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XAFS study on D+ irradiated Si surface

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Si K-edge XANES recorded in a total electron yield mode was applied to characterize silicon samples irradiated by deuterium ions accelerated to 5 and 15 keV. In XANES of samples irradiated at 5 keV, peaks showing the formation of displaced atoms and Si-D bonds were observed. For samples irradiated at 15 keV, such a appreciable change was not observed, indicating that the accumulations of defects and implanted deuterium are mostly out of the analyzing depth of XANES. Thus, XANES successfully distinguished deuterium irradiated samples with the difference in the depth distribution of implanted deuterium and produced damages.

Keywords: silicon; deuterium ion irradiation; Si K-edge XANES

1. Introduction

Ion implantation is commonly used as a method to modify the near-surface properties of materials. By controlling the fluence and energy of incident ions, one can introduce the desired amount of foreign species into suitable depth in host materials. Simultaneously 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. Moreover the amount of displaced atoms is usually much larger than that of implanted species, which makes the behavior of the implanted species very complex. Therefore characterization of the implanted materials with fine depth resolution is a very important task. In the present work, we have applied an X-ray absorption technique for characterization of silicon samples implanted by deuterium with the difference in the depth distribution of implanted deuterium and produced damages.

2. Experimental

Deuterium ion irradiation was 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^{-8} Torr during the irradiation. Mass analyzed deuterium ions (D^+) accelerated up to 5 or 15 keV were injected into a Si target (100) through a slit of 5 mm diameter with an incident angle of 22.5 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 to atmospheric oxygen. The depth profile of displacement damage in silicon was calculated with the TRIM92 code. (Kawai *et al.*, 1991)

Si K-edge XANES spectra were recorded under vacuum ($<10^{-7}$ Torr) at room temperature at the beam line 7A station attached with a two-crystal InSb monochromator at UVSOR, Institute for Molecular Science, Okazaki, Japan. The ring energy was 750 MeV and stored current was 100-200 mA during measurement. The sample was directly put on the first photocathode made of Cu-Be of the electron multiplier with the voltage of - 1.5 keV. Data were collected in a total electron yield mode, in which X-ray energy dependence of Si KLL Auger electron yield is mainly monitored.(Elam *et al.*, 1988, Erbil *et al.*, 1988). Although the escape depth of the Auger electrons is about 30 Å, the analyzing depth of XANES in the present experiment would be somewhat deeper than 30 Å due to the effect of high voltage of - 1.5 keV on the electron multiplier.

3. Depth profile of lattice damage in deuterium irradiated silicons

Generally hydrogen (deuterium) implantation in silicon is known to result in defects and Si-H layer formation (Doyle, 1982, Pankove & Jhnso, 1991). Under the medium energy (1-100 keV) deuterium irradiation, the amount of defects is expected to be much larger than that of implanted deuterium. Fig. 1 shows depth distribution of the number of displaced atoms per incident ion (dpa) which were calculated by the TRIM 92 code. One can clearly see that the distribution of the displaced atoms is much influenced by the incident energy of deuterium ions. Compared with the depth profile of the displaced atoms, the profile of implanted deuterium is generally considered to be distributed in the deeper region. However, it has been reported that most of implanted hydrogen (deuterium) moves to the damaged region assisted by defects. (Pankove & Jhnso, 1991, Cohen & McCracken, 1979). Therefore, it is expected that the accumulations of the defects and implanted deuterium occur in the near-surface of silicon under 5 keV irradiation while being deeper in silicon for 15 keV irradiation.

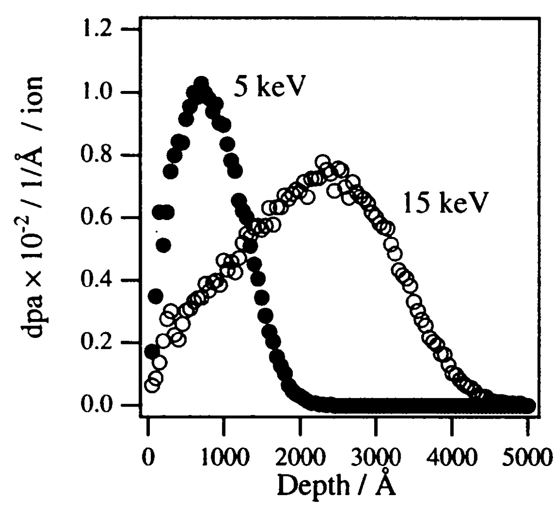

Figure 1
Depth distribution of the number of displaced atoms per incident ion (dpa) calculated by the TRIM code.

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4. XANES spectra of deuterium irradiated silicons

We applied Si K-edge XANES recorded in a total electron yield mode to the analysis of these two kinds of deuterium irradiated silicon samples. Fig. 2 shows Si K-edge XANES spectra of unirradiated silicon (a) and deuterium irradiated silicons with incident energy of 5 keV (b-d). The XANES spectrum of a pure silica glass is also shown in Fig. 2 (e) as a reference. The features of the XANES spectrum changed with increase of D^+ ion fluence. After the irradiation of 1.6×10^{18} ions/cm^2, characteristic peaks of unirradiated silicon disappeared [Fig. 2(b)], indicating that the regular tetrahedral structure of silicon was disordered by D^+ ion bombardment. In this spectrum, a pronounced peak at around 8 eV was also appreciable. Since the energy position of the peak agreed with that of the large characteristic peak of silica [Fig. 2(e)], this result clearly indicates that the target surface was oxidized to SiO_2. As shown in Fig. 2(a), the peak corresponding to SiO_2 was not observed for the XANES spectrum of unirradiated silicon. Accordingly, the appearance of SiO_2 species can be regarded as an indication of displacement of surface silicon atoms, which easily attract or bind oxygen in residual gas during the irradiation and/or in atmosphere during the transfer for the XAFS measurements.

In addition to the surface oxidation, as shown in Fig. 2 (c, d), when D^+ ion fluence was over ca. 2×10^{18} ions/cm^2, a remarkable change was observed in the XANES spectra. This strongly indicates that the electronic and atomic structures of these samples changed to others from those of a pure silicon, i.e., such a change is much considerable compared with the merely disordering of the regular tetrahedral structure of silicon as shown in Fig. 2 (b). Since the edge due to Si(0) state almost disappeared and simultaneously a sharp peak was observed at around 5 eV, it is likely that most Si(0) atoms changed to new Si species which are in higher valence states by the irradiation. On the basis of the energy position of the new peak, they must be in the intermediate states between Si(0) and Si(4+). However, less valenced silicon oxide like SiO is known to be unstable. (Yamamoto *et al.*, 1995) Therefore the new Si species should correspond to Si-D (SiDn species) formation with implanted deuterium as follows. As mentioned above, under irradiation at 5 keV, the amount of implanted deuterium is less than the number of the displaced atoms. Accordingly the peak due to the Si-D formation appeared after the deuterium irradiation over 2×10^{18} ions/cm^2, whereas the peak due to SiO_2 was clearly observed for the irradiation of 1.6×10^{18} ions/cm^2. Rather drastic structural change as observed between Fig. 2(b) and Fig. 2(c) would indicate abrupt formation of SiDn local structure after the implantation of a certain amount of deuterium ions. The formation of the SiHn species in which Si ions are in the intermediate states between Si(0) and Si(4+) has been reported to occur by the assist of the bubble or crack formation under hydrogen irradiation. (Doyle, 1982, Varma, 1997).

However, as already described above, the analyzing depth of the present XANES (around several nm) is much shallower than the damaged zone shown in Fig. 1. Therefore it is not possible to analyze the deuterium profile over the whole range. And observation of Si-D formation is very limited to the vicinity of the surface. The origin and cause of the Si-D formation very near the surface is still an open question. Similar observation of surface accumulation was reported by Yamamoto et al. for silicon irradiated by 5 keV O^+ ions with the fluence of 7×10^{20} / m^2 (Yamamoto *et al.*, 1996). Probably the surface works as a sink of vacancies which could carry implanted species and allow volume expansion easily to make deuteride or oxide.

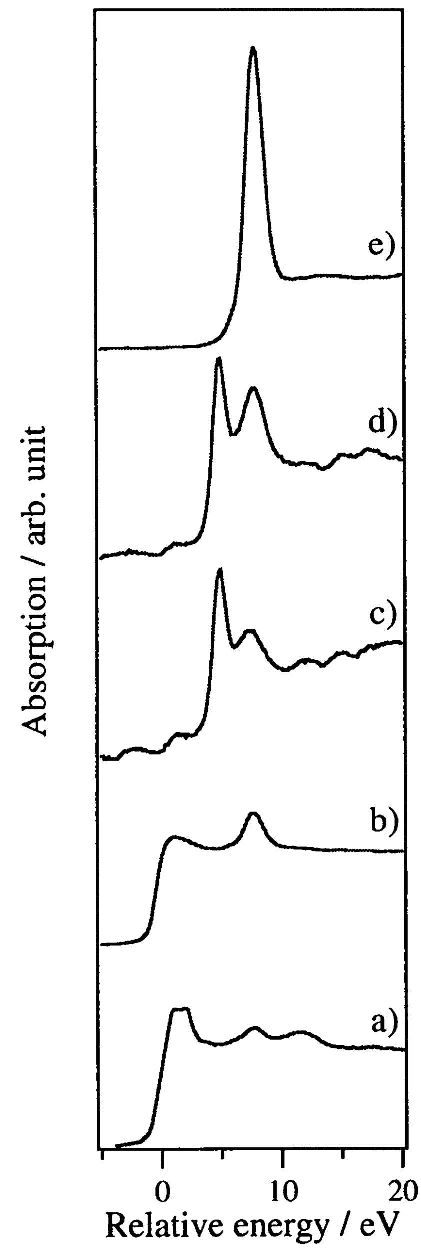

Figure 2
Si K-edge XANES spectra of a) unirradiated silicon, b-d) silicon samples irradiated by 5 keV deuterium ions, and e) a silica sample. The fluence of deuterium ions is b) 1.6×10^{18} / cm^2, c) 2.1×10^{18} / cm^2 and d) 2.9×10^{18} / cm^2. Energy offset is taken to be 1838 eV.

For the sample irradiated with 15 keV D^+ ion, such appreciable change in XANES spectra was not observed. As an example, the Si K-edge XANES spectrum of the sample after irradiation with 2.7×10^{18} ions/cm^2 is shown in Fig. 3(b). Except for the appearance of a small peak attributed to the surface SiO_2, the peak corresponding to Si-D layer was not observed at all. As depicted in Fig. 1, this is because under 15 keV irradiation the accumulations of the defects and implanted deuterium occurred deeper in silicon, which were not reflected in XANES spectra as their depth profiles were out of the analyzing depth of XANES (ca. 30 Å). Thus, the structural modification by ion implantation is very much dependent on the incident energy.

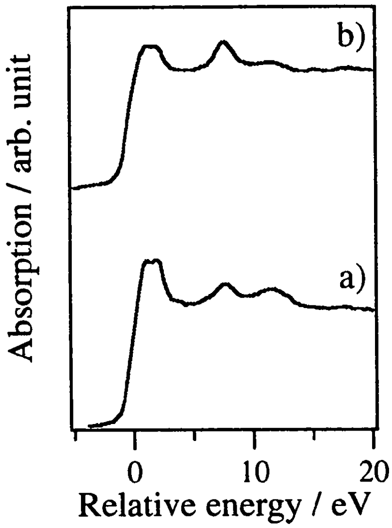

Figure 3
Si K-edge XANES spectra of a) unirradiated silicon and b) the silicon sample irradiated by 15 keV deuterium ions with the fluence of 2.7 × 10^{18} / cm^2. Energy offset is taken to be 1838 eV.

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