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Structural defects and chemical interaction of implanted ions with substrate structure in amorphous SiO_2

Hideo Hosono
Research Laboratory of Engineering Materials, Nagatuta, Tokyo Institute of Technology, Midori-ku, Yokohama 227, Japan

Noriaki Matsunami
Crystalline Materials Science, School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan

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Structural defects in SiO_2 glasses implanted with Li^+, N^+, O^+, F^+, Si^+, and P^+ ions were examined by vacuum-ultraviolet-absorption and electron-paramagnetic-resonance spectroscopies as well as thermal-gas-release analysis. The chemical interaction of implanted ions with substrate structure was considered on the basis of the obtained results. It is found that the type of predominant defects is controlled by the electronegative nature of implants. Silicon-silicon homobonds, which are oxygen-vacancy-type defects, are produced by electropositive implants (i.e., Li, P, and Si) at concentrations comparable to those of the implants. On the other hand, in the case of electronegative implants (F and O) O_2 molecules and peroxy radicals (POR), both of which may be regarded as oxygen-interstitial-type defects, are the major defects and the total concentrations of these two defects are comparable to implant concentrations. These results indicate that chemical interaction of implanted ions with SiO_2 is primarily controlled by the electronegative nature of implants. Electropositive implants (M) react chemically with oxygen atoms in the substrate structure to form M-O bonds, leaving Si-Si bonds. Electronegative implants (A) react chemically with silicon atoms to form Si-A bonds and oxygen atoms recoiled with implants combine with each other to form O_2 molecules or react with the silica-network structure to form POR's. Concentrations of these predominant defects relative to implants can be used quantitatively to describe the strength of chemical interactions. When the chemical interaction is strong, both concentrations are comparable. On the other hand, when the chemical interaction is weak, concentrations of these defects are much smaller than those of implants because the major fraction of implants occur in a neutral state without forming chemical bonds with constituents of the substrate. Nitrogen is an example of this category and the major fraction of implanted nitrogen atoms are present as N_2 molecules.

I. INTRODUCTION

Ion implantation is a processing technique to significantly modify surfaces and near-surface properties of materials.[1-3] Implantation in glass has been mainly used to modified optical properties such as refractive index. Various phenomena specific to implants, such as the formation of compounds between implants and constituents of substrates and colloid formation of implants, are known as chemical effects. The understanding and utilization of these phenomena are keys to the effective modification of glasses and the preparation of novel photonic glasses. For example, the increment of the refractive index of SiO_2 glasses implanted with N ions is greater by several times than that with other ions. This is explained as due to the formation of high-index clusters or phases such as SiON and Si_3N_4, besides densification effects which commonly occur in implanted SiO_2 glasses.[4] Recently, nanometer-sized colloid particles of metals and semiconductors embedded in glass have attracted attention because these composite glasses exhibit a large third-order optical susceptibility originating from quantum confinement effects. The elucidation of these chemical effects, is, therefore, indispensable for a comprehensive understanding of ion-beam interaction with solids, and the conclusions obtained should provide a fundamental basis for ion-beam modification of glasses as well as the creation of new photonic glasses. Various types of structural defects are produced in glasses along their trajectories as a consequence of the interaction of ion beams with glass. We examine structural defects in implanted glasses and consider chemical interaction of implanted ions with the substrate structure of glass on the basis of obtained results.

Amorphous SiO_2 (a-SiO_2) was used as a substrate appropriate for the present purpose for the following reasons: (a) it has a simple stoichiometry and the fewest impurities; (b) point defects are simple due to the strong localization of electrons. Knowledge about diamagnetic defects as well as paramagnetic defects in a-SiO_2 has accumulated over the past three decades;[5] (c) a-SiO_2 has a less dense-packed structure composed of building units of SiO_4 tetrahedra, hence, it is possible to identify and quantify *molecular species,*[6] which are expected to be created during implantation as an interstitial defect by using a vacuum extraction technique at elevated temperatures.[7]

II. EXPERIMENT

Substrates used were SiO_2 glasses (hydroxyl content: $\sim 4\times10^{19}$ cm^{-3}) prepared by hydrolysis of $SiCl_4$ with an O_2-H_2 flame. Some hydroxyl-free synthetic silica glasses prepared via a dechlorination process are known to have an intense absorption band peaking at around 7.6 eV even in the as-delivered state.[8] The presence of this band in virgin samples would obscure the effects we seek to observe. One side of the glass plate specimens ($2\times2\times0.05$ cm thick) was implanted at room temperature with Li^+, N^+, O^+, F^+, Si^+, and P^+ ions at 160 keV. Doses and dose rates were 3×10^{16} ions/cm^2 and ~3 μA/cm^2, respectively. This dose level was chosen because it is possible to identify and quantify relevant defects without serious errors. Substrates were wrapped with an Al foil to avoid charging effects. The temperature of substrates during bombardment measured by a thin-film-type thermocouple was ~40 °C.

Vacuum ultraviolet absorption (VUV) spectra were measured in the wavelength region of 150–250 nm with a single-beam spectrophotometer (light source: D_2 lamp). Electron paramagnetic resonance (EPR) spectra were measured at 300 and 77 K at the *X* band, applying 100 kHz field modulation and spin concentrations were evaluated by a comparison method using a $CuSO_4\cdot5H_2O$ crystal. Fourier-transform infrared-absorption (FTIR) spectra of implanted specimens were measured at an attenuated total reflection (ATR) configuration[9] to extract information on implanted layers. A germanium (refractive index=4) prism was used as an internal reflection element of ATR measurements. The calculated penetration depth of infrared radiation under these measurement conditions is 0.2–0.8 μm, depending on the wavelength.[9] Gases released from implanted substrates upon heating were analyzed with a thermal-gas analyzing instrument (Ushio, Tokyo, Japan), which consists of a high-vacuum system ($<5\times10^{-7}$ Pa), a quadrupole mass spectrometer (range $m/e=1-200$), where *m* and *e* denote mass number and charge, respectively), and an electric furnace. The detection limit of the instrument is $\sim2\times10^{14}$ molecules.[7] A heating rate of 5 K/min was employed.

III. RESULTS

Figure 1 (left) shows examples of implantation-induced VUV absorptions, which were obtained by subtracting the absorption spectra of substrates before implantation from those after implantation in order to compensate for reflection losses and absorptions due to the substrate itself. An absorption band centered at ~7.6 eV (7.6-eV band) is observed for all specimens but its intensity drastically varies with an implant as summarized in the Fig. 1 (right). Intensities in substrates implanted with Li^+, P^+, and Si^+ ions are larger by an order of magnitude than those in O- and F-implanted substrates.

Figure 2 (left) shows EPR spectra of implanted substrates. No perceptible signals were observed for substrates before implantation. In substrates implanted with F and O ions, intense signals of peroxy radicals (POR)[10] are seen in the spectra measured at high-microwave power levels (< 10 mW), while *E*′-type centers[11] associated with a Si-Si bond are observed distinctly in place of POR's in P-, Si-, and Li-implanted substrates. *E*′ centers[12,13] were observed in all the specimens at low-microwave power levels (1–10 μW). A concentration ratio of *E*′ centers relative to POR's in P-, Si-, and Li-implanted substrates was evaluated to be ~10, which is much larger than that (~0.1) in F- and O-implanted specimens. In N-implanted substrates this ratio is close to unity. Total concentrations of paramagnetic defects are, at most, 5% of concentrations of implants in each specimen.

Figure 2 (left) shows FTIR/ATR spectra of substrates before and after implantation of fluorine ions. Two changes are observed after implantation. The first is a shift of the two bands due to lattice vibrations. The peak position of the band centered at around 1100 cm^{-1} shifts distinctly to a longer wavelength side, while the peak at around 800 cm^{-1} shifts slightly to an opposite side. Both shifts are attributed to a decrease in the Si-O-Si bridging bond angle. The second is the appearance of a new band around 930 cm^{-1}, which is assigned to the bond-stretching mode of Si-F bonds.[14]

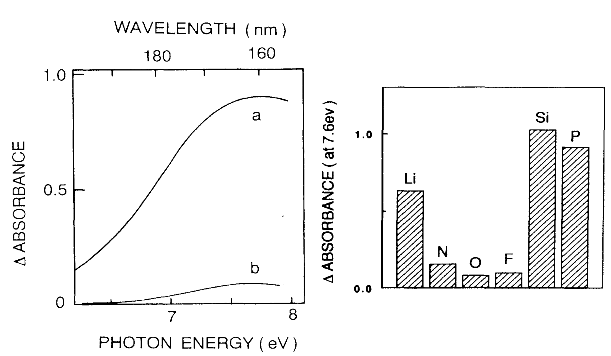

FIG. 1. (left) Vacuum ultraviolet absorptions induced by implantation. Each spectrum was obtained by subtracting the absorption spectrum before implantation from that after implantation. (a) P^+ (b) F^+. (right) Peak intensities of induced 7.6-eV band in implanted substrates.

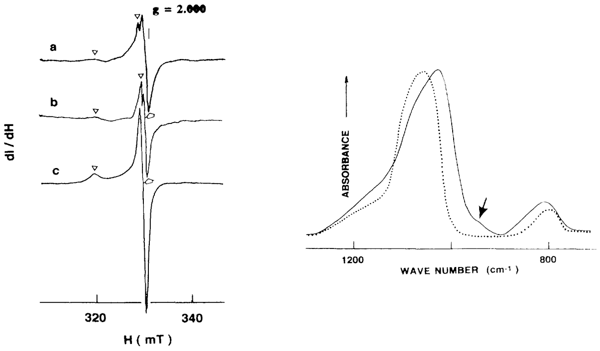

FIG. 2. (left) EPR spectra of implanted silica glasses. (a) P-implanted, (b) Si-implanted, and (c) F-implanted specimens. Measurement conditions: temperature, 77 K, microwave power, 100 mW, frequency, 9.3 GHz. Triangles and arrows indicate resonance fields characteristic of POR (Ref. 10) and *E*′-type center (Ref. 11) associated with a Si-Si bond, respectively. (right) FTIR/ATR spectra of substrates before and after implantation of F ions. — — —, before; ——, after. An arrow denotes a shoulder due to the stretching vibration of Si-F bonds. Shifts in the peak position of bands centered at around 1100 and 800 cm^{-1} are explained by a decrease in the Si-O-Si bond angle (Ref. 9).

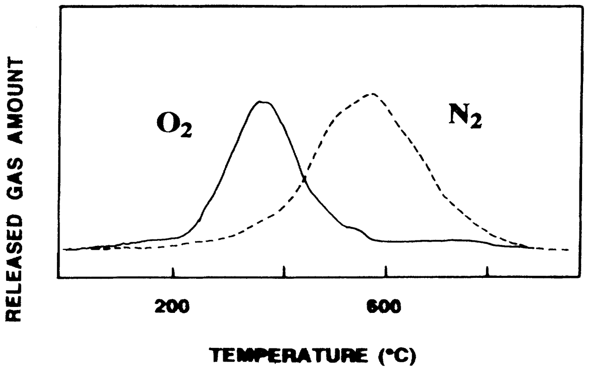

FIG. 3. Gas release of implanted specimen upon heating. — — —, N_2 gas from N-implanted substrate; ——, O_2 gas from F-implanted substrate.

Figure 3 shows thermal-gas-release spectra of substrates implanted with N and F ions. In N-implanted substrates, release of N_2 molecules (monitored by peaks of $m/e=28$ and 14, the latter peak being effective to discriminate N_2 from CO) was observed and the amount released from room temperature to 900 °C was approximately 80% of implanted N ions. Although no detectable amounts ($>2\times10^{14}$ molecules) of F_2 molecules ($m/e=38$) were detected in F-implanted substrates, the release of O_2 molecules ($m/e=32$) was observed in the range 150°–600 °C. Release of O_2 molecules was also observed in O-implanted substrates. No perceptible release of O_2, F_2, or N_2 gas was detected for substrates before implantation or substrates implanted with Li, P, and Si ions.

IV. DISCUSSION

A. Predominant defects produced by implantation

Peak intensities of implantation-induced VUV band centered at 7.6 eV in Li-, P-, and Si- implanted substrates are larger by an order of magnitude than those in O- and F-implanted substrates. It is known that two types of defects with entirely different nature give the 7.6-eV band POR's,[10,15] which is a paramagnetic defect and may be regarded as an oxygen interstitial, and a Si-Si bond,[8] which is a diamagnetic defect and may be regarded as an oxygen vacancy. Concentrations of POR's could be measured separately by EPR and the oscillator strength f of the 7.6-eV band due to POR's ($f=0.65$) (Ref. 15) and Si-Si bonds ($f=0.45$) (Ref. 8) was already reported. Thus, it may be possible to evaluate the participation of POR's and Si-Si bonds to intensities of the 7.6-eV band. The evaluated contribution of POR's is no more than 3% of the observed intensities in substrates implanted with Li, P, and Si. Concentrations of Si-Si bonds calculated from intensities of the 7.6-eV band by subtracting the concentrations of POR's are comparable to those of implants in Li-, P-, and Si-implanted substrates. On the other hand, in F- and O-implanted substrates, intensities calculated from POR concentrations measured by EPR are comparable to observed intensities of the 7.6-eV band, which are smaller by an order of magnitude than those in Li, P, and Si specimens. Concentrations of Si-Si bonds are estimated to be less than $\sim10^{15}$ cm^{-2} (per implanted surface area) in these specimens. On the other hand, numbers of O_2 molecules thermally released from F- and O-implanted substrates are $\sim3\times10^{15}$ cm^{-2} and $\sim7\times10^{15}$ cm^{-2}, respectively, both of which are larger than those of Si-Si bonds. It is, therefore, concluded that Si-Si bonds are not the predominant defect produced by implantation in F- and O-implanted silica. In these specimens, oxygen-surplus-type defects, O_2 molecules, and POR's, are the major defect in place of oxygen-deficient-type defects, Si-Si bonds.

Here we make the following assumptions to obtain quantitative relations between produced defects and implants; (i) fluorine and oxygen atoms occur nominally as -1 and -2 charge states, respectively (it is known that charge states of implants are easily changed after implantation), and thereby, an oxygen atom in the substrate structure is replaced by two implanted fluorine atoms due to the requirement of electroneutrality. This assumption is justified because the formation of Si-F bonds are confirmed by FTIR/ATR spectra (Fig. 2). (ii) A POR is created by reaction of a recoiled oxygen atom with silica network structure. POR's are not created in so-called "wet" (containing a large amount of Si-OHs) SiO_2 glasses irradiated with ionizing radiation such as x and γ rays,[8] but are predominant paramagnetic defects associated with oxygen atoms in the case of ion implantation.[2] Assumption (ii) is based on this result. Following these assumptions, we obtain that the amount of released O_2 molecules corresponds to $\sim45\%$ of $\frac{1}{4}$ of implanted F ions or $\sim40\%$ of $\frac{1}{2}$ of implanted O ions, and POR concentrations correspond to $\sim10\%$ of $\frac{1}{2}$ of implanted F ions or $\sim3\%$ of implanted O ions. Table I summarizes concentration ratios of the predominant induced defects relative to implants. It is evident that the type of predominant defect is classified into three groups, (a) Li, Si, P, (b) O, F, and (c) N. In group (a), concentrations of Si-Si bonds are comparable to those of implants. In group (b) the total concentration of O_2 molecules ($\times2$ for O^+, $\times4$ for F^+) and POR's ($\times2$ for F^+, $\times1$ for O^+), both of which are oxygen-surplus-type defects, are comparable to those of implants. In group (c) concentrations of both types of defects are much smaller than those of implants.

B. Chemical interaction of implants with substrate structure

Let us consider the primary factor to discriminate between the above three groups (a), (b), and (c). First, energy deposition is considered as a candidate. In many cases, defect creation in insulators with ion beams is closely related to nuclear energy deposition (NED) or electronic energy deposition (EED).[16] Table II summarizes the calculated NED and EED (TRIM code[17] was used) when relevant ions are implanted into SiO_2 glasses at an acceleration energy of 160 keV. Both NED and EED vary monotonically with atomic numbers of implants except for the case of Si, in which the efficiency of collisional momentum transfer becomes maximum because masses of both particles are almost the same.[18] We

TABLE I. Concentration ratios of major structural defects produced by implantation relative to implants.

Implants (Electronegativity)	Li (1.0)	N (3.0)	O (3.5)	F (4.0)	Si (1.8)	P (2.1)
$\frac{[\text{Si}-\text{Si}]^{a}}{[\text{Implant}]}$	0.65	~ 0.1	>0.05	>0.05	1.6	1.4
$\frac{n[O_2]+n/2[\text{POR}]^{b}}{[\text{Implant}]}$	$\sim 10^{-3}$	~ 0.1	0.49 $(=0.46$ $+0.03)^{c}$	0.48	$\sim 10^{-3}$ $(=0.38$ $+0.10)$	10^{-3}

[a] Brackets denote concentrations.

[b] POR and O_2 are assumed to be created from one and two oxygen atoms recoiled from substrates of a-SiO_2 (see text). Two F ions form two Si-F bonds, recoiling an oxygen atom. Thus, n is taken as 4 for F or 2 for O.

[c] The former and the latter values denote ratios of O_2 and POR to implants, respectively.

cannot find a correlation between the type of defect and the magnitude of NED or EED.

Next, electronegativity of implants is considered as a factor. Electronegativities (EN) of relevant implants in Pauling's scale are as follows: Li: 1.0, N: 3.0, O: 3.5, F: 4.0, Si: 1.8, and P: 2.1. We found that implants with $\text{EN} < 2.5$ and > 3.5 may be classified into groups (a) and (b), respectively. This indicates that the electronegative nature of implants controls the type of predominant defects created by implantation. Electropositive implants (M), such as Li ions, react chemically with oxygen atoms in the substrate structure to form M-O bonds, leaving Si-Si bonds at concentrations comparable to those of implants. On the other hand, electronegative implants (A), such as F ions knock oxygen atoms out from network structures to form Si-A bonds and the recoiled oxygen atoms combine with each other to form O_2 molecules or react with network structures to form POR's. When the chemical interaction of implants with silica substrates is weak, the major fraction of implants occur in a neutral state, such as elementary colloids and molecules, without forming chemical bonds with silicon or oxygen atoms in the substrate structure. Consequently, concentrations of Si-Si bonds or the total of O_2 molecules and POR's are much lower than those of implants. Nitrogen is an example of this category.

TABLE II. Electronic and nuclear energy depositions calculated with TRIM 85 code. Substrates: SiO_2 glasses (density $2.2 g/cm^3$); acceleration energy: 160 keV.

Implants	Atomic number	Energy deposition [keV(%)] Electronic	Nuclear
Li	3	142(89)	18(11)
N	7	116(73)	44(27)
O	8	108(68)	52(32)
F	9	97(61)	63(39)
Si[a]	14	63(40)	97(60)
P	15	74(46)	86(54)
Cu	29	28(18)	132(82)

[a] The contribution of nuclear energy deposition of $Si \rightarrow SiO_2$ is discontinuously large on going from small to large atomic numbers of implants. This is due to the maximum efficiency of momentum transfer in collision between particles (Si and Si) with the same mass. The mass of oxygen is so small compared to silicon that the enhancement due to this effect does not lead to discontinuity of order on the atomic number scale.

As found in this work (see Sec. III) the concentration ratio of POR's to E' centers varies drastically with implants. This ratio may be classified into three categories which are the same as those described above. Electronegative implants (A) replace oxygen atoms in the substrate structure to form Si-A bonds, causing a large number of oxygen atoms to recoil. Thus, concentrations of POR's, which are produced by a reaction of the recoiled oxygen atoms with silica network, are much larger than those of the E' center. In the case of electropositive implants, the situation is reverse. Implants (M) combine with recoiled oxygen atoms to form M-O bonds. As a consequence, POR concentrations are much smaller than those of E' centers. Implants with weak chemical interaction produce comparable amounts of E' centers and POR's, as in neutron bombarded SiO_2 glasses.[19] The major fraction of copper atoms occur as metal colloid particles in SiO_2 glasses implanted with Cu^+ at 160 keV at a dose of 3×10^{16} cm^{-2} (Refs. 20,21). Also in this case concentrations of POR's were comparable to those of E' centers. Therefore, this concentration ratio will be a good indicator to express the strength of the chemical interaction of implanted ions with SiO_2 substrates. Even when no information can be obtained from VUV absorption spectra due to strong coloration induced by implantation, this ratio will provide fruitful information.

V. CONCLUDING REMARKS

It is concluded that predominant defects produced by implantation in substrates of a-SiO_2 are controlled by the electronegative nature of implants and their concentrations are determined by the strength of chemical interactions. These defects are created by chemical reactions between implanted ions and the substrate structure. Results obtained here suggest that these chemical reactions occur at the final stage of energy deposition of implants. Implants which come to stop have an energy of the order of a few electron volts. Such an order of energy is below the displacement energy (25 eV) of an atom from the lattice site but is enough to induce chemical reactions. Examining relations between depth concentrations of Si-Si bonds and implants is in progress.

When the chemical interaction is strong, Si-Si bonds or O_2 molecules and POR's are created at concentrations comparable to those of implants. Thus, these defects may be regarded as main products rather than defects. Since resulting Si-Si bonds and O_2 molecules are chemically active, they will provide possibilities for coimplantation in realizing chemical bonds which cannot be formed by a simple implantation as exemplified in the formation of Si-N bonds.[22] We expect that application of the present conclusions to the preparation of highly efficient nonlinear optical glasses[23] utilizing photolytic changes of specific defects in a-SiO_2-base materials will be promising.

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