METASTABLE AMORPHOUS SiO_2 CREATED BY ION BOMBARDMENT

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Structural changes in thin amorphous SiO_2 (a-SiO_2) films induced by ion bombardment were examined with FT-IR and ESR techniques. 10MeV H^+, 15MeV He^+, 2MeV Li^+, 4MeV C^+ and 30MeV Si^{6+} ions, which traverse the 200nm thick of SiO_2 layer without chemical reaction with SiO_2, were used as ion beams with dosage of 10^{12}-$10^{16}cm^{-2}$. A decrease in the frequency of one peak in the infrared absorption spectrum from $1078cm^{-1}$ to $1041cm^{-1}$ and an increase of a second peak from $805cm^{-1}$ to $830cm^{-1}$ were simultaneously observed with cumulative ion dose. The concentration of E' centers has a maximum as a function of dosage in the region of 1-5×$10^{19}cm^{-3}$. We propose that a reduction of the Si-O-Si bond angle followed by displacement of oxygen is induced with ion bombardment.

INTRODUCTION

It is technologically as well as scientifically important to understand ion-beam-induced phenomena in silica glass (a-SiO_2). Yet, we still know very little about the structural changes in a-SiO_2 induced by MeV ions. For example, structural defects in latent tracks created with MeV ions remain unidentified. In this paper, structural changes in a-SiO_2 were examined with infrared (IR) spectroscopy and electron spin resonance (ESR) using various kinds of MeV ion beams. The results are discussed in term of densification and oxygen vacancies.

EXPERIMENT

SiO_2 films were formed on (100) silicon wafers by thermal oxidation at 1000°C for 3 hours. Commercial silicon wafers are usually doped with B or P and also contain oxygen impurities. To avoid oxygen impurity and dopants in silicon wafers, we used pure silicon wafers having high resistance and fabricated by the Floating Zone method and suitable for FT-IR and ESR. This specially made silicon wafer was fabricated by Shin-Etsu Semiconductor Co. LTD.. Oxidation was performed to obtain ≈200nm thick oxide film. Ion bombardment was performed at room temperature and at a residual pressure below 1×10^{-4}Pa. 10MeV H^+, 15MeV He^+, 2MeV Li^+, 4MeV C^+, 20MeV Si^{4+} , and 30MeV Si^{6+} beams were generated with the Université de Montréal 6MV Tandem accelerator. Electron spin resonance (ESR) measurements were carried out with a standard X-band Brucker ESP-300E spectrometer at room temperature. Absolute spin concentrations were obtained by double numerical integration of the experimental first-derivative spectra. The optimum power needed to obtain the spectra was 20μW. Relative

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error of the ESR signal intensity is within 30%. Infrared (IR) absorption was measured with a Fourier transform IR spectro-photometer using light at normal incidence. Isochronal annealing was performed at 350, 500, 600, and 800°C for 2 hours at a residual pressure below 1×10^{-4}Pa to avoid the effect of oxidation by residual air.

RESULTS

Fig. 1 shows the IR absorption spectra of an a-SiO_2 film before and after irradiation with 2MeV Li^+. There are two first order absorptions in the IR absorption spectra at 1078cm^{-1} and at 805cm^{-1}, which were labeled ω_4 and ω_3, respectively [1]. A decrease of frequency of ω_4 and an increase of frequency of ω_3 were observed to occur simultaneously with increase of dosage.

Fig.2 shows the frequency shift of ω_4 in the IR absorption spectra as a function of dosage. The closed circle stands for the frequency peak at 1078cm^{-1} of a virgin sample as occurring at a dose of 10^{12}cm^{-2}. No change of the IR-spectrum contour was observed after

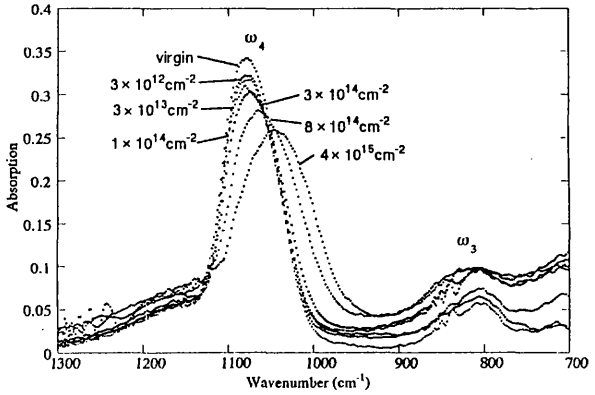

Fig.1 IR spectra of a-SiO_2 films before and after irradiation of 2MeV Li^+ ions. The two absorption peaks are labeled ω_3 and ω_4.

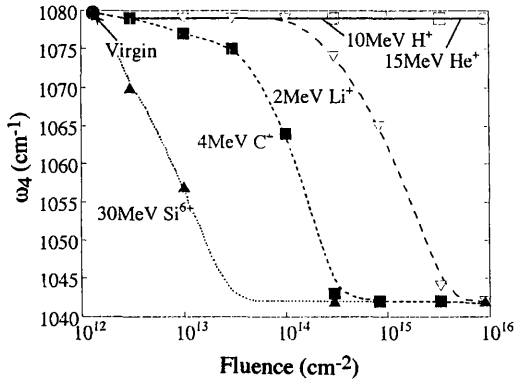

Fig.2 Frequency of ω_4 as a function of cumulative fluence of ion bombardment.

irradiation with either 10MeV H^+ or 15MeV He^+. In case of 2MeV Li^+, 4MeV C^+ and 30MeV Si^{6+} ions, in contrast, the frequency shift starts at dose of about $1\times10^{14}cm^{-2}$, $1\times10^{13}cm^{-2}$ and $1\times10^{12}cm^{-2}$, respectively. The frequency shifts were saturated at $1042cm^{-1}$ and no more change was observed with increase of dosage.

Fig.3 shows the IR spectra of the irradiated samples as a function of annealing temperature. The spectrum contour did not change with 350°C treatment for 2 hours. A frequency shift started from 500°C treatment and the peak frequency with 800°C treatment came back to almost the same position as virgin sample.

Fig.4 presents the concentration of E' centers as a function of cumulative dosage. In the case of 10MeV H+ and 15MeV He+, the E' defect concentration was below the detection limit ($<1\times10^{18}cm^{-3}$). We found that the E' center concentration as a function of cumulative dose had a maximum at $3\times10^{14}cm^{-2}$, $1\times10^{14}cm^{-2}$ and $1\times10^{13}cm^{-2}$ for 2MeV Li^+ , 4MeV C^+, and 30MeV Si^{6+} ions, respectively.

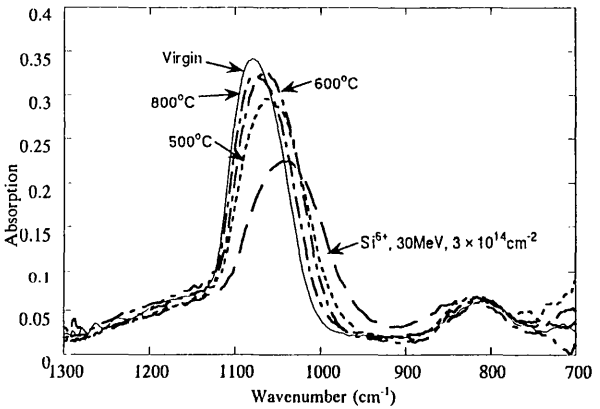

Fig.3 IR spectra of a-SiO with the heating temperature as a parameter. All thermal anneals were performed under residual pressure of $1\times10^{-4}Pa$ and for 2 hours.

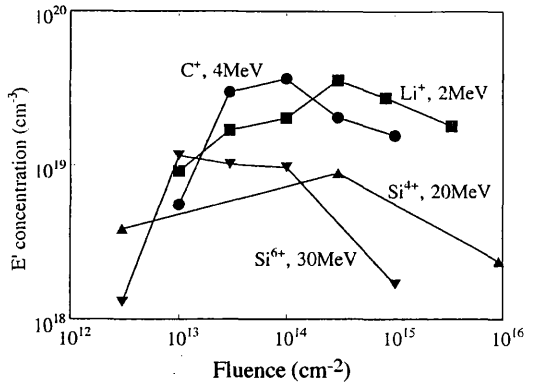

Fig.4 E' concentration as a function of cumulative fluence of ion bombardment.

DISCUSSION

The FT-IR spectra of a-SiO_2 exhibit two principal absorption bands connected to particular vibration modes: the bending vibration at about 805cm^{-1} (ω_3) and the asymmetric stretching mode at about 1078cm^{-1} (ω_4). In a central-force idealized continuous random network theory, the frequencies ω_3 and ω_4 are determined by the Si-O-Si bond angle [2]. The angular frequencies of the calculated modes as a function of bond angle are given by

$$\omega_3^2 = (\alpha/m_O)(1 + \cos\theta) + (4\alpha/3m_{Si}) \quad (1)$$

$$\omega_4^2 = (\alpha/m_O)(1 - \cos\theta) + (4\alpha/3m_{Si}) \quad (2),$$

where α is the central force constant, and m_O and m_{Si} are the atomic weights of O and Si, respectively.

Fig.5 shows the relation between ω_3 and ω_4 as determined from the IR spectra. Frequency ω_3 was increased and frequency ω_4 was decreased with increasing fluence. These results imply a decrease of θ from Eqs. (1) and (2). The solid line denotes the relation between ω_3 and ω_4 in a-SiO_2 at a range of densities, as has been reported in Ref [1]. Ion bombardment data in low dosage region corresponds to the data of densified silica. In contrast, ω_3 in high dosage region of ion bombardment is smaller than ω_3 in high pressure region of densified silica (left and upper side). We assume that the frequency shift can be explained by densification of silica induced by ion bombardment in the region of low dosage.

We now discuss what is happening in addition to densification as a function of dosage. As shown in Fig.4, the E' center concentration induced with each ion beam has maximum as a function of dosage. We notice that the dosage which gives a maximum peak of E' concentration also gives a frequency ω_4 of about 1060cm^{-1}. For example, in the case of 2MeV Li^+, 4MeV C^+ and 30MeV Si^{6+}, the maximum of E' concentration and 1060cm^{-1} value for ω_4 occur at fluence of about $3\times10^{14}cm^{-3}$, $1\times10^{14}cm^{-3}$ and $1\times10^{13}cm^{-3}$, respectively. We do not think that the decrease of E' concentration in the high dosage region implies a decrease of the concentration of defects. The maximum concentration of E' centers for each ion is located in the range of $1\text{-}4\times10^{19}cm^{-3}$ (≈0.05-0.2mol%). When the E' center concentration exceeds 0.05-

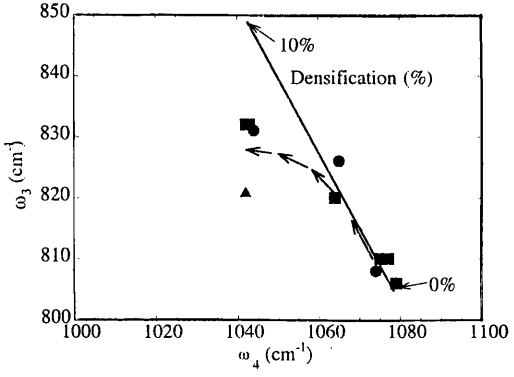

Fig.5 Relation between ω_3 and ω_4 in a-SiO_2 with ion bombardment. Arrows indicate increasing ion dose. Solid line denotes the relation in densified silica reported in Ref. [1].

0.2mol%, some E' centers transform to non-paramagnetic centers by interaction with one another (E'- E' interaction). If we would implant a small amount of oxygen into the damaged layer, we would find an increase in paramagnetic center.

The IR spectrum of a-SiO_2 irradiated and annealed at 800°C is almost the same as that of unirradiated a-SiO_2. It is unlikely that residual oxygen acts as the terminator of defects because the residual pressure during all annealing procedure was below 1×10^{-4}Pa. We assume that this recovery is responsible for two things, the relaxation of densification on the one hand, and that knock-on oxygen produced by ion bombardment diffuses and compensates vacancies such as E' center, on the other.

It was found that IR spectrum was not further affected with very high dosage. It seems that a sort of metastable structure is reached in SiO_2. We speculate that the saturation of the ω_4 peak shift is due to a thermal equilibrium reaction. The densified structure induced by ion bombardment is simultaneously annealed with ion bombardment. Oxygen displaced by ion bombardment is also expected to undergo dynamic annealing.

It is not obvious which aspect of the ion - solid interaction causes the damage. For the ion - energy combinations investigated here, similar damage levels are reached by scaling the ion dose with a factor of 10 (Si to C or C to Li) or 100 (Si to Li). The nuclear stopping, electronic stopping, and momentum each are different by a factor of about 3 (Si to C or C to Li) or 9 (Si to Li). No single parameter can be identified, nor is it clear whether a combination of the above parameters plays a role or whether other factors such as dynamic annealing come into play as well. Nevertheless, it is remarkable that the evolution of the damage with increasing ion dose is similar for all three ions in spite of the fact that the nature of the damage changes from compaction (at low fluences) to predominantly oxygen vacancies (at higher fluences until saturation).

CONCLUSIONS

The initial response of pure a-SiO_2 to irradiation with multi-MeV ions is a compaction and a decrease in Si-O-Si bond angles, as induced from the concerted frequency shifts of two absorption at 1078cm^{-1} and 805cm^{-1}. Continued irradiation leads to saturation in the density of E' centers as measured by ESR while at the same time the frequency shifts indicate damage other than compaction. The additional damage is thought to consist of oxygen vacancies, those being responsible for the E' signal. This would be consistent with the observation that annealing at temperatures of up to 800°C suffices to restore the network almost completely to the unirradiated state. The E' density saturates at roughly 0.1 mol%, and at ion dose where this occurs, the IR absorption bands shifting any further, indicating that a quasi-equilibrium (or metastable state) has been reached between the damage introduced by additional ions and dynamic annealing. It was found that heavier and more energetic ions require lower dosage to reach a certain level than do light or less energetic ions but no simple scaling law could be established.

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