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SURFACE AND BULK VIBRATIONS IN ION-IMPLANTED AMORPHOUS SILICA*

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ABSTRACT

Infrared reflection spectroscopy (IRS) has been used to identify the Si-O vibrational mode and confirm previous assignments of Si-OH, and Si-OD vibrational modes in porous amorphous silica implanted with heavy ions and with H^+ and D^+ ions. The Si-O stretching mode (∿ 1015 cm^{-1}) is produced by the damage cascade and is seen in all implanted bulk silicas as well as in porous silica. Implantation of porous silica with H^+ and D^+ ions produces bands at ∿ 985 cm^{-1} and ∿ 960 cm^{-1}, respectively. The position of all three bands is consistent with O, OH, and OD mass considerations. Implantation of D^+ ions into porous silica containing molecular water and OH^- groups results in D-H exchange. The Si-OH and Si-OD vibrations are also seen in bulk fused silica at low H/D fluences. These results suggest that intrinsic E′-type defects in bulk silica and dangling Si bonds at internal surface sites.

INTRODUCTION

Dangling-bond defects (e.g., Si-O) are formed in the near-surface region of ion-implanted silica and the vibrational modes of these defects can be readily identified using infrared reflection spectroscopy (IRS). Ion implantation further allows the incident ion to be chemically incorporated in the damage region formed by the stopping process. H and D implantations result in the formation of Si-OH and Si-OD modes in addition to the Si-O mode observed for heavy-ion implantation, and have been identified for the first time in this study. The identifications of the H and D modes agree with Raman studies of Hartwig, et al.[1] on gamma-irradiated fused silica loaded with H/D in overpressure soaking. We have also identified these modes in porous silica (CGW 7930). In this case, the H and D ions associate with dangling Si bonds at internal surface sites. The large internal surface area (200 m^2/g) greatly increases the number of these modes relative to bulk fused silica and makes investigation of such modes easy. Implantation of D ions into porous glass shows D-H exchange with surface species involving O, Si, and B. The results for Si-OH and Si-OD are in agreement with IR studies of Boccuzzi, et al.[2] on silica powders with and without H/D ambients, and with Raman studies of Murray, et al.[3] on porous glass exposed to H/D atmospheres. The removal of alkali from the near-surface region by inert-gas ion implantation and indiffusion of surface H further confirms the Si-OH assignment.

EXPERIMENTAL

Corning glasses 7940 and 7930 were used in this investigation. CFS 7940 is a high-purity silica glass (Type III) made by hydrolization of $SiCl_4$ in an oxyhydrogen flame. CGW 7930 is a porous silica glass ("thirsty" Vycor) in which a B_2O_3 phase

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has been leached out leaving a structure in which the pores are approximately 40 A diameter. Implantations were made using an Accelerators, Inc. implanter (50-500 keV). IRS measurements were made using a Beckman IR 12 spectrophotometer with a N. J. Harrick reflectance attachment at an angle of incidence of 20°.

RESULTS AND DISCUSSION

Figure 1 shows the IRS spectra after implantation of 3.5×10^{16} 200 keV A^{++}/cm^2 into bulk fused silica in the spectral region of the Si-O-Si vibrations between 400 and 1300 cm^{-1}. Decrease in intensity and an energy shift of the Si-O-Si stretching vibration is caused by the disorder introduced by implantation. In particular, the decrease in intensity is proportional to the product of energy density into displacement processes and the ion range.[4] The reflectance peak induced by the A^{++} and other heavy ions occurs near 1015 cm^{-1}. It is worth noting that, (1) a peak at this energy can be seen in the reflectance data of Simon[5] for fused silica after a fast-neutron fluence of 2×10^{20} n/cm^2, and (2) that the vibrational mode ascribed to dangling Si-O bonds in the alkali oxide-silica glass system occurs at 935-950 cm^{-1}. Since the latter is clearly seen only at molar concentrations of alkali oxide exceeding about 20%,[6] we believe that this mode is typical of phase separated alkali-rich regions of the binary glasses and that the 1015 cm^{-1} band represents that of the dangling Si-O species in pure silica. Experiments on a SiO_2:12%K_2O glass, implanted with 7×10^{16} 250 keV Xe^+ ions/cm^2 in order to remove the K ions,[7] show that the 935 cm^{-1} band in the unimplanted glass is replaced by a 980 cm^{-1} Si-OH band as H from the surface replaces the K ions.

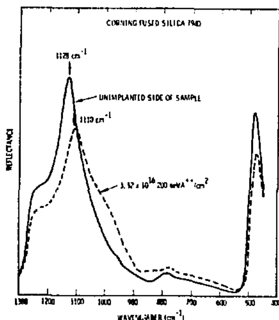

Fig. 1. Reflectance vs wavenumber for CFS 7940 after implantation of 3.5×10^{16} 200 keV A^{++}/cm^2 compared to the unimplanted side.

The results obtained by implantation of bulk fused silica with H- and D-ions are shown in Fig. 2. The reflectance maximum induced by H-implantation is at about 985 cm^{-1} which agrees with the expected value assuming that the 1015 value is that for the Si-O stretch. The D-ion also generates sufficient damage for this mode to be seen at 1015 cm^{-1}. Both the H and D implantations at these relatively low fluence levels produce dispersion in the reflectance curve. This dispersion is more clearly seen (different samples and fluences) in the difference spectra in Fig. 3. The positions of the two modes are clearly different even though the exact positions are difficult to determine in this case. These fluence levels cause little or no change in the intensity or position of the Si-O-Si band. At high fluence levels, the 1015 cm^{-1} damage band overwhelms the Si-OH and Si-OD modes.

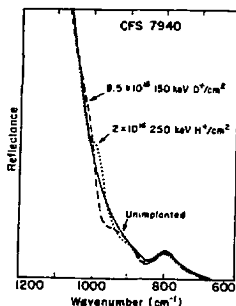

Fig. 2. Reflectance vs wavenumber for CFS 7940 after H- and D-implantation as shown compared to unimplanted sample.

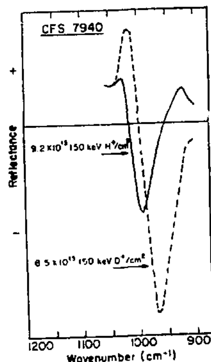

Fig. 3. ΔR vs wavenumber for CFS 7940 after H- and D-implantation as shown. ΔR is difference between implanted sample reflectance and that of the unimplanted side.

The use of porous silica glass (CGW 7930 Vycor) allows a much easier assignment to be made. In Fig. 4 are shown the results for Ne, H, and D implantations into 7930 glass. The samples were heated for 30 min. at 400°C prior to implantation. Induced bands at 1015, 985, and 960 cm^{-1} are clearly evident and are consistent with the assignment at Si-O, Si-OH, and Si-OD stretching modes, respectively. The effect of exchange of D for H is most evident at higher wavenumbers, as can be seen in Fig. 5 for the spectral region from 2000-3800 cm^{-1}. The easy exchange of D for H confirms the surface nature of the species. Before implantation the absorption at the H-bonded OH frequency of about 3650 cm^{-1} is the only apparent feature. After the D-ion implantation, however, the OD mode at about 2700 cm^{-1} is evident as

well as the other features labeled on the figure. Also observed, but no shown, are modes due to H-O-D, B-O, B-OH, and B-OD in the spectral range of 1200-2000 cm^{-1}. A common feature of all implants into porous glass is the increased intensity of reflection after implantation, which is evident from the data in Figs. 4 and 5. This increase is due to the known action of ion-implantation in reducing the interstitial alkali concentration in the near-surface region which results in increased strength of the fundamental SiO_4 tetrahedral vibrations.

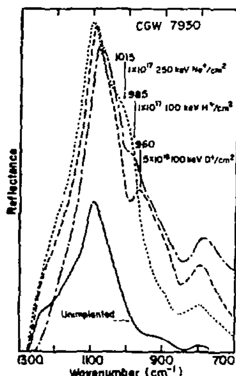

Fig. 4. Reflectance vs wavenumber for CGW 7930 porous glass after Ne-, H-, and D-implantations compared to an unimplanted reference sample.

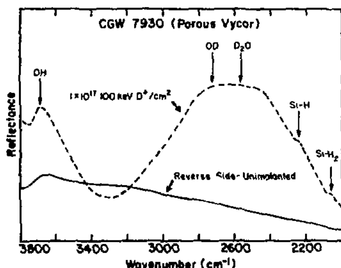

Fig. 5. Reflectance vs wavenumber for CGW 7930 porous glass after implantation with 1x10^{17} 100 keV D^{+}/cm^{2} compared to the unimplanted reverse side.

CONCLUSIONS

The results reported here indicate that a basic feature of the damage in ion-implanted silica is the dangling-oxygen bond (Si-O), producing a vibrational mode at about 1015 cm^{-1}. The results also show that the surface vibrational modes

Si-OH and Si-OD produced in porous glass by H- and D-ion implantation are seen, at nearly the same wavenumber, in bulk fused silica at low H- and D-fluences. This observation suggests that the H/D ions in fused silica are incorporated at sites which are similar to isolated surface sites. These internal surfaces represent sites for dangling Si valence bonds, i.e., intrinsic E′-centers, and the concentration of intrinsic defects is estimated to be from 10^{19}-10^{20} cm^3. The correspondence of irradiation produced E′-centers in bulk fused silica with those generated at the surfaces of ground silica powders has been noted by Arends, et al.,[8] and Hochstrasser and Antonini.[9] The present results and the earlier work of Boccuzzi, et al.[2] have also shown that the surface modes associated with Si-OH and Si-OD are readily seen by IR techniques in both porous silica glass and in silica powders. The bands were seen only in Raman scattering in the experiments of Murray, et al.[3] in which considerable care was taken to avoid atmospheric contaminants. Laughlin and Joannopoulos[10] used a Bethe lattice to model the surface sites in order to account for the non-appearance of this mode in the IR in these experiments.

The advantages of ion-implantation in glass studies have been exploited in the present experiments, i.e., (1) creation of a high-density damage region which allows the Si-O mode to be seen, (2) the incorporation of the incident ion (H/D) in the damaged region or at surface sites, and (3) the action of incident ions in sweeping out alkali network-modifier ions from the surface where the simultaneous in-diffusion of surface H allows a different means of establishing Si-OH modes.

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