleration voltage of Ar ion is 500 V. Take-off angle from sample surface was 80°.

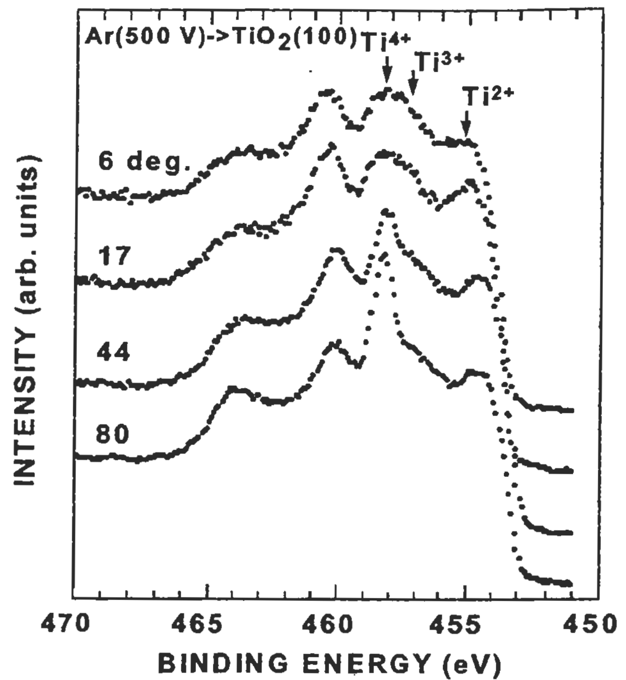

Fig. 2 Ti 2p XPS spectra of TiO_2 sputtered by Ar ion with acceleration voltage of 500 V as a function of take-off angle from sample surface.

with the acceleration voltage of 500 V as a function of sputtering time. Components for Ti^{3+} and Ti^{2+} as the reduced state appear in the XPS spectrum. The two states should be considered as $2\pm\delta$ and $3\pm\delta$ as shown in Ref. 6.

The Ti^{4+} component is still observed in TiO_2 after the intensities of the reduced states are saturated. The results suggest that the reduced state exists near the surface and the thickness is close to the information depth of photoelectrons.

3.2 Angle resolved XPS spectra of reduced states

The angle resolved measurement was performed for the sputtered TiO_2 after the surface chemical state becomes constant under the condition of the acceleration voltage of 500 V. The Ti 2p XPS spectra as a function of the take-off angle are shown in Fig. 2. The intensity ratio of the reduced state to the unchanged state (Ti^{3+} / Ti^{4+} or Ti^{2+} / Ti^{4+}) as a function of the take-off angle is shown in Fig. 3. The ratio of Ti^{3+} / Ti^{4+} monotonically decreases with increasing take-off angle. On the other hand, the ratio of Ti^{2+} / Ti^{4+} has a maximum at around 25°. The component of Ti^{2+} at the high take-off angle is more significant than that of Ti^{3+} and the Ti^{3+} states become intense at low take-off angle. These results suggest that the Ti^{2+} states exist at the deeper area than Ti^{3+}.

The intensity ratio (I_{TiOx}/I_{TiO_2}) of the reduced state (TiO_x) relative to the unchanged state (TiO_2) is given by eq. (1) using concentration of the reduced state, C(z), take-off angle from the surface, θ and information depth, λ_M [10].

$$I = \frac{\int_0^\infty C_{TiO_x}(z) \cdot \exp(-z / \lambda_{TiO_x} \sin\theta) \cdot dz}{\int_0^\infty (1 - C_{TiO_2}(z)) \cdot \exp(-z / \lambda_{TiO_2} \sin\theta) \cdot dz} \quad (1)$$

If the reduced state exists as one uniform layer and the information depth of TiO_x is equal to that of TiO_2, a logalism of the intensity ratio, $\ln(I_{TiOx}/I_{TiO2}+1)$ is proportional to reciprocal sine of the take-off angle, $\mathrm{cosec}\theta$.

Here, we consider 4 models for the depth profiles of the reduced layer. The maximum of C(z) is set unity using C_n as a normalizing constant.

(i) A uniform layer of thickness, a.:

$$C(z) = C_1 \ (C_1=1) \quad \text{for } 0 \le z \le a$$
$$C(z) = 0 \quad \text{for } a \le z \quad (2)$$

(ii) A gaussian distribution using projection range, Rp and straggle, ΔRp. The depth profile of the implanted ions has a gaussian distribution as predicted by LSS theory [11, 12].:

$$C(z) = C_2 \cdot \exp\left[(z - Rp)^2 / 2\Delta Rp^2\right] \quad (3)$$

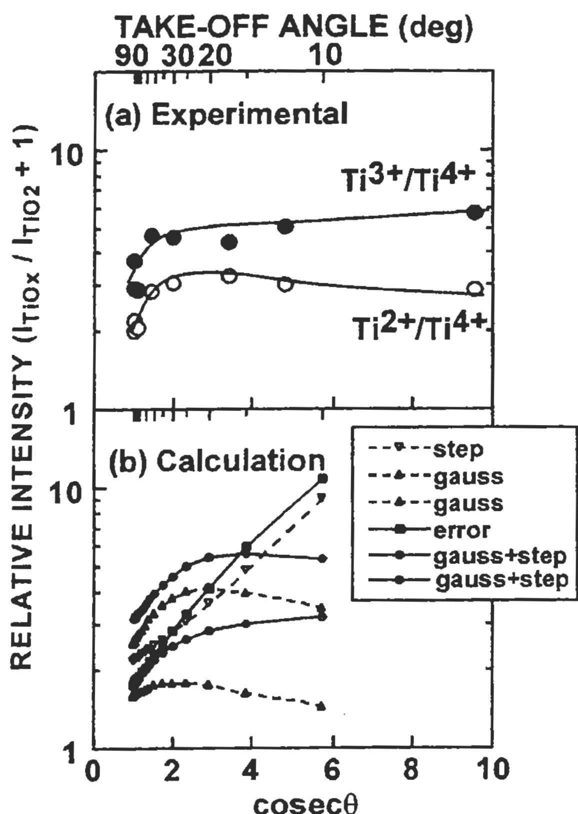

Fig. 3 Intensity ratios of Ti^{2+} and Ti^{3+} relative to Ti^{4+} state in Ar ion sputtered TiO_2 as a function of take-off angle of photoelectrons. ($I_{TiOx}/I_{TiO2}+1$) and cosecθ are expressed in y and x axis, respectively.
(a) Experiential results for Ar ion bombardment with acceleration voltage of 500 V.
(b) Calculations for models : step function (▽: a = 0.8.nm), gaussian function (Δ : Rp = 1.17 nm, ΔRp = 0.52 nm, ▲: Rp = 1.17 nm, ΔRp = 1.04 nm), error function(■: S = 0.2, Rp = 1.17 nm, ΔRp = 0.52 nm), modified gaussian (⊕: a=0.2nm, Rp = 1.17 nm, ΔRp = 0.52 nm, ●: a=0.1 nm, Rp = 1.17 nm, ΔRp = 1.04 nm).

(iii) An error function distribution with density of TiO_2, d, Ar dose, D (= 5.4×10^{16}) and sputtering yield, S (= 0.2) [7]. Considering the sputtering effect, the distribution of the implanted ions is modified to the error function [7, 12].

$$C(z) = C_3 \int_0^{\frac{d \cdot D}{S}} \exp\left[\frac{(z - Rp - l)^2}{2\Delta Rp^2}\right] \cdot dl \qquad (4)$$

(iv) A modified gaussian distribution (step at outer layer and gaussian at inner layer). The damage by the implantation exists at the outer layer of the projected range in the case of high energy implantation [13]. :

$$C(z) = 1 \qquad \text{for } 0 \leq z \leq a$$

$$C(z) = C_4 \cdot \exp\left[(z - Rp)^2 / 2\Delta Rp^2\right] \quad \text{for } a \leq z \quad (5)$$

Assuming that the information depth, 2.16 nm is an inelastic mean free path [14] and the content of the reduced state is 2.5, the angular dependence of the intensity of Ti 2p XPS line expected from these models was calculated, base on the calculated ion range for the normal incidence (Rp = 1.17 nm, ΔRp = 0.52 nm). The calculations are also shown in Fig. 3. The experimental angular dependence of Ti^{2+} is close to that derived from the gaussian function. This result suggests that the alternation is greatly related the ion implantation. The observed angular dependence of Ti^{3+} displays a monotonical but non-linear decay. The result means that the distribution is different from both of the simple layer model and the gaussian distribution. The measured angular dependence is close to error function or modified gaussian distribution. Thus, the present XPS results suggest that the reduced Ti^{3+} is strongly localized near the surface and is slowly distributed into the depth direction.

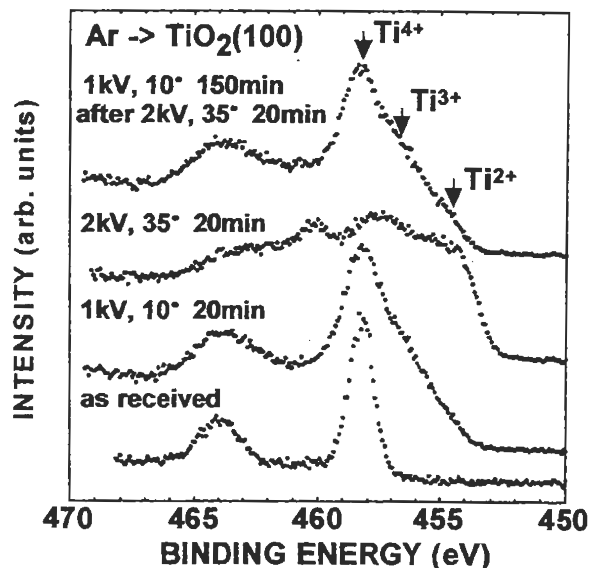

Fig. 4 Ti 2p XPS spectra of sputtered TiO_2 single crystal. As received TiO_2, ion sputtered TiO_2 (1 kV and 10° incidence), ion sputtered TiO_2 (2 kV and 35° incidence) and ion sputtered TiO_2 (1 kV and 10° incidence) after surface was reduced by sputtering (2 kV and 35° incidence).

3.3 Low angle incident ion bombardment

Fig. 4 shows the Ti 2p XPS spectra of TiO_2 which is sputtered with various conditions, namely 1kV and low-angle incidence, 2 kV and high-angle incidence, and 1kV and low-angle incidence for the reduced TiO_2. All spectra were measured after the alternation became constant.

The Ti^{4+} state of TiO_2 is observed as a major component in the case of Ar ion sputtering

Table 1 Calculated projected range (Rp) and straggle (ΔRp) of Ar implanted into TiO_2. Calculation is carried out using Monte Calro simulation (TRIM).

Acceleration voltage (V)	100	500	1000		2000
incident angle (deg)	35	35	10	35	35
Rp (nm)	0.34	0.76	0.73	1.12	1.68
ΔRp (nm)	0.19	0. 44	0.50	0.65	0.98

with 1 kV and the low angle incidence, although the intensities of Ti^{2+} and Ti^{3+} components as the reduced state are quite strong for the sputtering with 2 kV and high angle incidence. The calculated projection range and straggle for the ion implanted Ar is listed in Table 1. The projection range for 10° incidence of 1 kV acceleration is smaller than that for the 35° incidence of 500 V acceleration. The less reduction for the low angle incidence can be attributed to the smaller projection range of the implanted Ar ions.

The low angle incident Ar ions of 1 kV were irradiated to the altered TiO_2 by 2 kV sputtering with high angle incidence. The Ti^{2+} and Ti^{3+} components as the reduced state decrease and the Ti^{4+} component as the undamaged substrate increase. The feature is same as the results of the sputtering for as received TiO_2 with the same condition.

The results reveal that the layer reduced by the bombardment of 2 kV is removed by the low angle ion irradiation with the small projection range, and that the thickness of the reduced layer effectively is decreased.

The present results prove that with adequate conditions of the ion sputtering, the projection range becomes much smaller than the information depth of photoelectron thus giving a better depth profile of the chemical states for the compounds altered by the ion bombardment.

4. Conclusion

The angle resolved XPS measurements were performed for a TiO_2 single crystal, which was sputtered by Ar ion with 500 V, in order to examine the distribution of the reduced state. The results suggest that the thickness of the reduced layer is comparative to the information depth of Ti 2p photoelectrons. Comparing the experimental results with the calculation, the component of the Ti^{2+} state has a gaussian-like depth distribution and the component of the Ti^{3+} state is localized near surface and slowly distributed into inner layer.

Moreover, The intensities of the reduced states (Ti^{2+} and Ti^{3+}) by Ar ion sputtering of 1 kV decrease with lowering incident angle. The low angle incident ion bombardment was performed to the sputtered TiO_2 with 2 kV acceleration. The reduced states are decreased and the undamaged Ti^{4+} components are increased. The results prove that suitable conditions for the Ar ion sputtering will give a better depth profile of the compounds altered by the ion bombardment.

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References

[1] H. M. Nagiub and R. Kelly, *Rad. Eff.*, **25**, 1 (1975).
[2] S. Hashimoto, K. Hirokawa, Y. Fukuda, K. Suzuki, T. Suzuki, N. Usuki, N. Gennai, S. Yoshida, M .Koda, H. Sezaki, H. Horie, A. Tanaka and T. Ohtsubo, *Surf. Interface Anal.*, **18**, 799 (1992).
[3] K. S. Kim, W. E. Battinger, J. W. Amy and N. Winograd, *J. Electron Spectrosc. Relat. Phenom.*, **5**, 351 (1974).
[4] R. Kelly, *Surf. Sci.*, **100**, 85 (1980).
[5] U. Bardy, K. Tamura, M. Owari and Y. Nihei, *Appl. Surf. Sci.*, **32**, 352 (1988).
[6] S. Hashimoto and A. Tanaka, *J. Surf. Anal.*, **8**, 192 (2001).
[7] E. Taglauer, *Appl. Surf. Sci.*, **13**, 80 (1982).
[8] C. D. Wagner, D. A. Zatko and R. H. Raymond, *Anal. Chem.*, **52**, 1445 (1980).
[9] J. F. Ziegler, J. P. Bierzack and U. Littmark, in *The Stopping and Range of Ions in Solids*, Pergamon, New York, (1985).
[10] in *Practical Surface Analysis*, ed. by D. Briggs and M. P. Seah, Wiley, Chichester (1983).
[11] J. Lindhart, M. Scharff and H. E. Schiott, *K. Dan. Vidensk. Slsk. Mat. -Fys. Medd.*, **33**, 1 (1963).
[12] H. Ryssel, in *Ion Implantation Techniques*, ed. by H. Ryssel and H. Glawischnig, Springer-Verlag, Berlin (1982) p.177.
[13] T. Soeda, S. Matsumura, C. Kinoshita and N. Zaluzec, J. Nucl. Mater., **283-287**, 952 (2000).
[14] S. Tanuma, C. J. Powell and D. R. Penn, *J. Vac Sci. Technol.*, **A8**, 2213 (1990).