XANES analyses of silicon crystalline irradiated by nitrogen/oxygen ions

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X-ray absorption techniques have been applied to the characterization of 5 keV nitrogen / oxygen ions implanted silicon samples. The depth selective measurement of XANES by recording in PEY mode and the quantitative analysis by superposition of XANES spectra were carried out to elucidate the depth profile of implanted ions. It has been revealed that the silicon nitride phase were formed in silicon after prolonged N^+ irradiation and it extended over the deep part of the damaged region from the surface. On the ther hand, for the O^+ irradiation, silicon dioxide phase were produced only in the shallow part of the damaged region, i.e., the silicon dioxide phase likely broke off during the irradiation.

1. Introduction

Commonly, ion implantation is used as a powerful technique to modify the near-surface properties of materials (Pankove et al., 1991). By controlling the fluence and energy of incident ions, one can introduce the desired amount of foreign species into suitable depth in host materials. However, the kinetic energy of implanted ions introduces lattice damage through electron excitation and atomic displacement processes, sometimes resulting in undesirable modification of the near-surface structure. In addition, production of the huge amount of displaced atoms which are usually much larger than that of implanted species makes the behavior of the implanted species very complex. Therefore, to understand the near-surface properties of implanted materials, the characterization techniques with fine depth resolution as well as the quantitative analysis for the defects (atomic displaced) phase and ions implanted one are very important tasks. In the present work, we have applied X-ray absorption technique for characterization of silicon crystal implanted by nitrogen and oxygen ions, and carried out the quantitative and depth profile analyses of these samples.

2. Experimental

Nitrogen and oxygen ion irradiations were carried out in a standard vacuum chamber equipped with an ion source at room temperature (Tanabe et al., 1994). With an aid of differential pumping system, the pressure of the target chamber was kept below 10^{-6} Pa during the irradiation. Mass analyzed nitrogen or oxygen ions accelerated up to 5 keV were injected to a Si target (100) through a slit of 5 mm diameter with an incident angle of 45 degrees with respect to the target normal. The injected ion flux was monitored by a Faraday cup inserted in the beam line in front of the target. Since the samples were stored in air, they were exposed by atmospheric oxygen. The depth profile of implanted nitrogen or oxygen and number of displacement atom in silicon produced by 5

keV N^+ or O^+ injection was simulated by the TRIM92 code (Ziegler et al., 1985).

Si K-edge XANES spectra were recorded under vacuum ($<10^{-6}$ Pa) at room temperature at BL-27A station at Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK-PF) , using a two-crystal InSb(111) monochromator. The energy resolution of X-rays was about 0.7 eV at 2 keV. Data were recorded by a partial electron yield (PEY) mode or a photocurrent, in which X-ray energy dependence of Si KLL Auger electron yield is mainly monitored (Elam at al., 1988, Erbil et al., 1988). By considering the escape depth of the Auger electrons, the measured XANES spectrum is expected to give information on the near surface of a sample. In the measurement by PEY mode, a hemispherical electron energy analyzer (VSW. CLASS-100) was used as the detector. Each XANES spectrum was normalized by the photon intensity which was monitored by a Cu mesh located in front of the sample.
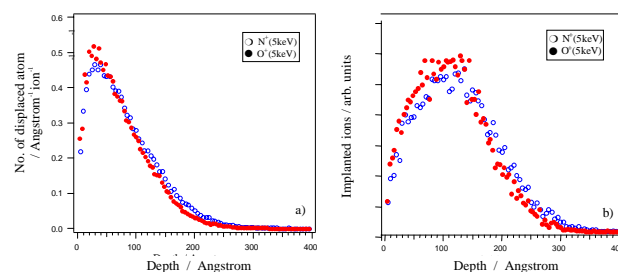

Fig.1(a) Depth distribution of the number of displaced atoms per incident ion (dpa) calculated for 5 keV N^+ or O^+ irradiated silicon by the TRIM 92 code.
Fig. 1(b) Depth distributions of implanted nitrogen or oxygen calculated for 5 keV N^+ or O^+ irradiated silicon by the TRIM 92 code.

3. Depth profile of lattice damage in nitrogen or oxygen irradiated silicons

Fig.1(a,b) shows depth distributions of the numbers of displaced atoms per incident ions (dpa) and the implanted nitrogen/oxygen which were calculated by the TRIM 92 code. Under the 5 keV N^+/O^+ irradiation, the amount of displaced atom is much larger than that of the implanted nitrogen/oxygen. In addition, the ions are generally implanted little deeper than the damaged region. It should be noted that the TRIM calculation with Kinchin-Pease model shows the similar depth distributions of dpa and implanted atoms for both N^+ and O^+ irradiation. The damaged region including the defects and implanted atom is likely to extend over the range to ca. 30 nm from the surface. On the other hand, the analyzing depth by the present X-ray absorption study is roughly estimated as several nm - 50 nm from the surface, which is suited for the analysis of the damaged region in the silica samples.

4. XANES spectra of N[+] irradiated silicons

Fig. 2 shows Si K-edge XANES spectra recorded by a photocurrent mode, of an unirradiated silicon (a) and N^+ irradiated silicons (b and c). After the irradiation of 1.2 x 10^{22} ions / m^2, a pronounced peak at around 8 eV was appreciable and relatively higher than the peak assigned to Si(0) species. Since the energy position of the 8 eV peak agrees with that of the main characteristic peak of silica (see Fig. 4(a)), the target surface must be oxidized to SiO_2. The surface oxidation likely occurred during the transport process in atmosphere from the irradiation chamber for XANES measurements. In a separate experiment, we found that the ion irradiated Si surface under the same condition as the present one was mostly kept oxygen free. It should be also noted that oxygen
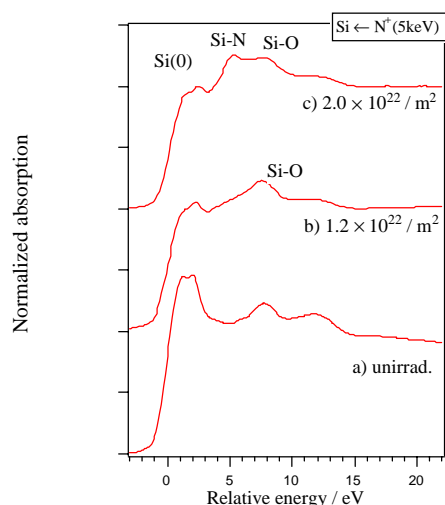
Fig. 2 Si K-edge XANES spectra recorded by a photocurrent mode of an unirradiated silicon (a) and silicon samples irradiated by 5 keV nitrogen ions (b and c). The fluence of nitrogen ions is (b) 1.2 x 10^{22} ions / m^2 and (c) 2.0 x 10^{22} ions / m^2. Energy offset is taken to be 1838 eV.

Fig. 3 Si K-edge XANES spectra of the silicon sample irradiated by 5 keV nitrogen ions with the fluence of 2.0 x 10^{22} ions / m^2. The spectra were obtained by recording the photocurrent (a), the yield of electrons having the kinetic energy of 50 eV (b) and 1500 eV (c). Energy offset is taken to be 1838 eV.

uptake for pure Si stored in atmosphere (Fig.2(a)) is far less than that appeared in Fig.2(b,c). This indicates that the surface oxidation was enhanced in the N^+ irradiated surface probably because of the damaging of Si tetrahedra by atomic displacement. Another appreciable peak at ca. 5 eV grew with the increase in the nitrogen ions fluence. Since less valenced silicon oxide than SiO_2 such as SiO is unstable (Yamamoto et al., 1995), the new Si species could be attributed Si-N formation with the implanted nitrogen. For the silicon sample after the irradiation of 2.0 x 10^{22} ions / m^2, the energy position of the new peak agreed with that of the main characteristic peak of Si_3N_4 (see Fig. 4(a)), and Si 1s XPS spectrum of this sample clearly showed the formation of nitride phase. The silicon nitride species like Si_3N_4 probably formed in the silicon samples after the prolong N^+ irradiation(Baba et al., 1993).

5. The depth profile and quantitative analysis by XANES

For the Si sample irradiated by N^+ with the fluence of 2.0 x 10^{22} ions / m^2, we also carried out the depth profile analysis by recording the XANES in PEY mode in order to understand the distribution of implanted nitrogen atoms. Fig.3(b) shows the XANES spectrum recorded by the electron yield mode but it was limited the electrons having the kinetic energy (K.E.) of ca. 50 eV. The 5 eV peak attributed to silicon nitride became higher compared with that recorded in a photocurrent (Fig.3(a)), although the feature of both XANES spectra were fundamentally the same. Taking into account the mean escape depth of the electrons with K.E. of ca. 50 eV (Seah, & Dench, 1979), the spectrum thus obtained should bring information within a few nm of the surface layers, which corresponds to the shallow part of the damaged region (Some electrons with K.E. of ca. 50 eV may come out from a little deeper region after scattering many times in the sample).

On the other hand, in the XANES spectrum recorded by the electron yield mode with limited electrons having K.E. of 1500 eV (Fig.3(c)), the 8 eV peak showing the oxidation to SiO_2 in the defect phase was reduced whereas the peak assigned to silicon nitride phase was clearly observed. The analyzing depth of this XANES spectrum would be roughly more than double of that for the electrons with K.E. of 50 eV (Seah, & Dench, 1979). On the
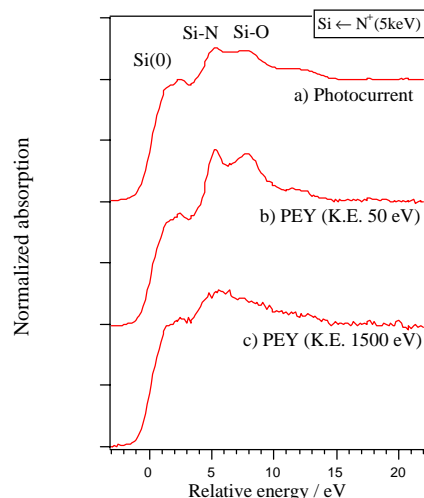
basis of these results, we can conclude that the silicon nitride phase extended over the deep part of the damaged region from the surface while the oxidation to SiO_2 occurred in the shallow part of the damaged region.

Similar results were also obtained in our separate depth profile analysis by Si 1s XPS spectra, suggesting that the present depth profile analysis by XANES is available and reasonable. The careful comparison of the depth profile analyses between XANES and XPS let us to notice that XANES reflected a little deeper range of samples compared with XPS. A small contribution of the scattering electrons may not be negligible especially for the XANES spectra recorded by PEY mode with limited electrons having K.E. of 50 eV. The detailed investigation of the analyzing depth may be required in future, although we can roughly estimate the analyzing depth in the present stage (as we described above).

Here we have attempted the simulation of XANES spectra in Fig.3 by superposition of XANES spectra of pure silicon, Si_3N_4 and SiO_2 with a suitable ratio. For the pure silicon, we used the silicon crystal after the Ar ion sputtering to exclude the oxygen uptake on the silicon surface. All of the spectra in Fig. 3 were able to be reproduced sufficiently as shown in Fig.4 (b) as an example. The results allow us to estimate the composition of silicon, silicon nitride (Si_3N_4) and SiO_2 phases. The composition was summarized in Table 1.

TABLE 1: Calculated fractions of Si(0), Si_3N_4 and SiO_2 species in Si irradiated with 5keV N^+ or O^+

Sample	Mode	Si(0)/%	Si_3N_4 /%	SiO_2 /%
Unirrad. Silicon	Photocurren	97	-	3
Si←N^+ (5keV) 2.0 x 10^{22} / m^2	PEY(K.E.50eV)	60	31	9
	Photocurrent	71	22	7
	PEY(K.E.1500eV)	75	22	3
Si←O^+ (5keV) 2.0 x 10^{22} / m^2	PEY(K.E.50eV)	78	-	22
	Photocurrent	84	-	16
	PEY(K.E.1500eV)	95	-	5

The simulation was performed by the sum of the spectra shown in Fig.4(a). The error is within ±2 %.
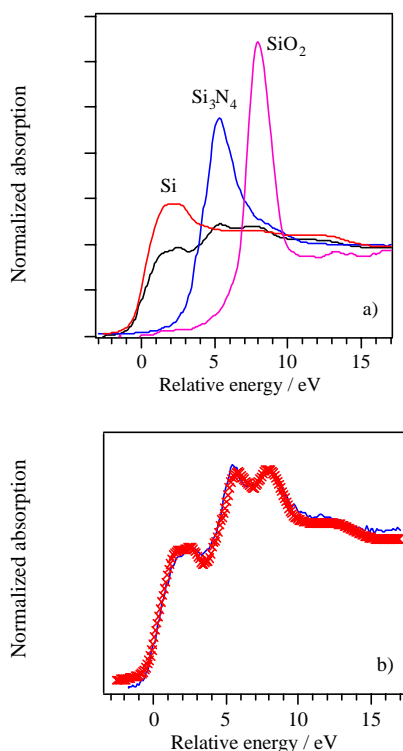
Fig. 4(a) Si K-edge normalized XANES spectra of a pure silicon (the silicon after the Ar ion sputtering to exclude the oxygen uptake on the surface) (a), Si_3N_4 (b) and SiO_2 (c). Energy offset is taken to be 1838 eV.
Fig. 4(b) The curve fitting of XANES spectrum of the silicon sample irradiated by 5 keV nitrogen ions with the fluence of 2.0×10^{22} ions / m^2. The simulation was performed by the sum of all the spectra shown in Fig.4(a). Energy offset is taken to be 1838 eV.

6. XANES spectra of O^+ irradiated silicons

Fig.5 shows Si K-edge XANES spectra of the silicon sample irradiated by 5 keV O^+ with the fluence of 2.0×10^{22} ions / m^2, recorded by a photocurrent and PEY modes. Two peaks attributed to silicon and SiO_2 phases were observed in these spectra. According to the quantitative analysis mentioned in the previous section, the composition of silicon and SiO_2 phases were calculated and also summarized in Table 1. The fractions of SiO_2 phase were evaluated as 22 % and 5 % for the XANES spectra recorded by the electron yield mode with limited electrons having K.E. of 50 and 1500 eV, respectively. This result surprisingly indicates that very few implanted oxygen ions existed in the deep part of the damaged region, which is in conflict with the presumption obtained by TRIM calculation where the depth distribution of dpa (defects) and implanted atoms were almost the same between 5 keV N^+ and O^+ irradiation.

The origin and cause of the discrepancy is still open question, but it may result from the difference in the volume expansion between silicon nitride (Si_3N_4) and silicon oxide (SiO_2). The densities of silicon atoms in silicon crystal, Si_3N_4 and SiO_2 are calculated as ca. 5.0×10^{22} / cm^3, 4.0×10^{22} / cm^3 and 2.5×10^{22} / cm^3, respectively, from the parameters of their crystal structures (Glemser et al. 1957, Young et al, 1962). Therefore, by the formation of SiO_2 phase, the volume is expected to expand 2 times as large as that of the unirradiated silicon whereas ca. 1.3 times by the formation of Si_3N_4 phase, which may result in the preferential break off of the SiO_2 phase during the O^+ irradiation.
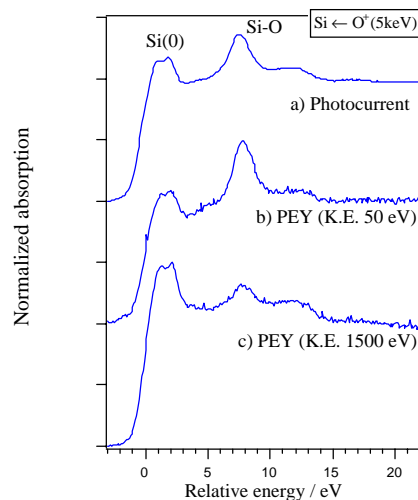

Fig. 5 Si K-edge XANES spectra of the silicon sample irradiated by 5 keV oxygen ions with the fluence of 2.0×10^{22} ions / m^2. The spectra were obtained by recording the photocurrent (a), the yield of electrons having the kinetic energy of 50 eV (b) and 1500 eV (c). Energy offset is taken to be 1838 eV.

In addition, the difference in the phase formation process between silicon oxide and silicon nitride may have some influence. Baba et al. investigated for silicon oxide and silicon nitride with nonstoichiometric compositions (SiOx, SiNx) produced by low-energy ion implantation in Si(100) by Auger and XPS techniques (Baba et al., 1993). They suggested the random-mixture model for the microstructure of nonstoichiometric SiOx, in which the SiOx phase is interpreted as a mixture of Si and SiO_2 phases. On the other hand, random-bonding model, in which each silicon atom is tetrahedrally coordinated to x nitrogen and (4-x) silicon atoms with the probability statistically determined, was considered for SiNx. According to their results, SiO_2 phase is easily formed even in the early stage of O^+ irradiation, which would result in the acceleration of the break off of silicon oxide phase. In the present study, the depth selective and quantitative analyses by using Si K-edge XANES clearly showed the difference in the depth profile of implanted nitrogen and oxygen in silicon.

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