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Annealing Effects in Reducing and Oxidizing Atmospheres**

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CARBON IMPLANTED IN OPTICAL GRADE FUSED SILICA: ANNEALING EFFECTS IN REDUCING AND OXIDIZING ATMOSPHERES

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ABSTRACT

Carbon is implanted into fused silica with doses of 1, 3, 6, 10×10^{16} ions/cm². Infrared spectroscopy identified the formation of CO and CO₂ molecules in the implanted glasses. The relationships among concentrations of carbon dioxide, carbon monoxide and carbon doses are established by the infrared measurements. Annealing under different atmospheres have dramatic effects on CO and CO₂ concentrations.

INTRODUCTION

Ion implantation has become an important technique to modify the electrical, optical and mechanical properties of insulator materials.¹⁻³ Ion implantation can create a supersaturated solution at the surface or near surface regions of insulators. This supersaturated material can be utilized to synthesize nano sized materials.⁴⁻⁵ Therefore, the understanding of the chemistry and nature of the interactions between the implanted ions and insulators become important.

In this paper, we have focused on the carbon implantation into fused silica. Unlike previous ion implantation studies, the implanted carbon is likely to produce many different chemical reactions. Previously, it has been observed that the implanted carbon in silica can form carbon dioxide and carbon monoxide molecules.⁶ It is intriguing that the CO and CO₂ formed in the fused silica have a very different spectroscopic behavior from that of the gas phase molecules. These differences may reveal the unique physical statuses of the CO and CO₂ embedded in the matrix. Additionally, it may be possible to synthesize SiC quantum dots under certain annealing conditions.

We applied both external reflectance and absorption infrared spectroscopy to characterize the various carbon compounds formed in the implanted systems. The infrared reflectance technique can only sample certain depth of materials below the surface. On the other hand, the infrared absorption technique can sample the whole sample thickness, if the absorption is not saturated. Both techniques revealed the formation of CO and CO₂ in the implanted systems and their concentrations varied with implantation doses and annealing conditions. The concentrations of CO increased linearly with ion doses, while the concentrations of CO₂ have reached its saturation. Annealing at different temperatures under oxygen suggests an increase of CO concentration and a decrease of CO₂ concentration. Annealing under hydrogen reduces both the concentrations of CO and CO₂. These observations will improve our understanding about the reactions between implanted carbon and silica matrix.

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page 1 of 2

EXPERIMENTAL

Carbon implantation into fused silica at room temperature was carried out at an energy of 160 KeV and at doses of 1, 3, 6, and 10×10^{16} ions/cm². The doses reported are nominal doses as determined by current integration.

Thermal annealing processes were performed at 600°C, 700°C, and 800°C for 30 minutes under both an oxidizing atmosphere (O₂ + Ar) and a reducing atmosphere (H₂ + Ar).

The XPS spectra were collected by a Perkin-Elmer PHI Model 560 ESCA. The 0.834 nm X-rays (Mg K α line) was generated by impacting the magnesium anode with 15 Kev electrons at a power level of 300 W. The base pressure of the instrument was maintained at $1-3 \times 10^{-9}$ torr. The pass energy of the double-pass cylindrical mirror analyzer was kept at 25 eV to achieve a 0.5 eV resolution. The shift of the binding energy was calibrated by assuming the binding energy of C 1s is always at 284.6 eV. To obtain depth profiles of the carbon implanted glass, XPS spectra were collected while the sample was sputtered by a 2.8 keV Ar ion beam with a size of 6×6 (mm)². The sputtering rate was around 60 Å/min, which was calibrated by using a 900 Å SiO₂ on Si standard sample. A curve fitting program was employed to calculate the peak areas of C 1s signals in the XPS spectra collected at different depth. The C 1s integrated area is directly related to the carbon concentration at different depth of the implanted sample.

The infrared spectra were measured by using a Bomem DA3 Fourier Transform Infrared Spectrometer. The instrument, as configured with a KBr beamsplitter and narrow band MCT detector, covers a range from 4000-800 cm⁻¹. Each spectrum is collected with 500 scans at 4cm⁻¹ resolution. The instrument is evacuated to a pressure of around 1 torr for both background and sample measurement. The reflectance measurements were carried out by using a homemade reflectance accessory. The incidence angle is around 10 degree. The intensities of the CO and CO₂ band were determined by using a Gram-386 software to integrate the area under the peak.

Fig. 1 Depth profile of carbon in 6×10^{16} ions/cm² sample.

RESULTS

The depth profile of the implanted carbon is determined by both TRIM calculations and XPS with ion sputtering technique. The TRIM calculation and XPS results are illustrated in Fig. 1. TRIM calculations indicate that the maximum carbon concentration is located at 4500 Å below the surface and the full width at the half height (FWHH) is 1300 Å. The carbon 1s peak areas of the XPS spectra demonstrate similar carbon distributions with the maximum carbon concentration also at 4500 Å below the surface and the FWHH is 1000 Å.

Birbring *et. al.* found that the implantation of carbon into fused silica leads to the formation of CO and CO₂.⁶ They identified this formation via infrared spectroscopy. The peak position for CO₂ is at 2329 cm⁻¹ and for CO is at 2121 cm⁻¹. These peak positions shift to lower wavenumbers than those of the gaseous phase and they appear as single bands unlike gaseous molecule that exhibit rotational fine structure. The reflectance spectra of substrates implanted with 1, 3, 6, and 10x10¹⁶ ions/cm² are plotted in Fig. 2a and the absorption spectra are in Fig. 2b. The humps located at 2200 cm⁻¹ in Fig. 2a b are due to uncompensated contributions from glass. Both CO and CO₂ appear in

Fig. 2a Reflectance spectra of the as-implanted silica with carbon concentrations of 1-10x10¹⁶ ions/cm².

Fig. 2b Absorption spectra of the as-implanted silica.

Fig. 3a CO₂ absorption intensity vs ion dose.

Fig. 3b CO₂ reflectance intensity vs ion dose.

Fig. 4 CO reflectance intensity vs ion dose.

the reflectance and absorption spectra at peak positions reported by Birbring *et. al.* Qualitative analyses from Fig. 2a,b indicate both the CO and CO₂ band intensities increase with the implantation dose and the CO intensities increase at a much faster rate than CO₂. In terms of quantitative analysis, the absorption spectra are used since the measurement probe whole thickness of the sample. The reflectance measurements, on the other hand, are limited to the penetration

depth of the light. For absorption spectra, only CO_2 band is available for quantitative intensity calculation. The CO band is located at a region where the absorption of glass is too strong for quantitative analysis. Fig. 3a shows plots of the CO_2 absorption peak intensities vs the ion implantation doses. Based on the Beer's law, the peak intensity is proportional to the concentration. Fig. 3a indicates that the peak intensities of CO_2 increase with carbon fluence and reach saturation at higher doses. The same result is also demonstrated in Fig. 3b which plots the reflectance CO_2 intensities with carbon doses. Fig. 4 plots the reflectance CO intensity for the ion doses of $1\text{--}10 \times 10^{16}$ ions/cm². Contrary to CO_2 , the intensities of CO increase linearly with the ion dose.

DISCUSSION

The preferred formation of CO at high carbon doses could be due to reactions of carbon and oxygen, carbon and carbon dioxide, or decomposition of carbon dioxide. To understand the reactions of CO_2 , CO and carbon, we performed annealing at different temperatures and characterize these samples by both reflectance and absorption infrared technique. The reflectance spectra of the

Fig. 5 Reflectance spectra show the annealing effect on CO and CO_2 .

Fig. 6 Absorption spectra show the annealing effect on CO and CO_2 .

6×10^{16} carbon implanted glass, that were stepwise annealed at 600, 700, and 800°C for 30 minutes at each temperature are shown in Fig. 5. Comparison of the spectra of the as-implanted sample with the one that is annealed under oxygen at 600°C indicates that the 600°C annealed sample has a stronger CO intensity than the as-implanted sample but the CO_2 intensity in the same sample has reduced to almost zero. As the annealing temperature reaches 700°C, the CO intensity reduces from the level observed at 600°C. Further annealing at 800°C causes both the CO and CO_2 bands to disappear. However, using absorption method, the CO_2 band intensity of the 800 °C annealed sample still retains 80% of the intensity of the as-implanted sample. This indicates that the disappearance of the reflectance of the CO_2 band for the 800°C annealed sample is partly due to the diffusion of CO_2 into a depth greater than the penetration depth of the reflectance technique. Since diffusion

Fig. 7 Reflectance spectra show the annealing effect on CO and CO₂.

reflectance technique. This may be the reason why we cannot observe CO₂ via infrared reflectance measurement for the 800°C annealed sample while we can observe CO₂ in the same sample via absorption. It is intriguing to notice that the 600°C annealed sample has a stronger CO reflectance intensity than the as-implanted sample, while the CO₂ reflectance intensity of the annealed sample is almost zero. Measurements on a 3×10^{16} sample annealed under O₂ were also performed. The absorption spectra of the 800°C annealed sample and as-implanted sample are plotted in Fig. 6. The 800°C annealed sample clearly has a weaker CO₂ peak intensity and a stronger CO intensity. The increased CO concentration of the oxygen annealed sample is most likely due to either a faster out-diffusion of CO₂ than CO or formation of CO from reaction between CO₂ and C.

The reflectance spectra of 6×10^{16} ions/cm² of as-implanted sample and the same sample under hydrogen annealing at 600°C and 700°C are plotted in Fig. 7. Clearly, at 600°C all the CO₂ and CO bands disappear. Both out-diffusion and conversions of CO and CO₂ into hydrocarbons are the possible mechanisms that could account for the decreased reflectance. Unlike the oxygen annealed samples, the CO₂ absorption intensity of the 700°C annealed sample retains only 15% of the intensity of the as implanted sample. Diffusion alone cannot generate such a large decrease in CO₂. The disappearance of the reflectance in CO band at 600°C strongly suggests that CO is not the product of reaction. Therefore, CO₂ and CO probably react with hydrogen.

CONCLUSION

Depth profile of carbon implanted fused silica was determined by both TRIM calculations and XPS with ion sputtering technique. CO and CO₂ molecules were formed during ion implantation. Significant spectroscopic differences between the embedded and gaseous CO and CO₂ molecules were observed. The formation of CO and CO₂ depends strongly on the ion implantation dose and annealing conditions. Different results based on infrared reflectance and

coefficients of CO and CO₂ in glasses are not known, we use the diffusion coefficient of argon in fused silica as an estimation. The diffusion coefficient in the damaged layer should be larger than the diffusion in fused silica. The diffusion coefficient of argon in fused silica at 600°C is 8×10^{-13} cm/s.⁷ Therefore, the diffusion length of argon in fused silica at 600°C for 30 minutes is $\sim 0.37 \mu\text{m}$, the diffusion length of Ar in silica annealed at 600, 700°C is $\sim 0.5 \mu\text{m}$. If annealed at 600, 700, 800°C sequence, the diffusion length will be $\sim 0.6 \mu\text{m}$. These mean that the CO or CO₂ formed at $0.45 \mu\text{m}$ below the surface where the maximum concentration of carbon is located may diffuse either out of the sample surface or diffuse into a depth that is not probed by the infrared

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absorption measurements are probably due to diffusion during annealing.

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