Change of Ti2p XPS spectrum for Titanium Oxide by Ar Ion Bombardment

Satoshi Hashimoto[1*], Aki Murata[1], Tsuguo Sakurada[1] and Akihiro Tanaka[2]

[1] *Kokan Keisoku K.K., 1-1 Minamiwatarida, Kawasaki 210-0855, Japan*
[2] *ULVAC-PHI, 370 Enzo, Chigasaki 253-0084, Japan*

e-mail : sahasimo@kks.keihin.nkk.co.jp

(Received: Nov. 17, 2002; Accepted: Jan. 20, 2003)

Change of Ti 2p XPS spectra for TiO_2 single crystal was measured during Ar ion sputtering. Acceleration voltage of Ar ion bombardment was from 10 V to 2 kV. Components of Ti^{2+} and Ti^{3+} as reduced states have appeared in addition to the Ti^{4+} state after the ion bombardment of 2 kV However, although small amount of Ti^{3+} has been observed in the case of 10 V bombardment, Ti^{2+} component have not appeared. The intensities of the reduced states which have appeared in each acceleration voltage have reached a constant after a long sputtering. The saturation shows that the surface reaches an equilibrium state between the sputtered atoms and implanted ions. Moreover, the intensities of the reduced states have increased with elevating accelerating voltage of the primary ions. The intensities of the reduced states by Ar ion bombardment with 1 kV acceleration voltage decreased with lowering incident angle. The ion bombardment with the low angle incidence decreased the amount of the reduced states by 2 kV sputtering. These present results emphasize that suitable conditions for the Ar ion sputtering will give a better depth profile of the chemical states for the compounds which are changed by the ion bombardment.

1. Introduction

Ar ion bombardment changes chemical state and composition of some compounds [1-6]. For example, oxides (TiO_2, NiO etc.) are reduced by ion bombardment and extra components appear in addition to an original XPS spectrum. Various transition metallic oxides reduced by the ion bombardment are important materials for a lot of applications; electronic devices, displays, catalyst, sensors, anti-corrosion coatings and so on. Therefore, it is difficult to determine the precise chemical states of the oxides.

On the other hand, it is reported that the ion sputtering with the lower energy improves depth resolution [7]. Preferential sputtering for the implanted ion with lower incidence angle is milder than that with higher incidence angle incidence [8]. However, the details of the ion bombardment with low energy or low angle incidence are not known.

In this paper, the XPS spectra of TiO_2 were measured during the Ar ion sputtering with the condition of various acceleration voltage and angle in order to estimate the change of the chemical state by the ion bombardment.

2. Experimental

A TiO_2 (100) single crystal (Furuuchi Chemical Corp.) was used as specimen for the XPS analysis during ion bombardment. The TiO_2 single crystals were sputtered with Ar ions with acceleration voltage of 10, 100, 500 V, 1 and 2 kV in two hemispherical XPS spectrometers (PHI-5800 / Φ, SSX100 / SSI).

Ti 2p, O1s and C 1s XPS spectra were measured with monochromatized Al Kα irradiation. Electrons were sprayed in order to compensate the charging. Energy scale was corrected using the binding energy of adventitious carbon (C 1s = 284.6 eV).

The Ar ion bombardment of 10, 100, 500 V and 2 kV acceleration was performed in the PHI-5800 spectrometer. Primary ions were 5° bent in the primary ion gun column in order to avoid the sputtering by fast neutral atoms or multiple charged ions. Incident angle of Ar ions was 36° from the sample surface. The ion bombardments with 10 V and 2 kV acceleration were performed on the as-received sample. The sputtering with 100 V was performed after the surface became constant by 10 V sputtering, then 500 V sputtering was performed. The base pressure was less than $4x10^{-8}$ Pa.

Sputtering of 1 kV acceleration with low angle incidence was performed for both of the as-received TiO_2 and sputtered TiO_2 with 2 kV in the SSX-100 instrument. The incident angle of Ar ions to the sample was 10 and 35°.

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

This paper was presented at the 4th KVS-SASJ Int'l Symposium in Hiroshima, Japan, November 18-19, 2002.

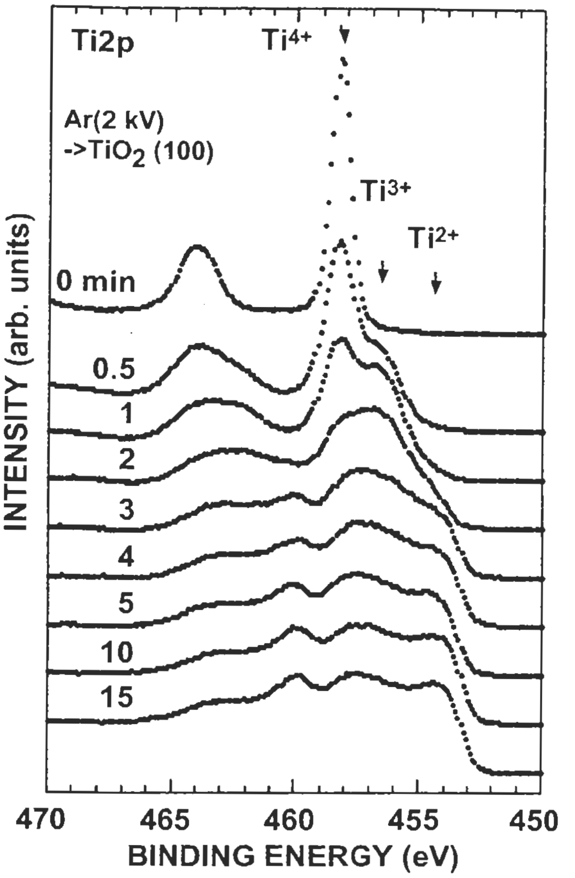

Fig. 1 Ti 2p XPS spectra of TiO_2 single crystal as a function of sputtering time. Acceleration voltage of Ar ion is 2 kV.

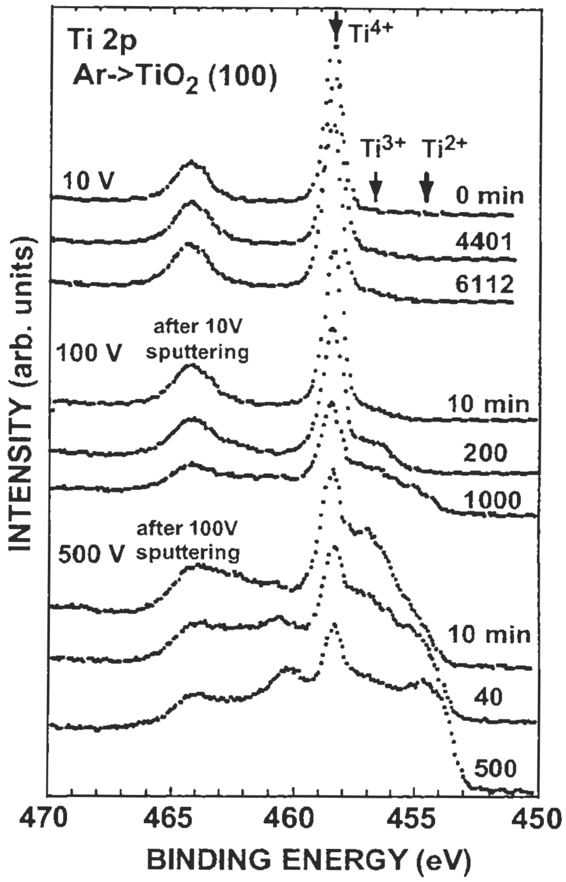

Fig. 2 Ti 2p XPS spectra of TiO_2 single crystal as a function of sputtering time. Ar ion sputtering with 10 V, 100 V and 500 V is performed in this order. Sputtering time is displayed as passage from start of each sputtering.

3. Results and discussion

3.1 Change of Ti 2p XPS spectra by ion sputtering

The changes of the Ti 2p XPS spectra from the TiO_2 single crystal during Ar ion sputtering as a function of sputtering time for the acceleration voltage of 2 kV is shown in Fig. 1. The Ti 2p XPS spectra in the case of the acceleration voltage of 10, 100, and 500 V is shown in Fig. 2. Components at 456.6 eV and 454.4 eV appear in addition to the Ti^{4+} component observed in as received TiO_2. According to previous result [10], two components of 456.6 eV and 454.4 eV can attribute to Ti^{3+} and the Ti^{2+}, respectively. Moreover, lower valence states than 2+ were not observed. TiO_2, Ti_2O_3, Ti_5O_3, TiO Ti_2O, Ti_3O and other phases (Ti_4O_5, Ti_4O_7, Ti_5O_9) are reported in Ti-O system [11]. Most of the oxides are coordinated from TiO_6 octahedrons or TiO_4 tetrahedrons, and the coordination of the oxide is similar to the others. The structures of the oxides suggest that the chemical states which have appeared after sputtering are not always assigned to Ti_2O_3 or TiO. The Ti^{3+} and Ti^{2+} state should be understood as the $3 \pm \delta$ and $2 \pm \delta$ state.

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

Components of Ti^{3+} and Ti^{2+} as the reduced state appear in the XPS spectrum except the case of 10 V sputtering. Only Ti^{3+} component was observed for the 10 V sputtering.

The Ti^{4+} component is still observed in TiO_2 after the intensities of the reduced states are saturated. If the depth distribution of the reduced layer is same as that of the implanted ions, the profile can be calculated [12, 13]. The calculated ion range and straggling is listed in Table 1. The values are close to the calculated inelastic mean free path (2.16 nm) [14]. LLS theory with sputtering effect predicts that the distribution of implanted ions moves to the surface by the removal of the substrate by the sputtering. The calculation suggests that some reduced molecules are removed by the sputtering and that the reduced oxides

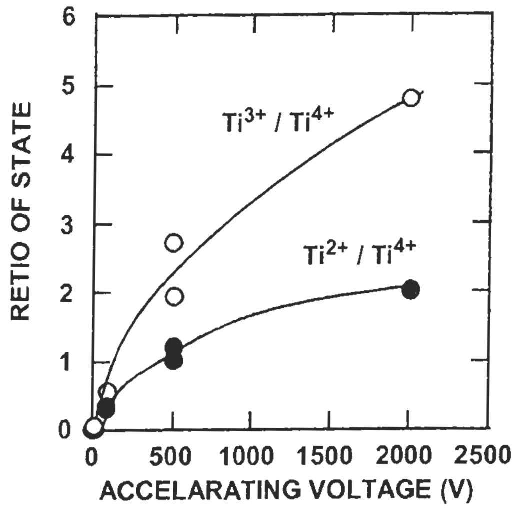

Fig. 3 Intensities of Ti^{3+} and Ti^{2+} state of sputtered TiO_2, that the surface reached a steady state, as a function of the acceleration voltage. The intensities of the states are normalized by that of Ti^{4+}.

and some of the TiO_2 beneath the reduced layer contribute the observed spectra.

Figure 3 shows the relationship between the intensities of the reduced state from TiO_2 and the acceleration voltage. The intensities of the reduced states are normalized by that of the Ti^{4+} state. The Ti^{3+} and Ti^{2+} state increases with elevating acceleration voltage in the whole range. The Ti^{2+} state is not observed at 10 V. The reduced state becomes a major state beyond 500V. These results suggest that the reduction from the Ti^{4+} state to the Ti^{3+} state can occur in a low energy bombardment but that a critical energy in the range between 10 and 100 V may exist for the reduction from the Ti^{3+} state to the Ti^{2+} state.

Moreover, the low energy ion sputtering can help to determine the chemical state of oxides which are reduced by the ion bombardment.

3.2 Low angle incident ion bombardment

Figure 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 until the change of the XPS spectra became constant.

The Ti^{4+} state of TiO_2 is observed as a major component in the case of Ar ion sputtering with 1kV 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. As 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.

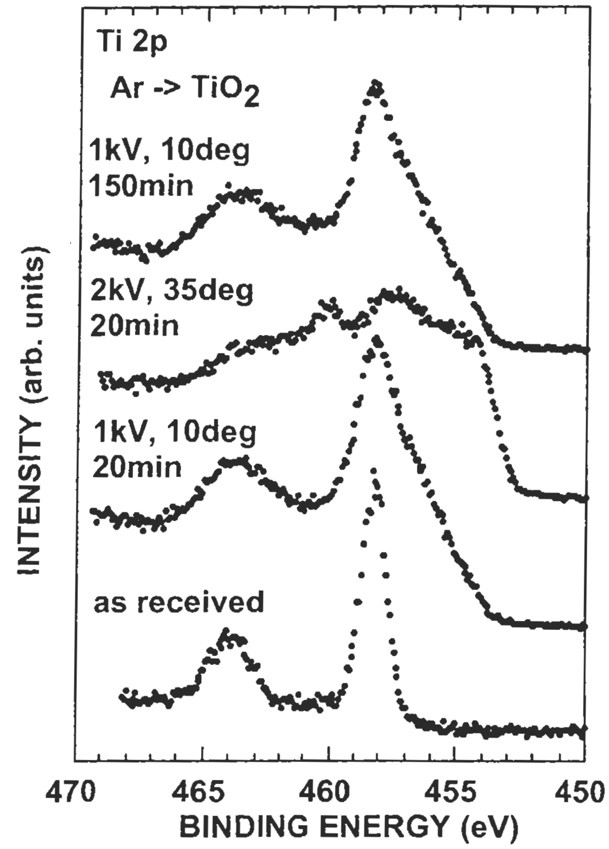

Fig. 4 Ti 2p XPS spectra of sputtered TiO_2 single crystal. As received TiO_2, ion sputtered TiO_2 (1 kV and 10° incidence), ion sputtered TiO_2 (2 kV and 35° incidence) and ion sputtered TiO_2 (1 kV and 10° incidence) after surface was reduced by sputtering (2 kV and 35° incidence).

The low angle incident Ar ions of 1 kV were irradiated to the reduced 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 from 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 bombardment with the small projection range, and that the thickness of the reduced layer effectively is decreased.

The present results show that suitable conditions of the ion sputtering, in which the projection range becomes much smaller than the information depth of photoelectron, will give a better depth profile of the chemical states for the compounds reduced by the ion sputtering.

4. Conclusion

The XPS spectra for a TiO_2 single crystal was measured during the Ar ion sputtering of 10 to 2 kV acceleration voltage in order to examine the effect of the ion energy and incident angle on the damage of such oxide by the sputtering.

The components of Ti^{2+} and Ti^{3+} as the reduced states have appeared in addition to the Ti^{4+} state after the ion bombardment except 10 V sputtering. The surface of TiO_2 reaches stable after Ar ion sputtering, because some reduced molecules are removed by the sputtering. A small amount of Ti^{3+} state is observed in the case of 10 V. The intensities of the reduced states are increased with elevating accelerating voltage of primary ion. The present results suggest that a critical voltage in the range between 10 and 100 V exists for the reduction of Ti^{2+} state from Ti^{3+} state.

The intensities of the reduced states (Ti^{2+} and Ti^{3+}) by Ar ion bombardment with 1 kV acceleration voltage 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.

These present results emphasize that suitable conditions for the Ar ion sputtering will give a better depth profile of the chemical states for the compounds which are changed by the ion bombardment.

Acknowledgement

We are grateful to Mr. K. Ohuchi for a part of XPS measurement.

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. and 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] K. Yoshihara, D. W, Moon, D. Fujita, K. J. Kim and K. Kajiwara, *Surf. Interface Anal.*, 20, 1061 (1993).

[8] E. Taglauer, *Appl. Surf. Sci.*, **13**, 80 (1982).

[9] J. F. Ziegler, J. P.Bierzack and U. Littmark, in *The Stopping and Range of Ions in Solids*, Pergamon, New York, (1985).

[10] R. Gouttebaron, D. Cornelissen, R. Snyders, J.P. Dauchot, M. Wautelet and M. Hecq, *Surf. Interface Anal.*, **30**, 527 (2000).

[11] P. Villards and C. D. Calvert, in *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*, American Society of Metals, Metals Park (1985).

[12] J. Lindhart, M. Scharff and H. E. Schiφtt, *K. Dan. Vidensk. Slsk. Mat. -Fys. Medd.*, **33**, 1 (1963).

[13] H. Ryssel, in *Ion Implantation Techniques* ed. by H. Ryssel and H. Glawischnig, Springer-Verlag, Berlin (1982) p.177.

[14] S. Tanuma, C. J. Powell and D. R. Penn, *J. Vac Sci. Technol.*, **A8**, 2213 (1990).