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Investigation of mixing effects of silicon isotopes under shave-off condition using atom probe tomography

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Shave-off depth profiling uses a Ga focused ion beam micro-machining process to provide highly precise depth profiles with nanometer-scale resolution. This method is a very unique process for acquiring a depth profile using the shave-off scan mode, in which the primary ion beam perpendicular to the direction of depth irradiates the sample. In our previous study, we confirmed by molecular dynamics simulation that the shave-off scan mode has a low mixing effect compared with the conventional scan mode, which uses the normal incident angle. However, the current understanding of measurement using the shave-off scan mode is insufficient. In this study, in order to estimate the sample damage in the shave-off scan mode, we investigated the degree of mixing effects after the primary ion bombardment under shave-off conditions using atom probe tomography. To evaluate the mixing effects, the intermixing of silicon isotope multilayers induced by ion beam irradiation was investigated. The depth of the damage from the sample surface caused by Ga focused ion beams was analyzed for both the shave-off scan mode and the conventional scan mode using the normal incident angle. Results showed that the shave-off scan mode has a significantly smaller mixing effect than the conventional scan mode. In addition, results showed that the attenuations of the damage and the Ga concentration exhibited almost the same tendency. Copyright © 2014 John Wiley & Sons, Ltd.

Keywords: SIMS; shave-off depth profiling; mixing effects; APT

Introduction

Shave-off depth profiling using a nano-beam secondary ion mass spectrometer (nano-beam SIMS[1]) achieves highly precise depth profiles with nanometer-scale depth resolution[2–5] using a focused ion beam (FIB) micro-machining process. This method is a very unique process for acquiring a depth profile using the shave-off scan mode (a fast horizontal sweep of FIB is combined with a very slow vertical sweep). In the shave-off measurements, the depth resolution mainly depends on the shape of the shave-off cross section.[2] The shape of the cross section is related to the following factors: the beam profile,[4] sample volume, sample composition (sputtering yield), and vertical scan speed.[5] For measurements with a high depth resolution, the introduction of the protection layers[2,5] and deconvolution of the obtained shave-off profile[3,4] are useful techniques. Using these techniques, the shave-off depth resolutions were estimated to be approximately 20 nm.[5] On the other hand, the mixing effects of the primary ion bombardment using the shave-off scan mode were investigated using molecular dynamics simulations,[6,7] and results suggested that the mixing effect under the shave-off scan mode was small. Compared with the shape of the cross section, this mixing effect (thickness of mixing layer) has the potential to be a very important factor for the estimation of the depth resolution under the shave-off condition.

Atom probe tomography (APT) is a technique of imaging materials three-dimensionally on a nearly atomic scale.[8] In APT, atoms at the apex of a needle sample are field-evaporated as ions when high positive voltages are applied to the sample. The elemental identities of the ions are determined from their time-of-flight. The *x*- and *y*-axis positions of the atoms in the sample are determined from the positions at which the ions arrive on a position sensitive detector, and the *z*-axis position is inferred from the evaporation sequence. A nearly atomic-scale image of the sample is reconstructed from these data as a three-dimensional image. APT is capable of measurement of interfaces between different elements and between isotopes.[9–13] Currently, APT is utilized to evaluate atomic mixing of interfaces caused by ion bombardments.[12,13] The evaluation of atomic mixing caused by Ga FIB irradiation at an angle normal to the direction of depth, as in the shave-off scan mode, has not been

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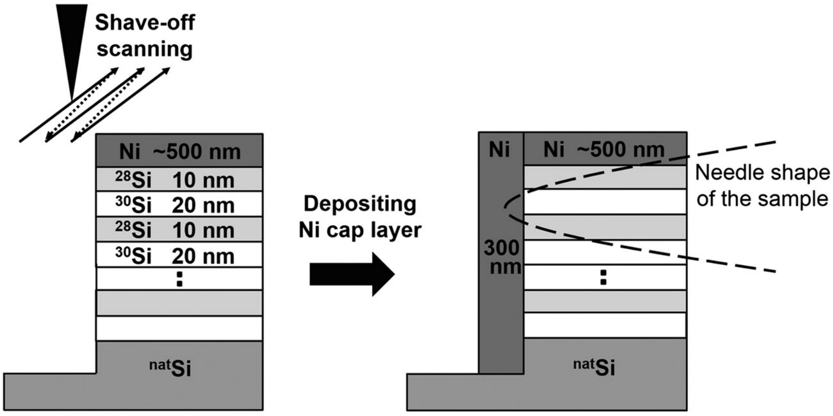

Figure 1. Sample preparation of shave-off sample.

performed. The incident angle in the shave-off scan mode is widely used for sample preparation and sectioning; therefore, evaluating the atomic mixing due to irradiation at this angle is essential.

In this study, in order to evaluate the sample damage (thickness of mixing layer) in the shave-off scan mode, the degree of mixing effects after primary ion bombardment under shave-off conditions was investigated using APT. To evaluate the mixing effects, the intermixing of silicon isotope multilayers was analyzed. Silicon isotope multilayers, which are composed of ^{28}Si and ^{30}Si heterostructures, are ideal samples for evaluating the atomic mixing caused by ion bombardment for the following reasons: ^{28}Si and ^{30}Si isotopes have same diffusion, migration, and field evaporation behavior, and ^{28}Si/^{30}Si multilayers have sharp interfaces and do not undergo chemical segregation owing to ion bombardment.[10,13]

Experiment

The ^{28}Si/^{30}Si isotope multilayers were composed of periodically stacked 10-nm-thick ^{28}Si-enriched and 20-nm-thick ^{30}Si-enriched layers on a naturally available Si (^{nat}Si) buffer layer.[14,15] A Ni protection layer approximately 500 nm thick was deposited on the top surface of the Si isotope multilayers in order to protect the sample from damage caused by the long tail of the FIBs during shave-off sectioning. Figure 1 shows the procedure of the sample preparation. A $50 \times 50 \times 50\ \mu m^3$ hole was milled, and the edge of the hole was sectioned using FIBs in the shave-off scan mode with a vertical scan speed of 7.8 nm/s. The shave-off sectioned volume was $10 \times 10 \times 2$ (t) μm^3. The acceleration voltage, current of the FIBs, and beam diameter were 30 kV, 35 pA, and 22 nm, respectively.

After shave-off sectioning, a Ni cap layer approximately 300 nm thick was deposited on the shave-off cross-section surface in order to protect the cross-section surface during annular milling, that is, the process of shaping the sample into a needle using Ga FIBs. This needle-shaped sample, called the 'shave-off sample,' was formed in a direction parallel to the multilayer planes and normal to the cross-section surface. The final annular milling process was performed using 2-keV FIBs.

As references, two types of sample were made from the Si isotope multilayer sample used to make the shave-off sample, on which a Ni protection layer approximately 500 nm thick was deposited. These samples were constructed using the lift-out method,[16] and no Ni cap layer was deposited on the apex. Two samples were formed in directions similar to that of the shave-off sample by a final annular milling process involving 8- and 30-keV FIBs. The samples shaped by 8- and 30-keV FIBs were labeled 'reference 8-keV sample' and 'reference 30-keV sample,' respectively. When shaping the reference samples by annular milling, the apexes of the samples were sufficiently sputtered, and the damage caused by the lift-out method was completely removed.

A laser-assisted local-electrode atom probe (LEAP3000XSi, AMETEK) with a green laser (wavelength: 532 nm) was used for

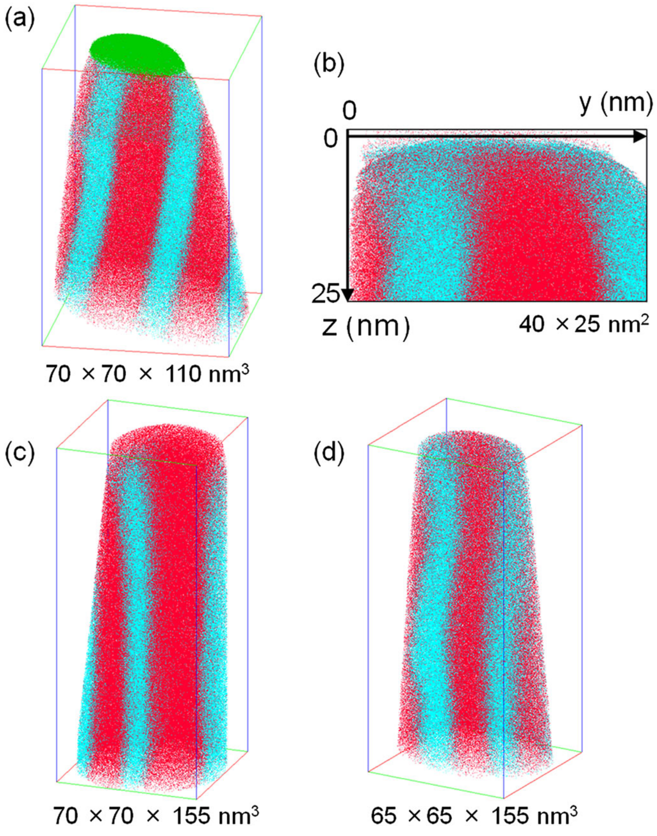

Figure 2. Three-dimensional reconstructed images of (a) shave-off sample, (b) shave-off sample near shave-off cross-section surface, (c) reference 8-keV sample, and (d) reference 30-keV sample. ^{28}Si, ^{30}Si, and Ni atoms are represented as light blue, red, and green dots, respectively.

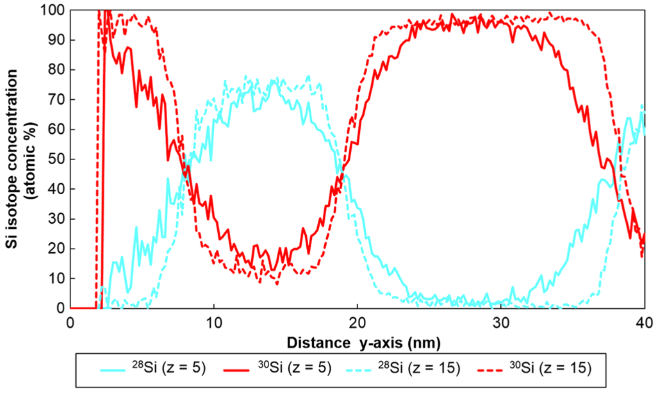

Figure 3. Concentration profiles of Si isotopes at depths of z = 5 and 15 nm in shave-off sample for lateral direction y. The analysis volume of each depth was x × y × z = 15 × 40 × 2 nm^3.

the APT analysis. The pulsed laser energy and base temperature of the sample were 0.3 nJ and 50 K, respectively.

Results and discussions

Figure 2 (a), (c), and (d) displays three-dimensional reconstruction images of the shave-off sample, reference 8-keV sample, and reference 30-keV sample, respectively. The ^{28}Si, ^{30}Si, and Ni atoms are represented by light blue, red, and green dots, respectively. The Ni atoms in Fig. 2 (a) were deposited on the shave-off sectioned surface before the annular milling. The thickness of this Ni cap layer was determined to be approximately 20 nm when the data was acquired. The interfaces of the ^{28}Si- and ^{30}Si-enriched layers parallel to the long axis of the needle were clearly observed. Figure 3 indicates concentration profiles of Si isotopes in the lateral direction at depths of z = 5 and 15 nm from the shave-off sectioned surface (see Fig. 2 (b)). As shown in Fig. 3, the interfaces between the ^{28}Si- and ^{30}Si-enriched layers became sharper in deeper regions. In general, the Gauss function is used for curve fitting, and the standard deviation is the important factor of the fitting curve. The value of the standard deviation represents the interface sharpness. To evaluate the interface sharpness, the ^{30}Si profiles near the central part of Fig. 2 (a) at a depth of approximately y = 20 nm were fitted by the least square

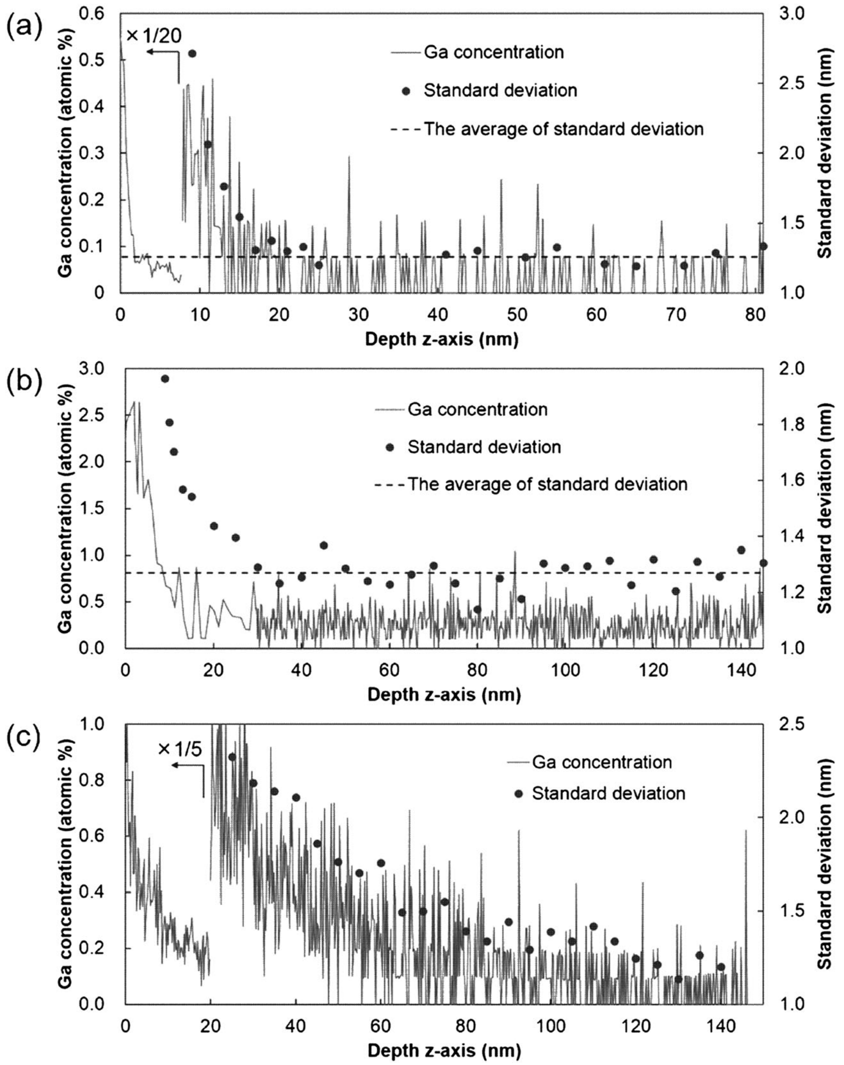

Figure 4. Standard deviations of fitted Gaussian integral and depth profiles of Ga concentration for (a) shave-off sample, (b) reference 8-keV sample, and (c) reference 30-keV sample.

method with a Gaussian integral, $F(x)$, which contains the fitting parameters Y and σ, as shown in the following equations.

$$S = \sum_{Y_{min}}^{Y_{max}} \left| C(y) - F(y) \right|^2$$

$$F(y) = B_{ave} + (T_{ave} - B_{ave}) \frac{\int_{-\infty}^{y} G(x)dx}{\int_{-\infty}^{\infty} G(x)dx}$$

$$G(x) = exp\left\{ \frac{-(x-Y)^2}{2\sigma^2} \right\}$$

S, $C(y)$, Y, and σ are the sum of the squared residuals, the concentration of the obtained profile, the center of the interface, and the standard deviation, respectively. B_{ave} and T_{ave} are the average concentration in the range of 2 nm including the bottom or top of the ^{30}Si concentration profile. The range of 2 nm was determined as the region where the slope of the approximation line was minimized. The fitting range from Y_{min} to Y_{max} was the range where B_{ave} and T_{ave} were calculated. Figure 4 (a) shows the standard deviation of the fitted Gaussian integral and the depth profile of the Ga concentration in a volume of $15 \times 15 \times 85\ \mathrm{nm}^3$ that contained a ^{30}Si interface fitted with the Gaussian integral. The standard deviation of the shave-off sample converged to 1.266 ± 0.055 nm, that is, the average of the standard deviation deeper than 25 nm from the shave-off cross-section surface, with increasing depth. To estimate the damage depth, the standard deviation was approximated by an exponential function. The depth below $1.266 + 0.055$ nm to which the approximated exponential function fell was defined as the damage depth. According to this estimation, the damage depth of the shave-off sample was 19.51 nm from the shave-off cross-section surface. Because the damage caused by annular milling was terminated within the Ni cap layer, this value represents the depth of damage caused only by shave-off scanning using Ga FIBs.

In the case of the concentration profiles of Si isotopes for the lateral direction in the reference 8-keV sample and reference 30-keV sample, the ^{30}Si profile at each depth was fitted in the same way as for the shave-off sample. Figure 4 (b) and (c) shows the standard deviation and Ga depth profile of the reference 8-keV sample and reference 30-keV sample, respectively. The damage depth of the reference 8-keV sample was estimated in the same way as that of the shave-off sample and was estimated to be 27.25 nm from the apex. In the reference 30-keV sample, the damage was quite deep, and the damage depth could not be estimated, because the standard deviation of the sample did not converge in the analyzed area. The damages in the reference 8-keV sample and the reference 30-keV sample were caused solely by the annular milling; the damage caused by the shave-off sectioning was removed during the annular milling. Therefore, the damage depth in the reference samples represents the depth of damage caused by Ga FIB irradiation at an incident angle normal to the surface of the Si substrate. These results suggest that the shave-off scan mode has a low mixing effect even with high FIB energy. From these data, we cannot evaluate the damage depth precisely and discuss the quantitative relationship between the degree of damage and Ga concentration. However, in each sample, the attenuations of the damage and the Ga concentration exhibited almost the same tendency.

Conclusions

In order to evaluate the sample damage (thickness of mixing layer) in the shave-off analysis, the intermixing of silicon isotope multilayers was investigated using APT. The damage depths of the shave-off sample and reference 8-keV sample were estimated to be 19.51 nm from the shave-off cross-section surface and 27.25 nm from the apex. The damage depth of the reference 30-keV sample could not be estimated by this analysis. These results indicate that the shave-off scan mode has a small mixing effect compared with ion beam irradiation perpendicular to the sample surface. The order of magnitude of the estimated damage depth under the shave-off measurement in this study (19.51 nm) is nearly equal to that of the observed depth resolution in reference.[5] Thus, we conclude that the mixing effect is a potentially important factor for determining the depth resolution under typical shave-off conditions.

References

[1] M. Nojima, M. Toi, A. Maekawa, B. Tomiyasu, T. Sakamoto, M. Owari, Y. Nihei, *Appl. Surf. Sci.* **2004**, *231–232*, 930.
[2] M. Toi, A. Maekawa, T. Yamamoto, B. Tomiyasu, T. Sakamoto, M. Owari, M. Nojima, Y. Nihei, *J. Surf. Anal.* **2005**, *12*, 170.
[3] K. Nakamura, Y. Ishikawa, K. Utsumi, H. Iigusa, R. Tanaka, Y. Ishizaki, T. Yamamoto, A. Maekawa, M. Owari, M. Nojima, Y. Nihei, *Surf. Interface Anal.* **2006**, *38*, 1734.
[4] M. Fujii, M. Nojima, M. Owari, Y. Nihei, *e-J. Surf. Sci. Nanotech.* **2010**, *8*, 237.
[5] M. Fujii, T. Imamura, M. Nojima, M. Owari, *J. Surf. Anal.* **2011**, *17*, 232.
[6] M. Fujii, M. Owari, *e-J. Surf. Sci. Nanotech.* **2012**, *10*, 463.
[7] M. Fujii, M. Owari, *Surf. Interface Anal.* **2013**, *45*, 122.
[8] T. F. Kelly, M. K. Miller, *Rev. Sci. Instrum.* **2007**, *78*, 031101.
[9] Y. Shimizu, Y. Kawamura, M. Uematsu, K. M. Itoh, M. Tomita, M. Sasaki, H. Uchida, M. Takahashi, *J. Appl. Phys.* **2009**, *106*, 076102.
[10] Y. Shimizu, Y. Kawamura, M. Uematsu, M. Tomita, T. Kinno, N. Okada, M. Kato, H. Uchida, M. Takahashi, H. Ito, H. Ishikawa, Y. Ohji, H. Takamizawa, Y. Nagai, K. M. Itoh, *J. Appl. Phys.* **2011**, *109*, 036102.
[11] S. Koelling, N. Innocenti, G. Hellings, M. Gilbert, A. K. Kambham, K. De Meyer, W. Vandervorst, *Ultramicroscopy* **2011**, *111*, 540.
[12] H. Gnaser, R. Schiller, M. Wahl, B. Reuscher, A. Zeuner, M. Kopnarski, R. Neb, B. Hillebrands, *J. Phys. D Appl. Phys.* **2012**, *45*, 50503.
[13] M. Tomita, M. Koike, H. Akutsu, S. Takeno, Y. Kawamura, Y. Shimizu, M. Uematsu, K. M. Itoh, *J. Vac. Sci. Technol. B* **2012**, *30*(1), 011803.
[14] T. Kojima, R. Nebashi, K. M. Itoh, Y. Shiraki, *Appl. Phys. Lett.* **2003**, *83*, 2318.
[15] Y. Shimizu, K. M. Itoh, *Thin Solid Films* **2006**, *508*, 160.
[16] K. Thompson, D. Lawrence, D. J. Larson, J. D. Olson, T. F. Kelly, B. Gorman, *Ultramicroscopy* **2007**, *107*, 131.