Laser-assisted atom probe tomography of ^{18}O -enriched oxide thin film for quantitative analysis of oxygen

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^{18}O -enriched SiO_2 thin film with the ^{16}O : ^{18}O ratio of around 1:1 has been analyzed by laser-assisted atom probe tomography (LA-APT) using 343 nm-wavelength ultraviolet laser or 532 nm-wavelength green laser in order to investigate the quantitateness of the oxygen concentration determined by LA-APT. No clear evidence for detecting $^{16}\text{O}^{18}\text{O}^{++}$ signals was found in mass spectra, implying that the peaks at mass/charge of 16 and 18 are dominated by O^+ , not by O_2^{++} . The calculated elemental composition indicated significant loss of oxygen in LA-APT analysis of SiO_2 .

Keywords:

Atom probe, Laser-assisted atom probe, Mass spectrum, Oxide, Isotope

1. Introduction

Laser-assisted atom probe tomography (LA-APT) opened up the possibility of investigation of microscopic structures of various materials, such as semiconductors, insulators, and those of complex structures including them, as well as metals. Recently, many LA-APT results examining semiconductive or insulative materials, multilayer structures on semiconductor substrates, or device structures have been reported [1-7]. On the other hand, difficulty concerning quantitative LA-APT measurement has also been recognized [8-11]. In particular, oxygen concentrations in oxide materials are important from the viewpoint of applying LA-APT to the development of semiconductor devices in which oxides such as SiO_2 are used as insulative components. Quantifying oxygen concentration of SiO_2 is receiving increasing attention also in the field of Li-ion batteries since SiO_2/Si is conceded as promising materials for their anode [12].

Fig. 1(a) shows a 3D reconstruction of part of a MOS-FET (metal-oxide-semiconductor field-effect transistor) device structure seen in an SEM (scanning electron microscopy) image (Fig. 1(b)), obtained with LA-APT, and Fig. 1(c) shows the concentration profile of the rectangular region indicated in Fig. 1(a) in the direction indicated by the arrow. The Si:O ratio at the sidewall region was around 1:1, significantly different from the expected one (~1:2). In this case the calculated oxygen concentration involves some ambiguousness derived from that of ion identification. In the mass spectrum that is the basis for the calculation of the concentration profile in Fig. 1(c), the peak that appeared at (mass/charge) ~ 16 was assumed to be O^+ , though it could also be assigned to O_2^{++} . Actually, if it were O_2^{++} , the ratio would become around 1:2, suggesting quantitatively successful measurement by

APT. It was unclear, however, if the peak is attributed to O^+ , O_2^{++} , or their mixture. This problem has been solved by considering which could give an expected stoichiometry [13], and the peak has been typically attributed to O_2^{++} [5, 14, 15, 16]. The former studies, however, have not discussed the variation of the elemental composition arising from possible peak assignments. In addition, the actual oxygen concentration of amorphous oxide, however, can deviate from the stoichiometry. So far, it has not been confirmed yet what the peak should be assigned as. It is a critical issue to apply LA-APT for the analysis of silicon oxides that are found in many semiconductor devices and Li-ion batteries.

Isotopic abundances are often utilized as a guide for identifying ion types from an acquired mass spectrum. The natural abundances of ^{17}O and ^{18}O , however, are too small to be detected by LA-APT measurements and not useful for resolving the ambiguousness mentioned above. In order to obtain chemically quantitative information of oxides with LA-APT, identification of detected oxygen ion types is critical. In this study, we propose a method using ^{18}O -enriched oxide in order to identify the types of ions including oxygen, and demonstrate it in the case of SiO_2 . A SiO_2 thin film with $^{16}O:^{18}O \sim 1:1$ was used in order to examine O_2^{++} ions in the resulting mass spectrum of LA-APT measurement. Our results indicate that parts of oxygen were lost in the LA-APT measurements, showing the limitation of the current LA-APT technique for the quantitative analysis of oxides.

2. Experimental

An ^{18}O -enriched SiO_2 thin film was formed on a Si substrate using secondary ion mass spectrometer (SIMS) (ATOMIKA SIMS4000). Oxygen ion beam was injected in the Si substrate as the primary ion beam with controlled supply of $^{16}O_2$ and $^{18}O_2$ gases. The mass around 34, corresponding to $^{16}O^{18}O^+$, was selected as the primary ion. The mass spectrum of

the secondary ion was monitored at the same time in order to control the gas flow making the $^{16}\text{O}^+ : ^{18}\text{O}^+$ ratio of the beam about 1:1. The injection direction was normal to the surface since it is well established that normal O_2^+ bombardment generates a synthetic SiO_2 layer at Si surface [17]. The injection energy for the $^{16}\text{O}^{18}\text{O}^+$ ion was 2 keV, and the SiO_2 thickness was expected to be ~6 nm. The Si: ^{16}O : ^{18}O concentration ratio of formed SiO_2 layer was confirmed to be ~1:1:1 with high-resolution Rutherford backscattering spectrometry (HR-RBS), as seen in Fig. 2.

LA-APT measurements were performed using a locally-built atom probe system (called Wide-Angle Tomographic Atom Probe (WATAP)) at the National Institute for Materials Science (NIMS) [7] and a commercial atom probe system (Cameca LEAP3000XSi). The former employs pulsed laser with wavelength $\lambda = 343$ nm (ultraviolet (UV) laser) and ~400 fs pulse duration with the spot size of ~100 μm in diameter at the specimen position, and the latter employs pulsed laser of $\lambda = 532$ nm (green laser) and ~12 ps pulse duration with the spot size of ~10 μm in diameter. The pulse repetition rate was set at 100 kHz with WATAP and at 500 kHz with LEAP3000XSi. WATAP had Cameca advanced delay line detector (ADLD) that controlled the trigger of the laser pulse. When a signal was detected on ADLD, the trigger was paused while data was processed [18]. Its substantial repetition rate, therefore, should be lower than the set value, typically around 80-90 kHz, though the detail of the trigger control was not recorded in our measurements. The specimen temperature was varied from 20 K to 100 K.

Needle-shaped specimens for LA-APT experiments were prepared by focused ion beam (FIB) fabrication. Prior to it, an amorphous Si (aSi) layer was deposited as a cover layer in an *ex-situ* process. Mikami *et al.* reported that a Si^{18}O_x layer formed on a Si substrate by $^{18}\text{O}_2^+$ injection using SIMS was suffered by ^{16}O in the air only within a depth of ~1 nm [19], and

our subsequent results were consistent with it. The specimens were prepared in cross-section mode, meaning that the SiO₂ layer was included in the direction of the needle axis, in order to raise the rate of successful measurements, particularly for those using green laser.

3. Results and Discussion

Fig. 3(a) shows an example of SEM images of prepared needle-shaped specimens, and 3(b) shows an example of the 3D reconstructions obtained with WATAP using UV laser. The laser pulse energy was set at ~0.2 μ J, and the specimen temperature was ~20 K in this case. The layered structure consisting of Si substrate, ¹⁸O-enriched SiO₂, and aSi cover is resolved in Fig. 3(b). The mass spectrum of the SiO₂ region compiled from the data set of Fig. 3(b) is shown in Fig. 4(a). The vertical axis is represented in a linear scale normalized by the peak height of ²⁸Si⁺⁺. Fig. 4(b) shows magnified spectra of the regions indicated by the dashed lines in Fig. 4(a). Although there can be found small peaks of complex ions such as SiO⁺, SiO⁺⁺, and SiO₂⁺, detected oxygen signals were predominantly involved in the peaks of O⁺/O₂⁺⁺ and O₂⁺. The peaks at (mass/charge) = 32, 34, and 36 correspond to ¹⁶O₂⁺, ¹⁶O¹⁸O⁺, and ¹⁸O₂⁺, respectively. The count ratio of these peaks was about 1:2:1. It is consistent with the ¹⁶O:¹⁸O concentration ratio of ~1:1. A minor peak can be found at (mass/charge) = 17, which could be assigned to ¹⁶O¹⁸O⁺⁺. Another minor peak at (mass/charge) = 19 is attributed to ¹⁸OH⁺. The count ratio of the peaks at 16 and 17 is almost the same as that at 18 and 19, suggesting that the peak at 17 is dominated by ¹⁶OH⁺. It is concluded that in this case ¹⁶O¹⁸O⁺⁺ signals are negligible, and that the peaks at 16 and 18 are dominated by O⁺, not by O₂⁺⁺. No significant difference was observed when the pulse energy was varied from ~0.05 μ J to ~0.3 μ J.

Fig. 5 shows the mass spectra of the SiO₂ regions obtained with LEAP3000XSi using

green laser. The laser pulse energy was set at ~0.5 nJ, and the specimen temperature was ~50 K. They are qualitatively degraded in comparison with Fig. 4(b). Such degradation was not observed with UV laser at ~50 K, and it is considered to be mainly due to the difference in laser wavelength, as previously reported [20, 21]. Detected oxygen signals were predominantly involved in the peaks of O^+/O_2^{++} and O_2^+ also in this case. There is no obvious peak at (mass/charge) = 17 in Fig. 5 and it is concluded that the peaks at 16 and 18 are dominated by O^+ and that O_2^{++} signals are negligible.

Consequently, no clear evidence for O_2^{++} signals could be found in any measurements using either UV laser or green laser. On this basis, we could calculate the depth profiles, assuming no detection of O_2^{++} . Fig. 6 shows a depth profile in the case of Figs. 3 and 4. While there are interface regions of aSi-cover/SiO₂ and SiO₂/Si-substrate, a region of stable composition with ~5 nm width can be found in SiO₂ layer. In this region, the effect of local magnification on calculated concentration ratio is thought to be insignificant (the mass spectra in Fig. 4 were compiled from this region). It can be seen in Fig. 6 that the oxygen concentration in SiO₂ layer measured by LA-APT is obviously lower than the stoichiometry of SiO₂. Then the bulk compositions of such stable regions in SiO₂ layers were calculated, as shown in Fig. 7. On this basis, we could calculate the bulk compositions of SiO₂ regions, assuming no detection of O_2^{++} . The result is shown in Fig. 5. It indicates that the calculated oxygen concentrations are obviously lower than the stoichiometry of SiO₂. It indicates that the calculated oxygen concentrations are lower than the SiO₂ stoichiometry in all the cases. It is considered that significant parts of oxygen were lost in the measurement processes of LA-APT. Note that the compositions calculated assuming that the signals of the peaks at (mass/charge) = 16, 17, and 18 had been all O_2^{++} ($^{16}O_2^{++}$, $^{16}O^{18}O^{++}$, and $^{18}O_2^{++}$, respectively), being incompatible with the present results, were found to be closer to the stoichiometry of

SiO₂ than those seen in Fig. 7. For instance, the calculated Si:¹⁶O:¹⁸O ratio based on this incompatible assumption was almost 1:1:1 in either case of (A) or (D) of Fig. 7, whereas in the case (C) the concentrations of ¹⁶O and ¹⁸O were overestimated and those in the case (B) were still underestimated.

It remains unclear how the oxygen atoms are miscounted. Losing atoms in atom probe analyses can be generally explained by the DC evaporation of atoms, i.e., field evaporation events unsynchronized with trigger pulses. In addition, the laser-assisted field evaporation process involves heating by laser irradiation, which can cause surface migration and degrade spatial resolution [22]. Considering this, the possibility of oxygen desorption as neutral gas should also be taken into account in the case of LA-APT measurements on oxide materials, as previously mentioned in the case of nitrogen from GaN surface [23]. Further study is necessary to clarify the mechanism that induces the oxygen loss in APT analysis.

Note that in Fig. 7, comparison with the other results obtained using the same laser suggests that the lower temperature leads to the composition closer to the stoichiometry. This cannot be attributed simply to thermal effect, since the effective pulse fraction contributed by laser irradiation should vary for each specimen mainly because of the variation of specimen shape. In our measurements, however, neither the detected area nor the voltage curve showed large difference as long as the same laser irradiation conditions were used, and it was supposed that there was no large variation in the pulse fraction. Lowering the specimen temperature would be one of the good strategies for obtaining improved quantitiveness of oxygen concentration in LA-APT analysis. Although no clear dependence of obtained composition on laser pulse energy was found in our experiments, pulse fraction can also affect the resulted concentration, and it is possible that experiments with wider variation of laser pulse energy would reveal the dependence.

Additionally, it is noticeable in Fig. 7 that the measured composition discrepancies using UV laser were larger than those using green laser. Their difference, however, is not considered to be due to only the wavelength. There were other conditions that could cause composition discrepancies, such as the irradiation spot size at specimen apex, pulse duration, repetition rate of the pulse, the trigger control of the laser pulse by ADLD. In order to investigate the influence of the wavelength, experiments are required in which such conditions are controlled.

4. Summary

We proposed a method using ^{18}O -substituted oxide in order to determine the types of oxygen ions detected with LA-APT. 343 nm-wavelength and 532 nm-wavelength laser were employed for laser-assisted atom probe analysis of ^{18}O -substituted SiO_2 thin film on a Si substrate with the $^{16}\text{O}:^{18}\text{O}$ ratio of around 1:1. The isotope analysis ruled out the possibility of the presence of O_2^{++} signals in atom probe mass spectra, implying that the peaks at mass/charge of 16 and 18 are dominantly O^+ . Calculated compositions of SiO_2 based on this mass assignment showed significant loss of oxygen in laser-assisted atom probe analysis. These results indicate the importance of further optimizing the measurement conditions.

Acknowledgments

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References

- [1] T.F. Kelly, D.J. Larson, K. Thompson, R.L. Alvis, J.H. Bunton, J.D. Olson, B.P.

- Gorman, *Annu. Rev. Mater. Res.* 37 (2007) 681.
- [2] S. Pinitsoontorn, A. Cerezo, A.K. Petford-Long, D. Mauri, L. Folks, M.J. Carey, *Appl. Phys. Lett.* 93 (2008) 071901.
- [3] K. Inoue, F. Yano, A. Nishida, H. Takamizawa, T. Tsunomura, Y. Nagai, M. Hasegawa, *Appl. Phys. Lett.* 95 (2009) 043502.
- [4] K. Inoue, F. Yano, A. Nishida, H. Takamizawa, T. Tsunomura, Y. Nagai, M. Hasegawa, *Ultramicroscopy* 109 (2009) 1479.
- [5] M. Gilbert, W. Vandervorst, S. Koelling, A.K. Kambham, *Ultramicroscopy* 111 (2011) 530.
- [6] Y.M. Chen, T. Ohkubo, M. Kodzuka, K. Morita, K. Hono, *Scripta Mater.* 61 (2009) 693.
- [7] K. Hono, T. Ohkubo, Y.M. Chen, M. Kodzuka, K. Oh-ishi, H. Sepehri-Amin, F. Li, T. Kinno, S. Tomiya, Y. Kunitani, *Ultramicroscopy* 111 (2011) 576.
- [8] G. Sha and S.P. Ringer, *Ultramicroscopy* 109 (2009) 580.
- [9] P. Ronsheim, P. Flaitz, M. Hatzistergos, C. Molella, K. Thompson, R. Alvis, *Appl. Surf. Sci.* 255 (2008) 1547.
- [10] P.A. Ronsheim, M. Hatzistergos, S. Jin, *J. Vac. Sci. Technol. B* 28 (2010) C1E1.
- [11] T. Kinno, H. Akutsu, M. Tomita, S. Kawanaka, T. Sonehara, A. Hokazono, L. Renaud, I. Martin, R. Benbalagh, B. Sallé, S. Takeno, *Appl. Surf. Sci.* 259 (2012) 726.
- [12] C. -M. Park, W. Choi, Y. Hwa, J. -H. Kim, G. Jeong, H. -J. Sohn, *J. Mater. Chem.* 20 (2010) 4854.
- [13] M. Bachhav, R.Danoix, F.Danoix, B.Hannoyer, S.Ogale, F.Vurpillot, *Ultramicroscopy* 111 (2011) 584.
- [14] M. Ngamo, S. Duguay, P. Pichler, K. Daoud, P. Pareige, *Thin Solid Films* 518 (2010)

2402.

- [15] S. Duguay, M. Ngamo, P.F. Fazzini, F. Cristiano, K. Daoud, P. Pareige, *Thin Solid Films* 518 (2010) 2398.
- [16] M. Gruber, C. Oberdorfer, P. Stender, G. Schmitz, *Ultramicroscopy*, 109 (2009) 654.
- [17] K. Wittmaack, *Surf. Interface Anal.* 29 (2000) 721.
- [18] G. Da Costa, F. Vurpillot, A. Bostel, M. Bouet, B. Deconihout, *Rev. Sci. Instrum.* 76 (2005) 013304.
- [19] A. Mikami, T. Okazawa, K. Saito, Y. Kido, *Appl. Surf. Sci.* 253 (2006) 1620.
- [20] J. Houard, A. Vella, F. Vurpillot, B. Deconihout, *Phys. Rev. B* 81 (2010) 125411.
- [21] Y.M. Chen, T. Ohkubo, K. Hono, *Ultramicroscopy* 111 (2011) 562.
- [22] B. Gault, M. Müller, A. La Fontaine, M. P. Moody, A. Shariq, A. Cerezo, S.P. Ringer, G.D.W. Smith, *J. Appl. Phys.* 108 (2010) 044904.
- [23] D.W. Saxey, *Ultramicroscopy* 111 (2011) 473.

Figure captions

Fig. 1

(a) 3D reconstruction of MOS device structure obtained by LA-APT measurement. Only 1% of detected Si atoms are represented for clarity. The dashed line and the arrow represent the region and the direction used in data processing of (c). (b) An SEM image of the MOS device structure. (c) Concentration profile of the region represented in (a).

Fig. 2

Depth profile of ^{18}O -enriched SiO_2 layer on Si substrate obtained by HR-RBS analysis.

Fig. 3

(a) An SEM image of an LA-APT specimen fabricated with FIB. (b) 3D reconstruction obtained by LA-APT measurement using UV laser ($\lambda = 343 \text{ nm}$) with the pulse energy of $\sim 0.2 \text{ }\mu\text{J}$. A specimen temperature was $\sim 20 \text{ K}$. Only 10% of detected Si atoms are represented for clarity.

Fig. 4

(a) Mass spectrum compiled from the oxide region seen in Fig. 3(b). The vertical axis is represented in a linear scale normalized by the peak height of $^{28}\text{Si}^{++}$. (b) Magnified mass spectra of the regions indicated by the dashed lines in (a).

Fig. 5

Mass spectra of the oxide region, measured under the usage of green laser ($\lambda = 532 \text{ nm}$) with the pulse energy of $\sim 0.5 \text{ nJ}$. A specimen temperature was $\sim 50 \text{ K}$. The vertical axis is represented in a linear scale normalized by the peak height of $^{28}\text{Si}^{++}$.

Fig. 6

Depth profile in the case of Figs. 3 and 4, calculated based on an assumption of no O_2^{++} detection.

Fig. 7

Bulk compositions of the oxide regions obtained by LA-APT measurements varying the specimen temperature, calculated under an assumption of no O_2^{++} detection. The pulse energy was set at $\sim 0.2 \mu J$ for UV laser and at $\sim 0.5 nJ$ for green laser. The case (A) and the case (C) correspond to those of the mass spectra shown in Fig. 4 and Fig. 5, respectively.

Fig. 1

Fig. 2

Fig. 3

(a)

(b)

Fig. 4(a)

(a)

Fig. 4(b)

(b)

Fig. 5

Fig. 6

Fig. 7