Paper

Auger Crater Edge Profiling by Water Droplet Impact

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The charged water droplets used in electrospray droplet impact (EDI) are extremely large cluster ions with masses of about a few 10^6 u. When a target is etched by EDI, the physical sputtering of the target does not take place to the recognizable extent. The etched surfaces of TiO_2 thin film on Si(100) by EDI were evaluated by AES crater edge profiling. We found that TiO_2 thin film do not suffer from de-oxygenation by EDI etching.

1. Introduction

Auger Electron Spectroscopy (AES) depth profiling is the most useful technique for observation of the cross sectional elemental distribution in micro-area analysis. AES depth profiling is usually coupled with Ar^+ ion sputtering in many instruments. The depth profiles are obtained by alternately recording specific peaks and removing material from the sample surface by Ar^+ ion beam sputtering. However, the Ar^+ ion beam sputtering induces the degradations and preferential sputtering of the samples. For reducing these degradations, the cluster ion projectiles are now being used in cluster-secondary ion mass spectrometry (SIMS). The ion sputtering by Ar_n^+ and C_{60} clusters guarantees the high sputtering rate, the smooth surface sputtering and low sample degradations [1,2]. Recently, a new ionization method, the electrospray droplet impact (EDI) ionization has been developed for matrix-free SIMS [3,4]. The projectiles used in EDI are extremely large water cluster ions with masses of about a few 10^6 u. The charged water droplets impact on a target, and molecular-level etching is realized without damaging the sample underneath the surface. In the related work, the SiO_2 on Si, poly ethylene terephthalate (PET), and InP samples etched by EDI were examined by XPS in detail. It was found that the etched surfaces by EDI were extremely smooth and no degradation and no preferential sputtering took place. This is a marked contrast to Ar^+ ion sputtering [5-7]. The occurrence of de-oxygenation for the metal oxide samples such as TiO_2 or Ta_2O_5 by Ar^+ ion sputtering was reported previously. The degradations of metal oxide samples induced by Ar^+ ion bombardment were also observed using X-ray photoelectron spectroscopy (XPS) [8]. In this paper, the surfaces of metal oxide sample etched by EDI were evaluated by using AES crater edge profiling. We examined whether de-oxygenation takes place or not for TiO_2 etched by EDI etching.

2. Experimental

AES crater edge profiling by EDI etching was performed by the two steps of etching and surface analysis. At the first step, the samples were etched in an orthogonal time-of-flight mass spectrometer (TOF-MASS) (JEOL: Accu-TOF) equipped with EDI gun as shown in Fig. 1. The charged water droplets formed by electrospraying 1M acetic acid aqueous solution at atmospheric pressure were sampled through an orifice with 400 μ m diameter into the first vacuum chamber, and transported into a quadruple ion guide. The charged water droplets after exiting the ion guide were accelerated by 10 kV, focused by the Einzel lens and impacted on the target [9].

The charged water droplet projectiles are the cluster ions with masses of about a few 10^6 u. The *m/z* estimated is in the range of 1×10^4–5×10^4. The cluster ions can be represented as $[(H_2O)_{90000}+100H]^{100+}$ with z=100. The kinetic energy of impacting projectile is ~10^6 eV for the acceleration potential of 10 kV. An energy per nucleon is about 0.6 eV/u. The impact angle is 60 degrees from the surface normal. The secondary ions formed by EDI were transported into a second quadruple ion guide and mass-analyzed by an orthogonal time-of-flight mass spectrometer [10].

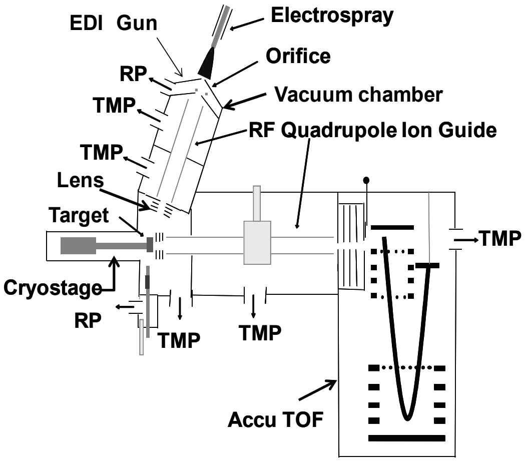

Fig. 1. Schematic diagram of the time-of-flight mass spectrometer equipped with an EDI Gun.

After etching by EDI, AES crater edge profiles were measured using a Scanning Auger Microscope (SAM) (JEOL: JAMP-7810) with the hemi-spherical energy analyzer. This energy analyzer is used to obtain the information on the Auger chemical shift between the oxide metal and metal [11]. In this experiment, AES spectra were measured with the energy resolution of 0.13 % to observe the changes in the line shapes. The electron beam conditions were an accelerating voltage of 10 kV and beam current 0.5 nA with beam diameter of 60 nm. At this beam conditions, the electron induced de-oxygenation for TiO_2 was not observed.

The measurements of the depth profiling by Ar^+ ion sputtering and crater edge profiling were performed using SAM with Ar ion gun. Auger crater edge profiles were obtained by Auger line scan analysis across the “crater edge” formed by the Ar^+ and EDI sputtering [12]. The evaluation of etched surface by EDI was carried out by comparing the surface etched by EDI with that by Ar^+ ion sputtering.

3. Results and Discussion

In this experiment, the sample of TiO_2 film deposited on Si(100) was prepared by the sputtering coating. The thickness of TiO_2 measured by the ellipsometer (SE800: SENTECH Instrument) was 30 nm. The experimental condition of Ar^+ ion sputtering was adjusted to suppress the de-oxygenation of TiO_2 deposited on Si as described in the following sections.

Figure 2 shows the TiO_2 Auger spectra for as-received and after 20, 40 and 60 s sputtering by the Ar^+ ion at 3 keV energy and incidence angle of 55 degrees from the surface normal. The sputter rate for 3keV Ar^+ ion was 10 nm/min for SiO_2. The as-received spectrum shows the double peaks of Ti-$L_3M_{23}M_{45}$ (408.9 and 417.7 eV). The Ti-$L_3M_{23}M_{45}$ (408.9 eV) peak is TiO_2 and Ti-$L_3M_{23}M_{45}$ (417.7eV) is metallic Ti. We estimated that the double peaks of Ti-$L_3M_{23}M_{45}$ with almost comparable intensity were TiO_2 in this experiment. “STD Ti” denotes the standard spectra of metallic Ti and shows the single peak of Ti-$L_3M_{23}M_{45}$ (417.7eV). After 20 s, 40 s and 60 s sputtering, the intensity of Ti-$L_3M_{23}M_{45}$ (408.9 eV) were decreased and changed to the single peak. Figure 2 clearly indicates that the ion induced de-oxygenation for TiO_2 takes place by the 3 keV Ar^+ ion bombardment.

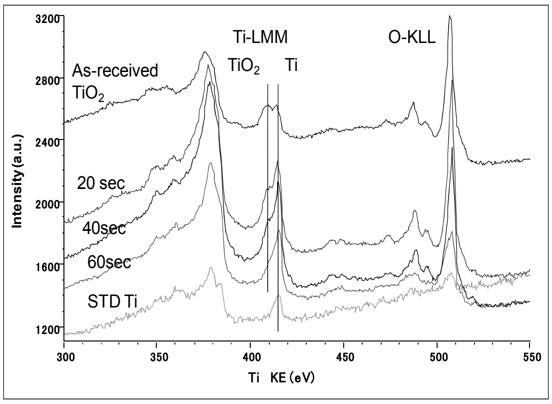

Fig. 2. TiO_2 Auger spectra of as-received and after 20, 40 and 60 s sputtering by the 3 keV Ar^+ ion. STD Ti is the standard spectra of metallic Ti.

Figure 3 shows the TiO_2 Auger spectra of as-received and those for 90 and 150 s sputtering by the 1 keV Ar^+ ion for the sample of TiO_2 on Si(100). The sputtering rate for 1 keV Ar^+ ion was 4 nm/min for SiO_2. After etching for 90 and 150 s, the intensity of Ti-$L_3M_{23}M_{45}$ (408.9 eV) were slightly decreased, and de-oxidized. In this experiment, we estimated Ti-$L_3M_{23}M_{45}$ double peaks with slightly different intensity were the almost TiO_2. The TiO_2 film was sputtered with slightly de-oxidization by 1 keV Ar^+ ion sputtering. These results indicated that the ion induced de-oxygenation of TiO_2 was highly depended on the energy of Ar^+ ion.

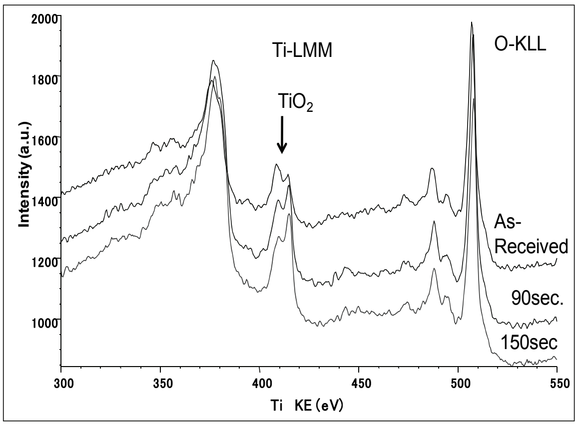

Fig. 3. TiO_2 Auger spectra of as-received and after 90 and 150 s sputtering by the 1 keV Ar^+ ion sputtering.

We selected 1 keV Ar^+ ion sputtering to decrease the ion induced de-oxygenation for the following depth profiling and crater edge profiling of TiO_2 on Si. The correlation between the depth profile and the crater edge profile of TiO_2 on Si etched by 1 keV Ar^+ ion was examined.

Figure 4 shows the depth profile of TiO_2 obtained by 1 keV Ar^+ ion sputtering. Figure 4 shows that the top surface of the sample was contaminated by carbon and oxygen. After the removal of contaminants, the layer structure of TiO_2 on Si substrate appeared.

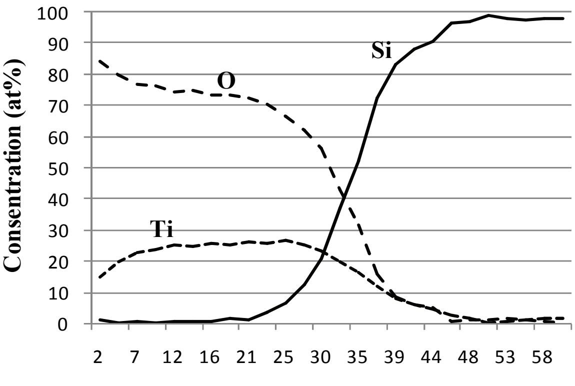

Fig. 4. Depth profile of TiO_2(30nm) on Si(100) etched by 1 keV Ar^+ ion.

Figure 5 shows the SEM image of the sputtered crater for the TiO_2 on Si after Ar^+ ion sputtering. Auger crater edge profile was obtained by measuring Auger spectra on the line across the crater edge formed by Ar^+ ion sputtering.

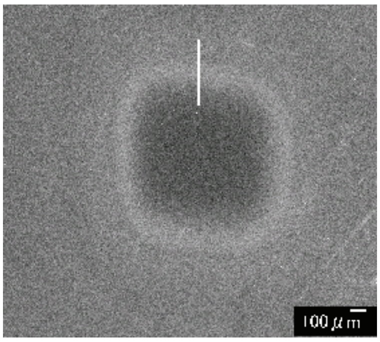

Fig. 5. SEM image of crater formed for TiO_2(30nm) on Si(100) etched by 1keV Ar^+ ion sputtering. White line is the position of Auger 26 multi-points analysis.

Figure 6 shows the AES crater edge profile of TiO_2 on Si, which was measured by Auger 26 multi-points analysis on the white line shown in Fig. 5. The horizontal axis of Fig. 6 is represented as the depth by estimating the thickness of TiO_2 as the distance from the top surface to the interface determined by the intensity of the Ti signal reaching 50% of its value from the plateau level.

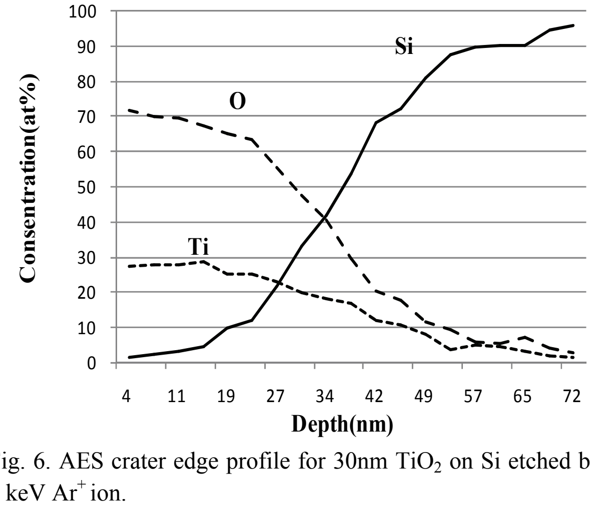

Fig. 6. AES crater edge profile for 30nm TiO_2 on Si etched by 1 keV Ar^+ ion.

By comparing Ar^+ ion sputtering depth profile with crater edge profile, the profiles of TiO_2 thin film and Si substrate are almost the same. At the top surface, the sample was contaminated for the Ar^+ ion etching depth profile. But, for the crater edge profile, the contamination was not observed at the top surface, because the wide area over the crater was cleaned or sputtered by the irradiation of the neutral or un-focused Ar ion.

We have already reported that the EDI is an extremely soft etching method and it can avoid the de-oxygenation for PET [5]. The etching process of TiO_2 thin film by EDI was monitored by the EDI-SIMS apparatus as shown in Fig. 1. The etched surfaces by EDI were evaluated by AES. The SEM image of TiO_2 on Si crater etched by EDI is shown in Fig. 7. The crater has an ellipse shape which is formed by the EDI projectiles of glancing incident angle with 60 degrees from the surface normal.

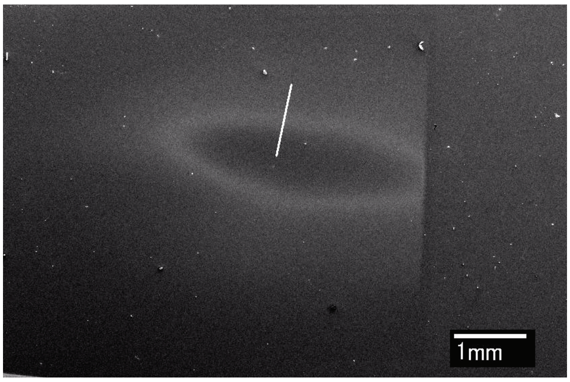

Fig. 7. SEM image of crater for TiO_2(30nm) on Si(100) etched by EDI. White line is the position of Auger 26 multi-points analysis.

Auger crater edge profiling was obtained with 26 multi-points analysis across the crater edge. The results are shown in Fig. 8. By comparing the crater edge profile made by Ar^+ ion with the crater edge profile by EDI, the profiles of Ti for TiO_2 thin film and Si substrate are almost the same. For the oxygen profile by EDI, much oxygen is distributed on the crater edge profile. The reason of much oxygen will be discussed in the next paragraph.

For confirmation of de-oxygenation in TiO_2 by EDI etching, we examined from the following Auger spectra analysis. Figure 9 shows the Auger spectra of 1, 7, 24 and 26 points from Auger 26 multi-points analysis. The 1 point corresponds to the spectrum at the top surface, and the 26 point is the spectrum at the bottom on the crater edge etched by EDI as shown in Fig. 7. $\text{Ti-L}_3\text{M}_{23}\text{M}_{45}$ Auger peaks of 1 and 7 points are the double peaks corresponding to TiO_2. The intensity of $\text{Ti-L}_3\text{M}_{23}\text{M}_{45}$ peaks were decreased with keeping the double peaks of TiO_2 in the case of EDI etching. This indicates that the TiO_2 film was etched without the occurrence of de-oxidizations by 10 keV EDI irradiation. At the crater bottom etched by EDI, the $\text{Ti-L}_3\text{M}_{2,3}\text{M}_{4,5}$ Auger peaks disappear at 24 and 26 points. It confirms de-oxygenation of TiO_2 does not take place in EDI etching.

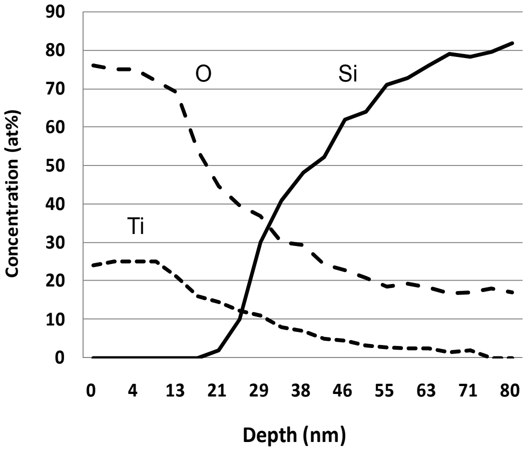

Fig. 8. AES crater edge profile for TiO_2(30nm) on Si(100) etched by EDI.

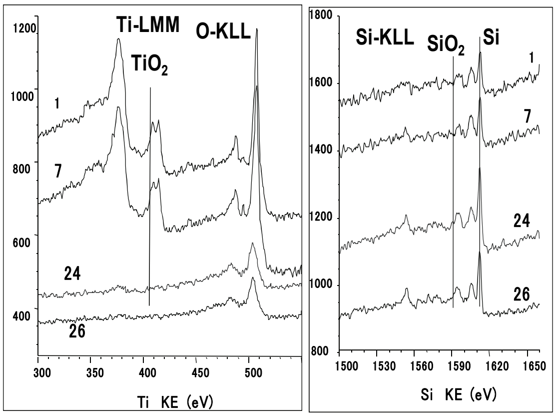

Fig. 9. Auger spectra from 26 multi-point analysis on the crater edge etched by EDI. The 1 point position is the spectrum at the top surface and the 26 is the spectrum at the bottom of the crater etched shown in Fig. 7.

From the oxygen profile shown in Fig. 8, the oxygen concentration at the depth corresponding to TiO_2 thin film is almost same as that in Fig. 6. But, much oxygen is distributed at the bottom of the crater on Si substrate. In Fig. 9, the Si-KLL Auger peaks at 24 and 26 points at the crater bottom are not due to the silicon oxide but to the metallic Si. It indicates the origin of much oxygen was not oxidization of Si.

We speculated that high oxygen signal at the crater bottom in Fig. 8 comes from the adsorbed water. This is because after the charged water droplets were impacted on the sample, the most or scattered water droplets were evacuated, and a little water was absorbed on the surface. We confirmed that the AES intensity of oxygen on EDI irradiated area was higher than that of un-irradiated area. And in this experimental conditions, the electron induced desorption of the adsorbed water was not observed.

In this experiment, the surface etched by EDI was exposed in air before AES measurement. When the metallic Ti etched by Ar^+ ion was exposed to air during 15min for transporting it between two instruments, Ti-$L_3M_{23}M_{45}$ (408.9 eV) peak grown up about 20% of TiO_2. We confirmed Ti was slightly oxidized by exposing to air but Ti peak was not changed to the double peaks due to TiO_2. Generally, the more precise evaluation for oxidation of metal requires in-site experiment, we will perform the chemical state analysis of TiO_2 etched by EDI under in-site experimental condition. From these result obtained by AES crater edge profile, it was confirmed that TiO_2 film does not suffer from de-oxygenation (i.e., reduction), and Ti and Si are not oxidized by EDI. Thus, EDI makes it possible to perform the molecular-level etching without causing any chemical modification of the target.

4. Conclusion

The TiO_2 thin films on Si substrate etched by EDI were examined by AES crater edge profiling. De-oxygenation by EDI is not observed for TiO_2 thin film as same as the case of PET etched by EDI. The EDI can etch TiO_2 thin film with no degradation underneath the surface. That is, EDI is confirmed to be a unique technique for the surface etching with almost damage-free. For more precise evaluation for oxidation of metal, EDI etching instrument is necessary to combine with AES for in-site experiment. The crater edge profiling method is useful for the depth profile measurement by using the ion gun with large ion beam diameter.

5. Acknowledgments

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6. References

[1] J.Matuo, C.Okubo, T.Seki, T.Aoki, N.Toyoda, and I.Yamada, *Nucl. Instr. and Meth. B* **219,** 463 (2004).

[2] N.Sanada, A.Yamamoto, R.Oiwa, and N.Ohashi, *Surf. Interface Anal.* **36**, 280 (2004).

[3] K.Hiraoka, D.Asakawa, S.Fujimaki, A.Takamizawa, and K.Mori, *Eur.Phys.J.D* **38,** 225 (2006).

[4] K.Hiraoka, K.Mori, and D.Asakawa, *J. Mass Spectrom.* **41,** 894 (2006).

[5] Y.Sakai, Y.Iijima, K.Mori, and K. Hiraoka, *Proceedings of 6th International Symposium on Atomic Level Characterizations for New Materials and Devices '07 (ALC'07)*, (to be published).

[6] Y.Sakai, Y.Iijima, K.Mori and K. Hiraoka, *Proceedings of International Symposium on Practical Surface Analysis '07 (PSA'07),* (to be published).

[7] Y.Iijima, M.Kudou, Y.Sakai and K. Hiraoka, *Proceedings of International Symposium on Practical Surface Analysis '07 (PSA'07),* (to be published).

[8] S.Hashimoto, *J. Surf. Anal.* **10**, 136 (2003).

[9] K.Mori, D.Asakawa, J.Sunner, and K.Hiraoka, *Rapid Commun. Mass Spectrom.* **20**, 2596 (2006).

[10] D.Asakawa, S. Fujimaki, Y. Hashimoto, K.Mori and K.Hiraoka, *Rapid Commun. Mass Spectrom.* **21**, 1579 (2007).

[11] Y.Sakai, *J. Surf. Anal.* **13**, 239 (2006) (in Japanese).

[12] D.Briggs and J.Grant(Eds), *Surface Analysis by Auger and X-Ray Photoelectron Spectroscopy* (2004) IM Pubrication and SurfaceSpectra Limited.