Structure of Br Ions in Br-Ion-Implanted Silica Glass

K. Fukumi1, A. Chayahara1, H. Kageyama1, N. Kitamura1, J. Nishii1, K. Handa2, J. Ide2 and K. Kadono3
1National Institute of Advanced Industrial Science and Technology, Ikeda, Osaka Japan
2Kyoto University, Institute for Chemical Research, Uji, Kyoto Japan
3Kyoto Institute of Technology, Sakyo-Ku, Kyoto Japan

Structure of implanted Br ions has been studied in 2.4MeV 6x10^16 Br ions cm^{-2}-implanted silica glass by X-ray absorption spectroscopy. It was found that most of implanted Br atoms form Br-Si bonds in as-implanted glass. Br atoms were substituted for oxygen atoms in SiO_4 tetrahedra to form SiO_3Br tetrahedra. About 60% of Br atoms formed Br_2 molecules in the glass after heating at 600°C.

Key words: Structure, Br ions, Silica Glass, X-ray absorption

1. INTRODUCTION

Ion implantation is a useful method for doping ions in materials because of its control of ion beam position and of ion concentration. Various kinds of ions have been implanted in silica glass to modify surface properties of glasses and chemical structure of implanted ions has been studied extensively in silica glass. Most of studies have been concerned with implanted atoms which have low electronegativity and act as cations in glass network. The structure of implanted atoms of high electronegativity which act as anions in glasses has scarcely been studied. It is interesting to study the structure of implanted atoms of high electronegativity. In the present study, we have examined the structure of implanted bromine ions in silica glass by X-ray absorption fine structure (XAFS) spectroscopy, both the extended X-ray absorption fine structure (EXAFS) and the X-ray absorption near-edge structure (XANES).

2. EXPERIMENTAL

6x10^{16} 2.4MeV Br^{+} ions cm^{-2} were implanted in a silica glass plate (Yamaguchi Nippon Silica Glass Co., Ltd., direct method, OH content = ca. 1000 ppm, 25x25x2.3 mm in size) which was silver-pasted on a water-cooled aluminum sample holder within a sample chamber of an NT-1500 tandem type accelerator. SRIM code simulation showed that the concentration of Br^{+} ions had maximum at a depth of 1.36 mm with a full width at half maximum of 0.50 mm. The average concentration of the implanted ions was about 15 times greater than the OH concentration.

The fluorescent x-ray excitation spectra of the Br^{+} ion implanted silica glass around a Br K-absorption edge were measured at a BL-12C station of Photon Factory, the National Laboratory for High Energy Physics. The spectra were measured by a Lytle-type ionization chamber equipped with an Se filter. The incident and take-off angles of x-rays were kept at 45° against the sample surface. The measurement was repeated three times at room temperature. The x-ray absorption spectra of liquid SiBr_4 (Wako Chemicals, reagent grade) and liquid Br_2 (Wako Chemicals, 99%) were measured at room temperature for comparison.

The absorption coefficients of X-ray obtained from the fluorescent and absorption measurements were reduced to the interference function, \( \chi(k) \), by the usual method. Then, the interference function, \( \chi(k) \), was multiplied by \( k^2 \) (k: photoelectron wave vector), multiplied by Hanning window function and fourier-transformed into R space. The fourier transformation was carried out over the range of k from 3 to 12 Å^{-1}. The k dependences of the phase shifts and the backscattering amplitude were ignored in the fourier-transformation. For XANES spectra, the absorption intensity was normalized to the atomic absorption at 13500eV that was evaluated from the asymptotic trend at larger energy.

3. RESULTS

Figure 1 shows XANES spectra of Br_2, SiBr_4, as-implanted glass and glass after heating at 600°C. An intense pre-edge peak was observed at about 13465 eV in Br_2 and the glass after heating at 600°C. On the other hand, no such peaks were observed in SiBr_4 and as-implanted silica glass.

Figures 2 and 3 shows the k^2 \( \chi(k) \) curves and the magnitude of fourier transform of k^2 \( \chi(k) \) of Br_2, SiBr_4 and Br-ion implanted silica glass. A peak was observed at 1.98, 1.74, 1.72 and 1.86 Å in the magnitude curves of Br_2, SiBr_4, as-implanted glass and glass after heating at 600°C, respectively.

Figure 4 shows the \( \chi(k) \) curves of SiBr_4 and Br-ion implanted silica glass at low k region. It can be seen that a peak was located at 2.25 and 2.75 Å^{-1} in SiBr_4 and Br-ion implanted glass.

4. DISCUSSION

An intense pre-edge peak due to 1s-4p transition was observed in XANES spectrum of Br_2, as shown in fig. 1. This peak has been observed in solid, liquid and gaseous Br_2. Such a peak was not observed in SiBr_4 and Br^{+} ion implanted glass. The absence of the pre-edge peak indicates that Br_2 molecules were not formed in the as-implanted glass. On the other hand, the pre-edge peak was observed in the glass after heating at 600°C. The intensity of the pre-edge peak in the glass was,
however, lower than that of Br2. The presence of pre-edge peak with low intensity shows that the implanted Br atoms partially formed Br2 molecules in the glass after heating at 600°C.

In the magnitude curves of Fourier transform of k2χ(k), shown in fig.3, a peak was observed at 1.98 and 1.74 Å in Br2 and SiBr4, respectively. These peaks correspond to Br-Br bonds (bond length = 2.30 Å7)) and Br-Si bonds (bond length = 2.15 Å7), respectively. A peak due to Br-O bond should be observed at 1.35 Å, assuming the linear dependence of phase shifts on k8). A peak was observed at 1.72 Å in the as-implanted glass. Since the distance of this peak in the glass was similar to that in SiBr4, shorter than that in Br2 and longer than that of Br2O, it was inferred that the peak at 1.72 Å in the as-implanted glass was assigned to Br-Si bonds, that is, the implanted Br atoms were mainly coordinated with Si atoms. The intensity of the peak at about 1.7 Å in the as-implanted glass was similar to that in SiBr4. Since a Br atom is coordinated with an Si atom in SiBr4, it was deduced that an implanted Br atom was also coordinated with an Si atom in the as-implanted glass. The distance of the peak in the glass after heating at 600°C was shorter than that in Br2, but was longer than that in SiBr4, indicating that Br2 molecules were partially formed. The fraction of Br atoms which form Br2 was obtained by the least-square fitting in R space within the region from 1.08 to 3.46 Å, on assumption that the k2χ(k) of the glass after heating at 600°C can be expressed by the weighed average of k2χ(k) of Br2 and k2χ(k) of as-implanted glass. The magnitude of k2χ(k) obtained from the least-square fitting agreed well with that of the glass after heating at 600°C, as shown in fig. 3. The fraction of Br atoms forming Br2 molecules was about 60%.

Figure 5 depicts the scattering paths calculated by FEFF.

The magnitude curves of BrOBr and Br2-Br model structures at low k region were calculated theoretically from Ab initio self-consistent real space multiple-scattering code (FEFF8.0).11) The latter model implies that oxygen atoms are substituted by Br atoms, since silica glass has three-dimensional random network structure of SiO4 tetrahedra. In this calculation, an SiBr4 tetrahedron has Td symmetry with a Br-Si distance of 2.15 Å. An SiBr2 tetrahedron has C3v symmetry with a Br-Si distance of 2.15 Å, an O-Si distance of 1.62 Å and a Br-Si-O angle of 109°28’ degree. Figure 5 depicts the scattering paths calculated by FEFF. The 1st and 2nd paths are the single scattering paths and the 3rd path is the multiple scattering path. As shown in fig.4, the sum of χ(k)’s of 1st, 2nd and 3rd paths of SiBr4 model structure agreed fairly well with the empirical χ(k) curve for SiBr4, although χ(k) of 1st path or the sum of χ(k) of 1st and 2nd paths did not agreed with the empirical χ(k). The sum of χ(k)’s of 1st, 2nd and 3rd paths of SiBr2 model structure, however, did not agreed with the empirical χ(k) of as-implanted glass. The sum of χ(k)’s of 1st, 2nd and 3rd paths of SiO3Br model structure agreed fairly well with the empirical χ(k) curve of as-implanted glass, although χ(k) of 1st path or the sum of χ(k) of 1st and 2nd paths did not agreed with the empirical χ(k). These findings indicate that the difference in χ(k) in the region from 2 to 3 Å-1 was due to the effect of 3rd path. The third path is Br-Si-Br and Br-Si-O in the SiBr4 and SiO3Br models, respectively. Therefore, the difference in χ(k) in the region from 2 to 3 Å-1 shows that Br-Si-O was mainly formed in the as-implanted glass, but Br-Si-Br was scarcely formed. In other words, more than one Br
atom was not included in one tetrahedron.

In a previous study, it was proposed that implanted ions form elemental colloid particles in silica glass when free energy of formation of oxides of implants is greater than that of silica at 3000K. The extension of this idea suggests that the chemical structure of implanted ions depends on the thermochemical stability of the system of implanted ions-matrix at 3000K. The most stable state is the state that Br atoms are present as Br monoatomic gas in the Br-SiO₂ system at 3000K. Translational movement of Br atoms must, however, be permitted in silica glass in order to act as gas, that is, silica glass must be swollen to form cavities filled with Br monoatomic gas. Such a condition would not be attained at low local concentration of Br atoms, since the number of Si and O atoms is much greater than that of Br atoms and the bond strength of Si-O is high. On the other hand, it is expected that the chemical state in which Br monoatoms dissolve in silica glass network isolatedly has lower entropy and higher Gibbs energy of formation due to the lack of translational movement. These considerations suggest that the chemical state in which Br-Si bonds are formed has the lowest Gibbs energy of formation at 3000K among all the chemical states except for the formation of monoatomic Br gas.

On the other hand, it was deduced that the formation of Br₂ molecules were more stable than the formation of Br-Si bonds at 600°C.

5. CONCLUSION
Structure of implanted Br ions has been studied in Br²⁺-ion implanted silica glass by X-ray absorption spectroscopy. It was found that most of implanted Br atoms form Br-Si bonds in the as-implanted glass. Br atoms were substituted for oxygen atoms in SiO₄ tetrahedra to form SiO₃Br tetrahedra. About 60% of Br atoms formed Br₂ molecules in the glass after heating at 600°C.

Acknowledgment:
This work has been performed under the approval of the Photon Factory Program Advisory Committee (Proposal No.2006G316).

References
Structure of Br Ions in Br-Ion-Implanted Silica Glass


(Received January 15, 2009; Accepted February 15, 2010)