Journal of Surface Analysis Vol. 22, No. 2（2015）pp. 97 - 103
C. Park, et al. Application of Ar Gas Cluster Ion Beam to Oxide Thin Films

Review

Applications of Ar Gas Cluster Ion Beam to Oxide Thin Films

Chanae Park,[1] Hongchol Chae,[2] Nam Seok Park,[3] and Hee Jae Kang[1,*]
[1]*Department of Physics, Chungbuk National University, Cheongju, 28644, Korea*
[2]*Center for Research facility, Chungbuk National University, Cheongju, 28644, Korea*
[3]*Department of Semiconductor Electroengineering, Chungbuk Health & Science University, Cheongju, 28150, Korea*
[*]*hjkang@cbu.ac.kr*

(Received: June 17, 2015; Accepted: August 31, 2015)

The electronic structure of a Ta_2O_5 thin film on SiO_2/Si (100) after Ar Gas Cluster Ion Beam (GCIB) sputtering was investigated using X-ray photoemission spectroscopy and compared with those obtained via mono-atomic Ar ion beam sputtering. The Ar ion sputtering had a great deal of influence on the electronic structure of the oxide thin film. Ar GCIB sputtering without sample rotation also affected the electronic structure of the oxide thin film. However, Ar GCIB sputtering during sample rotation did not exhibit any significant transition of the electronic structure of the Ta_2O_5 thin films. Ar GCIB can be useful for potential applications of oxide materials with sample rotation.

1. Introduction

Ion beam sputtering has been widely used in secondary ion mass spectrometry (SIMS), X-ray photoelectron spectroscopy (XPS), and Auger electron spectroscopy (AES) for depth profiling or surface cleaning. One of the drawbacks of ion beam sputtering is an induced matrix effect such as surface segregation, surface composition change and surface damage, which causes difficulties in characterization of organic/inorganic interfaces and oxide materials [1,2]. Therefore, the surface matrix effects caused by ion beam sputtering should be minimized to use facile surface analysis. C_{60} ion sputtering has been used for low damage surface cleaning and depth profiling of many organic materials, but the depth profiling of organic has not been successful because of a composition change due to preferential sputtering as well as degradation of chemical states of C 1s, N 1s, and O1s [3]. Recently, Ar GCIB has attracted a lot of attention as a promising method for depth profiling of organic thin films due to extremely low degradation of surface during depth profiling [4,5]. The effects of an Ar GCIB sputtering process on the structural and chemical properties of an organic material as well as the energy level alignment at the interface between the organic semiconductor and the electrode were studied. The molecular structure and the orientation of pentacene stayed the same after the Ar GCIB process. Furthermore, there was no change in the chemical bonding states in the organic materials including pentacene and poly (3, 4-ethylene dioxy thiophene) polymerized with poly (4-styrene sulfonate) (PEDOT: PSS). The Ar GCIB sputtering process did not cause any variation in the primary valence band structure including the chemical state and the configuration of pentacene/PEDOT:PSS and pentacene/Au. The Ar GCIB sputtering is a damage-free process for organic thin films [6, 7]. In our previous work, we applied GCIB sputtering to measure the damage profile on Si (100) surfaces [8]. The damage thickness was about 10 nm, 6.4 nm and 4.2 nm for 20, 10, and 5 keV Ar GCIB sputtering, respectively. We also applied Ar GCIB sputtering to SiO_2 thin films [9]. The Ar GCIB sputtering at surface normal incidence had a deal of influence on the surface potential and the chemical structure of a SiO_2 thin film. However, the Ar GCIB sputtering at the grazing incidence angle during sample rotation did not cause any transition of a chemical bonding state or any work function change in the SiO_2 thin film. In this work, we applied Ar GCIB to the Ta_2O_5 thin film since Ar ion beam sputtering used for the removal of surface contamination or depth profiling caused severe oxygen reduction such as the phase change from Ta_2O_5 to metal Ta [10]. The electronic structure of Ta_2O_5 thin films on SiO_2/Si (100) during Ar GCIB sputtering process has been studied and compared with those obtained via mono-atomic Ar ion sputtering.

2. Experimental

The XPS measurements were performed using an Ar GCIB gun equipped with scanning X-ray Microprobe-PHI Quantera II system and with 20 keV beam energy at the incident angles of 40° from the surface normal. The mean size of one cluster was approximately 2500 atoms, the scanning area of the GCIB beam was about 2 mm × 2 mm, and the beam current was about 50 nA. Ta_2O_5 thin films were deposited on Pt substrate and 2.5 nm-thick SiO_2/Si (100) substrates by sputtering method. The Si (100) substrates weare Boron-doped (*p* type). The change in the electronic structure of a Ta_2O_5 thin film during Ar GCIB sputtering was examined using *in situ* XPS measurements. The sample rotation mode during Ar GCIB sputtering was adopted to prevent the sample surface from ripple formation, which can be a critical factor distorting depth profiling and the electronic structure [8,9]. The rotation speed of the sample holder during Ar GCIB sputtering was fixed at 6 rpm. The changes in the electronic structures during 1 kV Ar ion beam sputtering were also measured for comparison. The scanning area of the Ar ion beam was about 3 mm × 3 mm and the beam current was about 0.8 μA. The changes in the electronic structures in Ta_2O_5 thin films during Ar GCIB sputtering with or without the sample rotation were investigated by *in-situ* XPS. Monochromatic Al *Kα* (1486.6 eV) sources were used for the XPS measurements. The pass energy of hemispherical analyzer for the XPS measurements was fixed at 69 eV. The surface morphology of the thin films after Ar GCIB sputtering was also measured using scanning electron microscope (SEM). SEM was measured with a Carl Zeiss ULTRA PLUS microscope at 20.0 kV acceleration voltage.

3. Result and Discussion

Figure 1 shows XPS Ta 4f and the valence band spectra at each sputtering time during 1.0 keV monomer Ar ion beam sputtering at the incident angle of 45° from the surface normal. The peak at about 27 eV and 22.5 eV are assigned to Ta $4f_{7/2}$ from Ta_2O_5 and to metal Ta, respectively. The Ta metal peak appears right after Ar ion beam sputtering. The Ta peak of Ta_2O_5 phase decreases and the metal Ta peak increases as the sputtering time increases. In general, XPS core-level spectrum mainly depends on the core-level structure of materials due to its relatively deep probing depth (2~5 nm). It does not reveal information about small variations in the valence band structure, which can be obtained from the valence band spectrum. In the valence band spectra, the metal Ta peak at

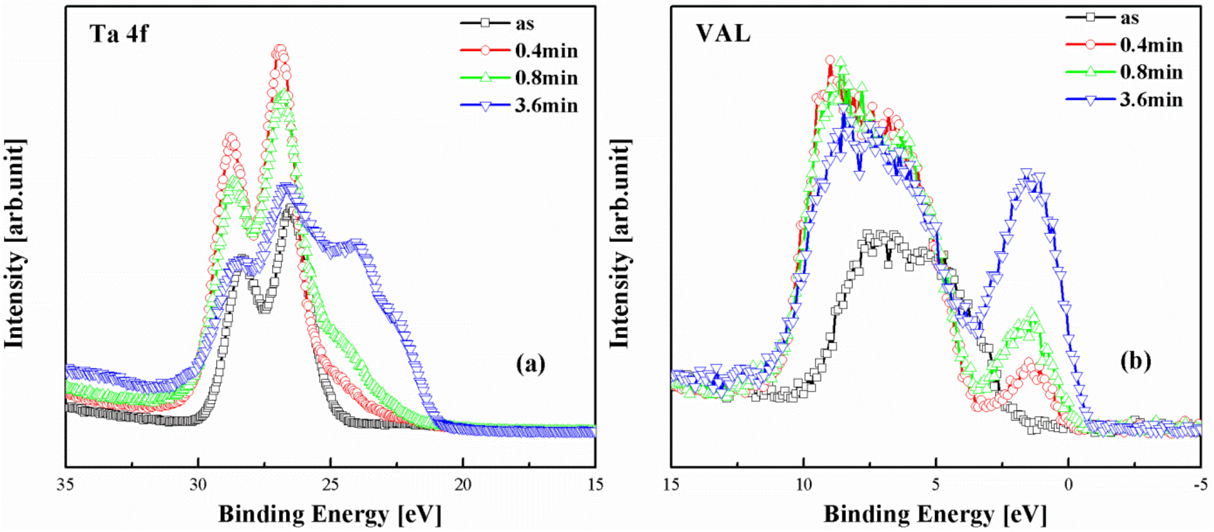

Figure 1. XPS Ta 4f (a) and valence band spectra (b) obtained from Ta_2O_5 films on Pt substrate for each sputtering time during 1 kV Ar ion beam sputtering at the incident angle of 45° from the surface normal. (color online)

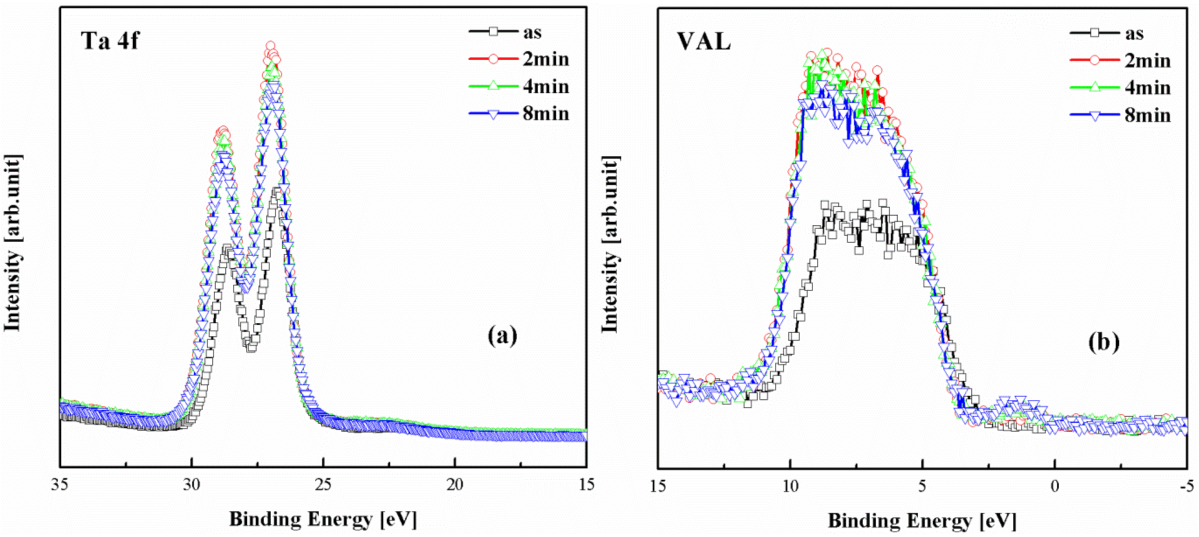

Figure 2. XPS Ta 4f (a) and valence band spectra (b) obtained from Ta_2O_5 films on Pt substrate for each sputtering time during 20 kV Ar GCIB sputtering at the incident angle of 40^o from the surface normal without sample rotation. (color online)

around Fermi level of 0 eV clearly appears right after ion beam sputtering and increases as sputtering time increases. It indicates that the electronic structure of the Ta_2O_5 layer was destroyed immediately by monomer Ar ion beam sputtering due to induced the sever oxygen reduction effects on the surface of Ta_2O_5 thin films.

Figure 2 shows Ta 4f and valence band spectra of Ta_2O_5 films on Pt substrate at each sputtering time during 20 keV Ar GCIB sputtering at the incident angle of 40^o from the surface normal without sample rotation. Ta 4f peaks at 27 eV corresponding to Ta_2O_5 slightly decrease as the sputtering time increases. But the binding energy of Ta_2O_5 did not shift and thereby the metal Ta peak did not appear as the sputtering time increases. The valence band spectra corresponding to the Ta_2O_5 phase right after removing carbon contamination at the initial stage of Ar GCIB sputtering does not change, but the peak at Fermi level corresponding to the Ta metal phase in the valence band spectrum faintly appears at the sputtering time of 8 min.

Figure 3 shows Ta 4f valence band and Si 2p spectra of Ta_2O_5 films when it was deposited on 2.5 nm-thick SiO_2/Si (100) sample for each sputtering time during 20 keV Ar GCIB sputtering at the incident angle of 40^o from the surface normal without sample rotation. The Ta peak shifted to 27 eV corresponding to the Ta_2O_5 phase right after the removal of the carbon contamination by Ar GCIB sputtering. The intensity of the peak decreases as the sputtering time increases, but the binding energy stayed the same. The peak at 22.5 eV corresponding to the metal Ta phase starts to appear after Ar GCIB sputtering time for 20 min. The peak at Fermi level corresponding to the Ta metal phase in the valence band spectrum appears at sputtering time for 20 min. The existence of a small metal Ta peak indicates that Ar GCIB sputtering lead to a preferential sputtering effect, which is not critical in comparison to Ar ion beam sputtering. The peaks at 103.5 eV and 99.0 eV in Si spectra correspond to the SiO_2 phase and the Si phase, respectively. As seen in Si 2p peak, the peak at 103.5 eV appears after sputtering time for 10 min. and then shifted to 99.0 eV. The intermediate SiO_2 layer between the Ta_2O_5 thin film and the Si substrate cannot be clearly distinguished from the Si substrate. This is caused by the surface morphology change during the Ar GCIB sputtering due to the non-uniform surface layers from inhomogeneous sputtering.

Figure 4 shows Ta 4f, valence band and Si 2p spectra of Ta_2O_5 films on 2.5 nm-thick SiO_2/Si (100) sample at each sputtering time during 20keV Ar GCIB sputtering at the incident angle of 40^o from the surface normal with sample rotation. Ta 4f peaks at 27 eV corresponding to Ta_2O_5 decrease as the sputtering time increases. But the binding energy of Ta_2O_5 did not shift and then the metal Ta peak did not appear. The valence band spectra corresponding to the Ta_2O_5 phase right after removing carbon

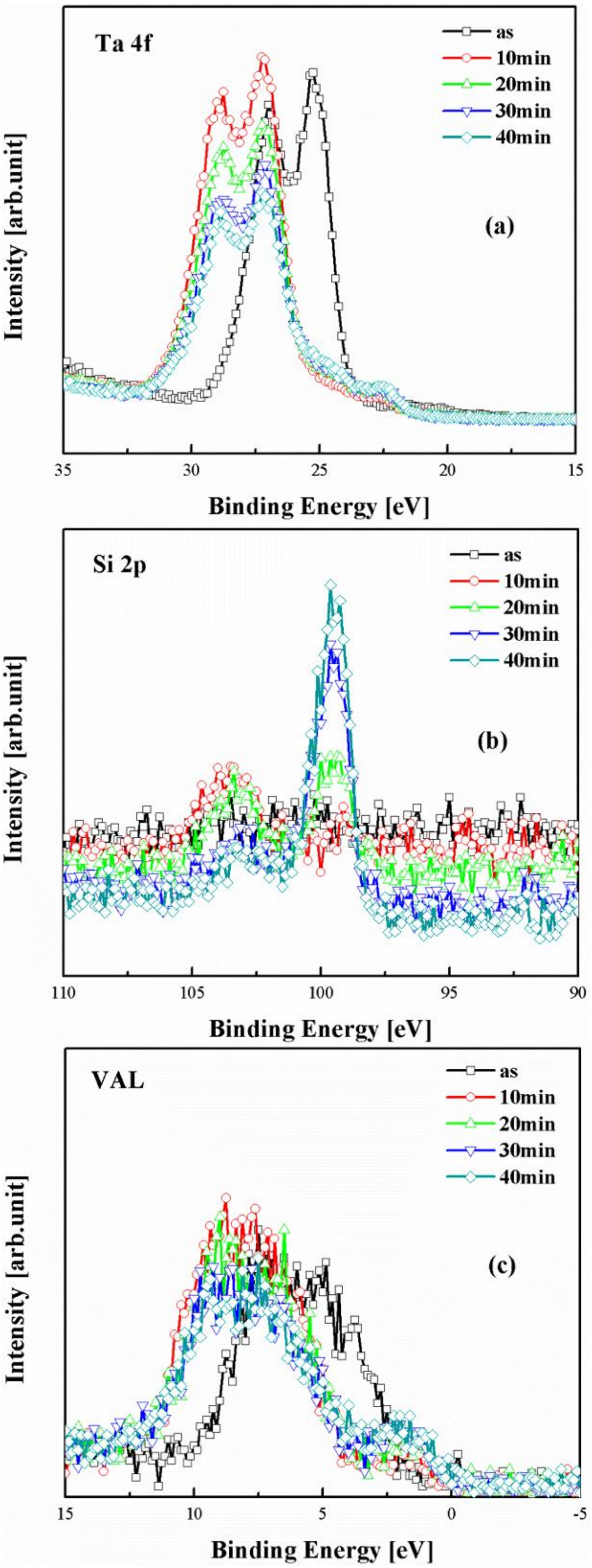

Figure 3. XPS spectra of Ta 4f (a), Si 2p (b), and the valence band (c) obtained from Ta_2O_5 films on SiO_2/Si(100) substrate for each sputtering time during 20 kV Ar GCIB sputtering at the incident angle of 40 ° from the surface normal without sample rotation. (color online)

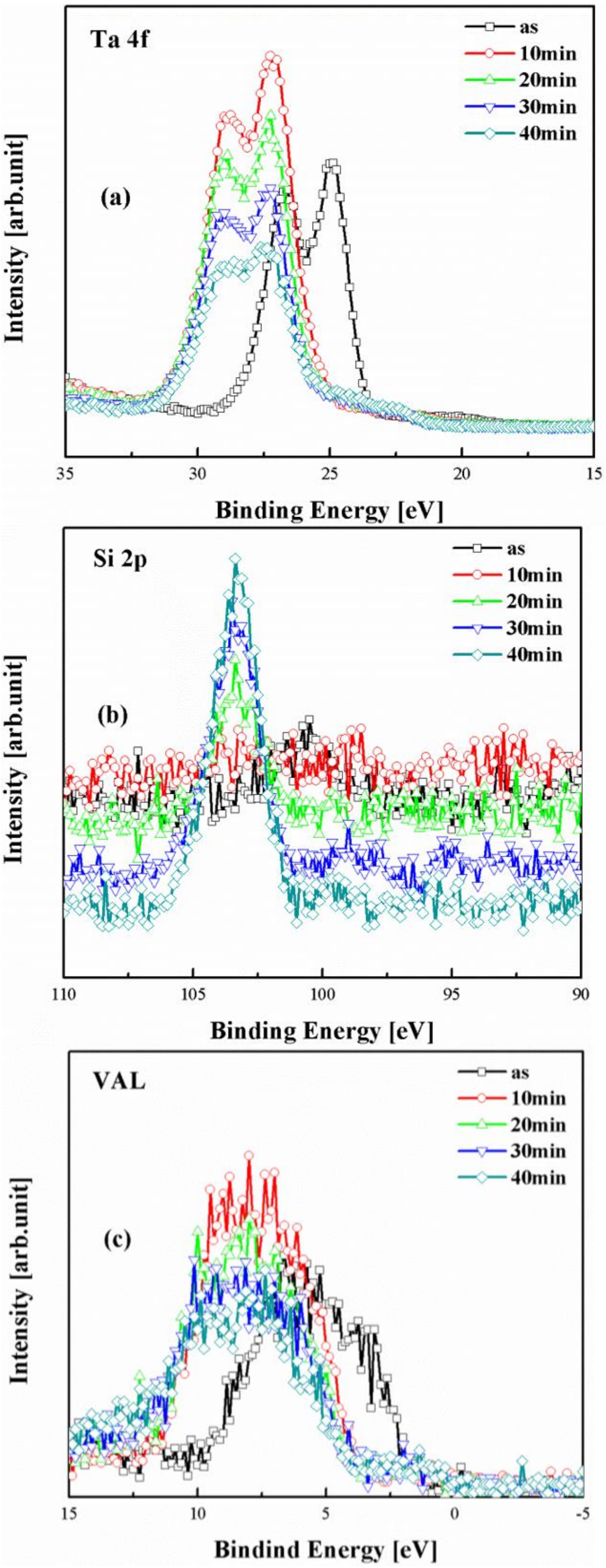

Figure 4. XPS spectra of Ta 4f (a), Si 2p (b), and the valence band (c) obtained from Ta_2O_5 films on SiO_2/Si(100) substrate for each sputtering time during 20 kV Ar GCIB sputtering at the incident angle of 40° from the surface normal with sample rotation. (color online)

contamination at the initial stage of Ar GCIB sputtering does not change even though the intensity decreased because of the sputtered out of Ta_2O_5 layers. As can be seen in Si 2p, the electronic structure of the intermediate SiO_2 layer was not destroyed during Ar GCIB depth profiling. It means that the electronic structure of the Ta_2O_5 layer does not destroy during Ar GCIB sputtering with sample rotation. Under this experimental condition, Ar GCIB can be applied to the oxide materials without any electronic structure change.

Changes in surface morphology during ion beam or cluster ion beam sputtering can influence on depth profiling and the electronic structure in the surface analysis. In our previous studies [8,9], we demonstrated that Ar GCIB sputtering develop ripples and the orientation of the ripples was perpendicular to the GCIB beam direction. The ripples can be minimized by rotating samples during Ar GCIB sputtering. In this work, we measured the morphology changes after Ar GCIB sputtering of the Ta_2O_5 thin film on the SiO_2/Si (100) substrate with and without sample rotations. Figure 5 shows the SEM images obtained after Ar GCIB sputtering without sample rotation mode (a) and with sample rotation mode (b) at the incident angles of 40^o from the surface normal. The ripples were developed periodically without sample rotation and their orientation was perpendicular to the GCIB beam direction as shown in Fig. 5(a). However, the ripples were not developed during the sample rotation and a smooth surface was maintained as shown in Fig. 5(b).

The change in the surface morphology is strongly correlated with the change in the electronic structure of oxide materials. As shown in Fig. 3 and 4, the electronic structure of the Ta_2O_5 thin-film layers and the intermediate SiO_2 layer did not change during the sample rotation. However, the electronic of the film destroyed without sample rotation during Ar GCIB sputtering, which can result from the surface morphology change during sputtering. Ar GCIB may be useful for potential applications of oxide materials, if using sample rotation mode.

4. Conclusions

We studied the effect of Ar monomer ion beam and Ar GCIB sputtering processes on the electronic structure of Ta_2O_5 thin films on Pt substrate and SiO_2/Si (100) using XPS. Monomer Ar ion beam sputtering at the incident angle of 45^o from surface normal had a great deal of influence on the electronic structure of the thin film. Ar GCIB sputtering at the incident angle of 40^o from surface normal without sample rotation caused the surface morphology changes, which can also affect the electronic structure of a Ta_2O_5 thin film. However, the Ar GCIB sputtering during sample rotation did not cause any transition of the electronic structure of Ta_2O_5 thin films and the SiO_2 layer. Our results proved that Ar GCIB sputtering during sample rotation offers a damage-free environment for chemical analysis of oxide thin films.

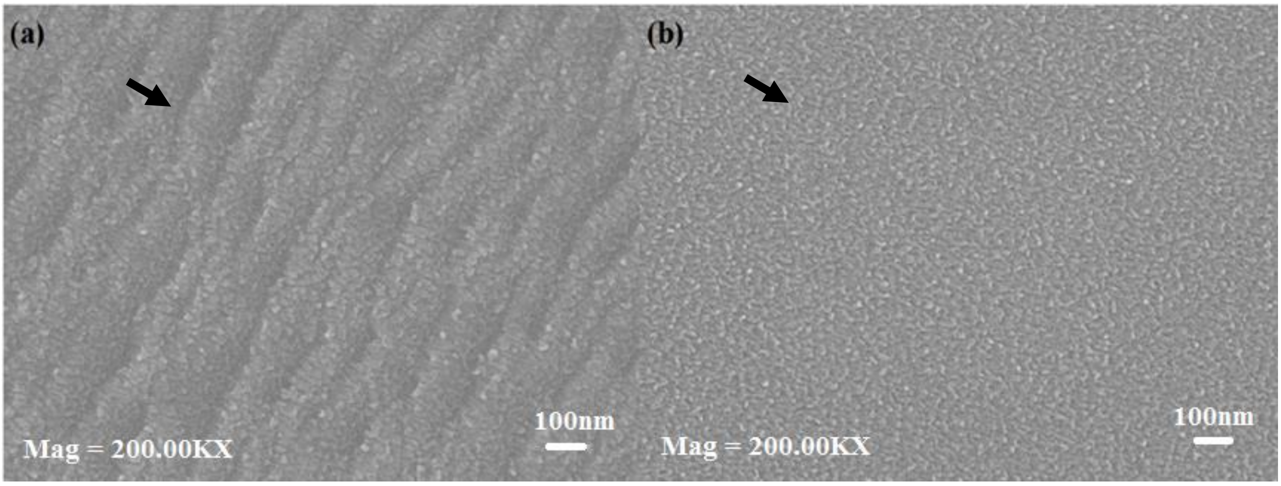

Figure 5. SEM images obtained after Ar GCIB sputtering without sample rotation mode (a) and with sample rotation mode (b) at the incident angles of 40^o from the surface normal. The arrow represents the incident Ar GCIB direction.

5. Acknowledgment

This work was conducted during the Research Year of Chungbuk National University in 2014.

6. References

[1] K. Wittmaack, *Surf. Interface Anal.*, **29**, 721 (2000).

[2] Hyung-Ik Lee, Hee Jae Kang, and Dae Won Moon, *J. Appl. Phys.*, **99**, 123507 (2006).

[3] K. Tanaka, N. Sanada, M. Hikita, T. Nakamura, T. Kajiyama, and A.Takahara, *Appl. Surf. Sci.*, **254**, 5435 (2008).

[4] T. Miyayama, N. Sanada, M. Suzuki, J. S. Hammond, S.-Q. D. Si, and A. Takahara, *J. Vac. Sci. Technol. A* **28**, L1 (2010).

[5] T. Miyayama, N. Sanada, S. R. Bryan, J. S. Hammond, and M. Suzuki, *Surf. Interface Anal.*, **42**, 1453 (2010).

[6] Dong-Jin Yun, Changhoon Jung, Hyung-Ik Lee, Ki-Hong Kim, Yong Koo Kyoung, Anass Benayad, and JaeGwan Chung, *J. Electrochem. Soc,*. **159**, H626 (2012).

[7] Dong-Jin Yun, JaeGwan Chung, Changhoon Jung, Ki-Hong Kim, WoonJoong Baek, Hyouksoo Han, Benayad Anass, Gyeong-Su Park, and Sung-Hoon Park, *J. Appl. Phys.*, **114**, 013703 (2013).

[8] Y. K. Kyoung, H. I. Lee, J. G. Chung, S. Heo, J. C. Lee, Y. J. Cho, and H. J. Kang, *Surf. Interface Anal.*, **45**, 150 (2013).

[9] Yong Koo Kyoung, Jae Gwan Chung, Hyung Ik Lee, Dong-Jin Yun, Jae Cheol Lee, Yong Su Kim, Suhk Kun Oh, and Hee Jae Kang, *Surf. Interface Anal.*, **46**, Supp. 1, 58 (2014).

[10] Dae Won Moon and Kyung Joong Kim, *Appl. Phys. Lett.*, **62**, 3094 (1993).

Discussion and Q&A with the reviewers

The figures and line numbers referred to below indicate those in the original manuscript.

Reviewer #1 Mineharu Suzuki (Tsukuba University)

The advantage of Ar GCIB applied to the oxide films of Ta_2O_5 and SiO_2 is very clearly introduced in this article. The electronic states of these film materials are kept during sputtering by Ar GCIB with sample rotation. J. Surf. Anal. shall accept this article as the report of a new sputtering technique with less destruction. Here are several comments to help readers' understandings.

[Q1_1]

The analyte structure in this study is Ta_2O_5 (20 nm)/SiO_2 (2 nm)/Si(100). When Si 2p oxide peak is detected, is Ta 4f peak simultaneously detected or not? The question is for (a) the SiO_2 layer co-exists with the residual Ta oxide layer at the top-most surface, (b) Si 2p is detected through thinned Ta oxide layer, or (c) SiO_2 layer is appeared at the surface after completely removal of Ta oxide layer.

[A1_1]

First of all, I sincerely appreciate the referee's precise and helpful comments on our manuscript entitled "Applications of Ar Gas Cluster Ion Beam to Oxide Thin Films".

The Ar GCIB sputtering yield on Ta_2O_5 and SiO_2 thin films was too low to remove. Therefore Ta_2O_5/SiO_2 thin film was not removed yet after 40 min. sputtering since Ta 4f peak gradually decreases and Si 2p peaks gradually increase as can be seen in fig. 4.

[Q1_2]

The reviewer thinks that the spectra of as-received surfaces for Figs. 1, 2, and 3 prior to sputtering processes should be the same. Ta 4f peaks and valence band peaks are shifted for about 2.5 eV from those obtained at the sputtered surfaces in Figs. 2 and 3, but they are not shifted in Fig. 1. The authors are recommended to explain this phenomenon.

[A1_2]

We used two types of Ta_2O_5 thin films. One is Ta_2O_5 thin films on Pt substrate, and the other is Ta_2O_5 thin films on SiO_2/Si substrate. There are almost no peak shifts of Ta 4f between before and after sputtering on

Ta_2O_5/Pt substrate as shown in XPS spectra (Figure 1 and 2) but there are peak shifts of Ta 4f between before and after sputtering as shown in Figure 3 and 4. It could be coming from charging up on Ta_2O_5/ SiO_2/Si sample only.

[Q1_3]

The authors clearly show the relationship between spectra and sputtering conditions (Ar^+, GCIB without sample rotation, and GCIB with sample rotation). The reviewer is expecting that the authors will investigate actual surface roughness in future, using, for example, AFM for short and long period of texture information.

[A1_3]

Thank you for your comments. I will investigate actual surface roughness in the future work by using AFM.

Reviewer #2 Yoshimi Abe (Mitsubishi Chemical Holdings Corp. R&D Synergy Center, Inc.)

Applications of Ar-GCIB to oxide thin films with sample rotation are briefly reported. The article is an informative review for JSA readers, because the application of Ar-GCIB for inorganic materials is one of the most interested issues for surface analysis scientists to discuss with.

Minor revisions are requested for the help of the readers.

[Q2_1]

In the last line in Experimental, measurement condition of SEM should be supposed to be described. The measurement conditions including the instrument model name and the acceleration voltage are preferable.

[A2_1]

We described the instrument model name and the acceleration voltage of SEM in the revised manuscript as follows:

“Scanning Electron Microscope (SEM). SEM was measured with a Carl Zeiss ULTRA PLUS microscope at 20.0kV acceleration voltage”

[Q2_2]

In the 14th line in Results and Discussion, could you please describe why the Ta peak was shifted to 27 eV right after the removal of the carbon contamination? In Fig. 1, the Ta peak was located at 27 eV before sputtering.

[A2_2]

(The editor removed the author's answer, which was the same as **[A1_2])**.

[Q2_3]

In Fig.3, Si 2p peak appears after the 20 min sputtering. After the 40 min sputtering, Si 2p peak of the SiO_2 phase still remains. Why the 2.5nm thin layer of SiO_2 still remains after the sputtering? Is the sputtering rate of SiO_2 too low to remove it? Has the sputtering stopped at the interface between Ta_2O_5 and SiO_2? Would you please comment?

[A2_3]

(The editor removed the author's answer, which was the same as the last paragraph of **[A1_1])**.

[Q2_4]

In Fig.4, information such as magnification, scale bar and the direction of Ar-GCIB should be added.

Additional SEM image after Ar monomer ion sputtering may be informative.

[A2_4]

We put the magnification, scale bar and the direction of Ar-GCIB in Fig.5 in the revised manuscript. Unfortunately we did not measure the SEM image after Ar monomer ion sputtering at this time but the surface morphology change was not observed after Ar monomer ion sputtering on oxide materials.