Optical and structural properties of Ge-ion-implanted fused silica after annealing in different ambient conditions*

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Ge^+ ions are implanted into fused silica glass at room temperature and a fluence of 1×10^{17} cm^{-2}. The as-implanted samples are annealed in O_2, N_2 and Ar atmospheres separately. Ge^0, GeO and GeO_2 coexist in the as-implanted and annealed samples. Annealing in different atmospheres at 600 °C leads each composite to change its content. After annealing at 1000 °C, there remains some amount of Ge^0 in the substrates. However, the content of Ge decreases due to out-diffusion. After annealing in N_2, Si–N composite is formed. The absorption peak of GeO appears at 240 nm after annealing in O_2 atmosphere, and a new absorption peak occurs at 418 nm after annealing in N_2 atmosphere, which is attributed to the Si–N composite. There is no absorption peak appearing after annealing in Ar atmosphere. Transmission electron microscopic images confirm the formation of Ge nanoparticles in the as-implanted sample and GeO_2 nanoparticles in the annealed sample. In the present study, the GeO content and the GeO_2 content depend on annealing temperature and atmosphere. Three photoluminescence emission band peaks at 290, 385 and 415 nm appear after ion implantation and they become strong with the increase of annealing temperature below 700 °C, and their photoluminescences recover to the values of as-grown samples after annealing at 700 °C. Optical absorption and photoluminescence depend on the annealing temperature and atmosphere.

Keywords: nanoparticles, optical absorption, photoluminescence, ion implantation

PACC: 8140T, 6146, 6170T

1. Introduction

Owing to their unique optical and electronic properties, semiconductor nano-materials have attracted much attention in recent years, and possess great potential applications in non-linear optical devices, photoelectric functional material, etc. Fused silica, as a useful optical material, has been used in optical fibre and other optical devices. Research on germanium has an important application background as a typical semiconductor. The optical properties of the composite structure, Ge–SiO_2, have aroused much interest, especially in luminescence.

Silica has widely been employed in silicon devices and integrated circuits.[1,2] In addition, some impurities, defects, and their complexes in SiO_2 are radiative centres;[3–5] therefore light emission can be obtained by embedding semiconductor nano-crystallites in the SiO_2 substrates. Up to now, many methods, e.g. ion implantation and modified chemical vapour deposition process (MCVD), have been used to fabricate Ge-doped SiO_2 materials and investigate their structural and optical properties, especially, the strong photoluminescence. The SiO_2 substrate used for doping includes SiO_2 film, glass and islands array.[6–10] Ion implantation combined with subsequent annealing has become a good method to form metallic and oxide nanoparticles in insulators. In the present study, Ge^+ ions are implanted into fused silica and then the as-implanted samples were annealed at different temperatures in O_2, N_2 and Ar atmospheres. The charge state, optical absorption and photoluminescence (PL) are investigated for the as-implanted and annealed samples.

2. Experiment

Optically polished fused silica glass with dimensions of 10 mm × 10 mm × 0.5 mm were implanted by Ge ions of 56 keV in a vacuum chamber of 1.8×10^{-3} Pa. The Ge ion implantation was performed at a fluence of 1×10^{17}. The samples were

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kept at room temperature with water cooling during the ion implantation. The ion flux was controlled below 5 μA/cm^2 to avoid overheating the samples. After implantation, the samples were annealed in a quartz tube furnace for 30 min at temperatures from 300 to 1000 °C in increment steps of 100 °C in flowing O_2, N_2, and Ar atmospheres separately. The heating rate was kept at 10 °C/min.

X-ray photoelectron spectra (XPS) of the as-implanted samples were obtained at room temperature with a KRATOS X SAM 800 x-ray photoelectron spectrometer with monochromatic Al Kα ($h\nu$ = 1486 eV). The sample had been etched to a depth of 2 nm with Ar^+ ions before measurement in order to remove surface contamination. A JEM 2010F field emission gun electron microscope operating at 200 keV was used to obtain a cross-sectional bright field transmission electron microscopic (TEM) image and a selected area electron diffraction (SAD) pattern. Optical absorption measurements in the UV–visible range were made in a SHIMADZU UV-2550 spectrophotometer at room temperature, with a deuterium lamp for UV and a tungsten halogen lamp for visible regions. Room temperature photoluminescence (PL) measurements were performed with a SHIMADZU RF-5301PC photo-luminescence spectrophotometer, with a 150 W Xe lamp used as an excitation source.

3. Results and discussion

Figure 1 shows the XPS spectra of the $Ge_{3d5/2}$ energy level of the as-implanted (a), annealed in O_2 (b) and N_2 (c) atmospheres at 600 °C, and annealed in Ar atmosphere at 1000 °C (d) samples separately.

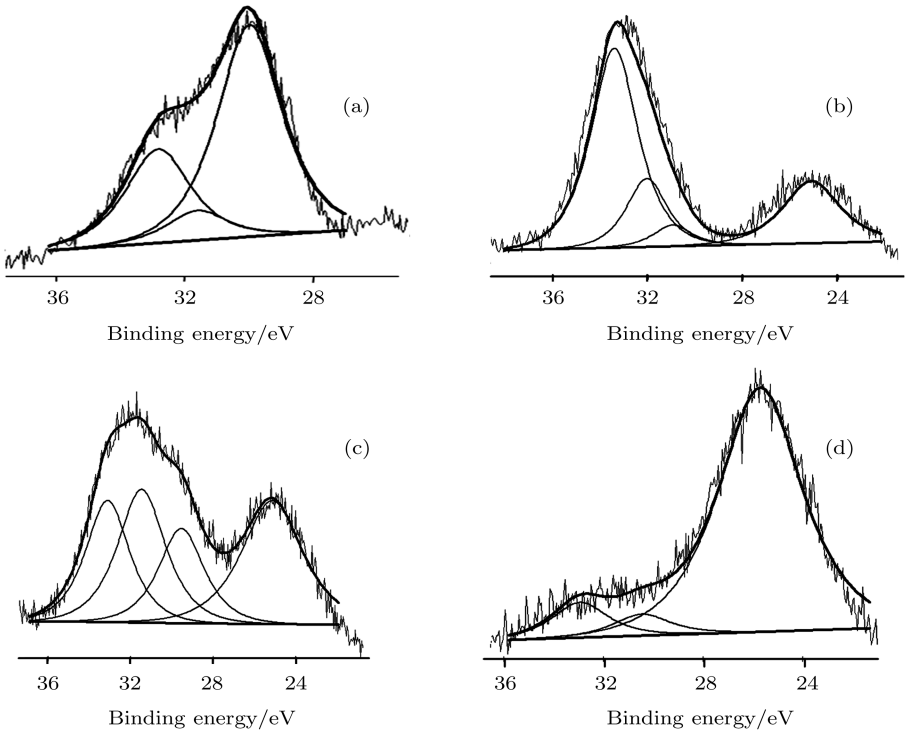


Fig. 1. XPS spectra of $Ge_{3d5/2}$ energy level of the samples as-implanted (a), annealed in O_2 atmosphere (b) and N_2 atmosphere (c) at 600 °C, and annealed in Ar atmosphere at 1000 °C (d).

The C_{1S} peak at 285.0 eV is used to calibrate the spectra. The XPS peaks of different samples are summarized in Table 1. Ge^0, GeO and GeO_2 coexist in the as-implanted and annealed samples. After annealing at 600 °C in different atmospheres, each composite changes in content. Ge^0 dominates in the as-implanted sample, and GeO_2 dominates in the annealed sample in O_2 atmosphere. For the samples annealed in N_2 atmosphere (Fig. 1(c)) and Ar atmosphere (not shown) separately, the Ge^0, the GeO content and the GeO_2 content are nearly close

to each other. After annealing at 1000 °C there is still some Ge^0 existing in the samples annealed in three atmospheres. In this paper, only the XPS spectrum of samples annealed in Ar atmosphere at 1000 °C is shown in Fig. 1(d). However, the content of Ge decreases heavily due to out-diffusion at this temperature. Since silicon nitride forms after annealing in N_2 atmosphere, the XPS spectra of the $Si_{2p3/2}$ energy level of the sample annealed at 600 °C in N_2 can be observed as shown in Fig. 2. The Gaussian peak at 103.3 eV is due to Si–Si (103.45 eV) and Si=O (103.65 eV) in SiO_2, for they are very close to each other in binding energy. The peak at 102.2 eV is due to a Si–N chemical bond, indicating that Si–N composite forms, which may be Si_3N_4 (102.2 eV) or SiO_xN_y (102.3 eV).[11]

Table 1. XPS peaks of the as-implanted and annealed samples.

sample	binding energy of $Ge_{3d5/2}$/eV		
	Ge	GeO	GeO_2
as-implanted	29.90	31.600	32.820
annealed in O_2 at 600 °C	30.56	31.820	33.500
annealed in N_2 at 600 °C	29.539	31.469	33.116
annealed in Ar at 1000 °C	30.470	-	32.950

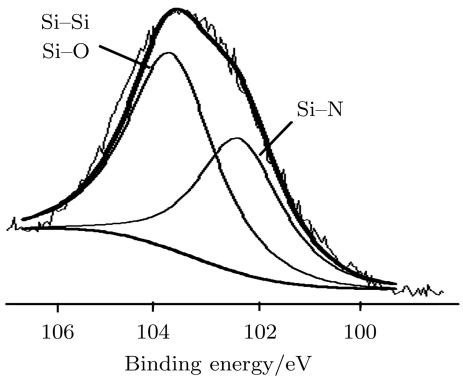


Fig. 2. XPS spectra of $Si_{2p3/2}$ energy level of the sample annealed at 600 °C in N_2 atmosphere.

Figure 3 shows the cross-sectional bright field TEM images of the samples as-implanted (a) and annealed (b) at 600 °C in O_2 atmosphere. The insets show the corresponding selected area electron diffraction (SAD) patterns. Face-centred cubic (fcc) Ge nanoparticles distribute near the surface of the substrate in the as-implanted samples. After annealing, a large number of Ge atoms near the surface diffuse out of the substrate. At the same time, some Ge atoms migrate into the deep depth of the substrate and GeO_2 nanoparticles form in a deeper area of the substrate. The polycrystalline ring can be observed in the SAD pattern of the as-implanted sample. However, only several diffraction spots can be observed in the annealed sample. This may be due to the low content of GeO_2 after annealing. High resolution TEM images of the as-implanted (a) and annealed (b) sample are shown in Fig. 4. Spherical Ge nanoparticles with good crystallinity distribute in the amorphous silica substrate after ion implantation. After annealing, GeO_2 nanoparticles are still in a round shape but the crystallinity seems not as good as that of the as-implanted sample.

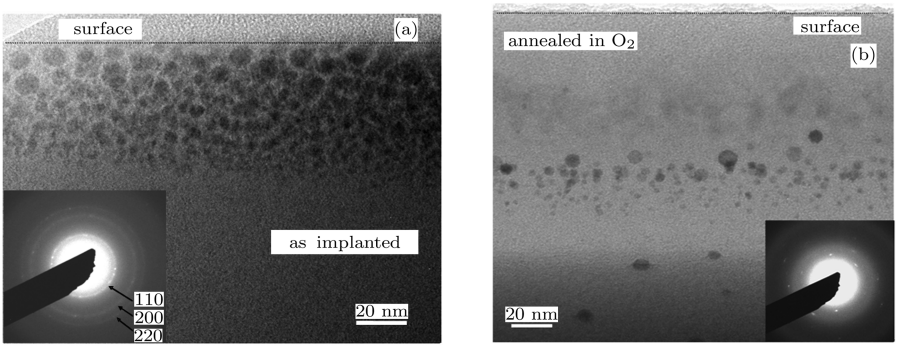


Fig. 3. Cross-sectional bright field TEM images of the as-implanted (a) and annealed (b) sample at 600 °C in O_2 atmosphere.

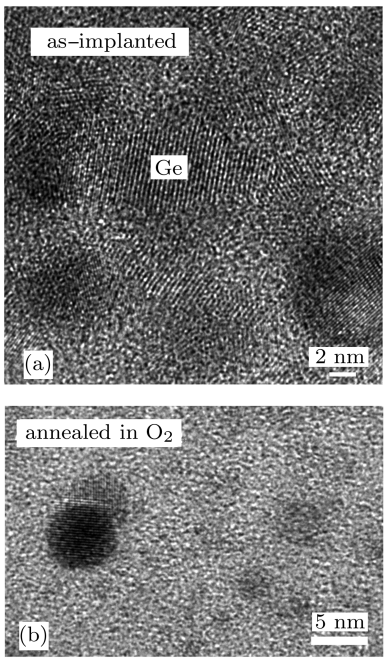


Fig. 4. High resolution TEM images of the as-implanted (a) and annealed (b) samples.

The optical absorption spectra of as-grown, as-implanted and annealed samples in O_2 (a) and N_2 (b) atmospheres are shown in Fig. 5. The spectra have been vertically offset to avoid overlapping. Ion implantation has induced many defects. As a result, the background absorption of the as-implanted samples increases in the UV range. The background absorption decreases with annealing temperature increasing. A weak absorption peak at 240 nm appears after annealing at 600 °C in O_2 atmosphere. Actually, this absorption peak has widely been studied in the Ge doped SiO_2, and a general conclusion has been drawn that this absorption band is correlated with a singlet-to-singlet transition of GeO centre.[8,12–14] The GeO centre is a Ge^{2+} ion coordinated with only two oxygen atoms instead of four as in the normal structure. Usually, this absorption peak is composed of two absorption peaks, one at 245 nm (5.06 eV), and the other at 240 nm (5.17 eV), according to the previous studies.[9,15,16] It is not easy to identify them because they are very close to each other. Furthermore, the two absorption peaks at 5.06 eV and 5.17 eV are known as the $B_{2\alpha}$ and the $B_{2\beta}$ bands, respectively. The $B_{2\alpha}$ band is attributed to a neutral oxygen vacancy (NOV).

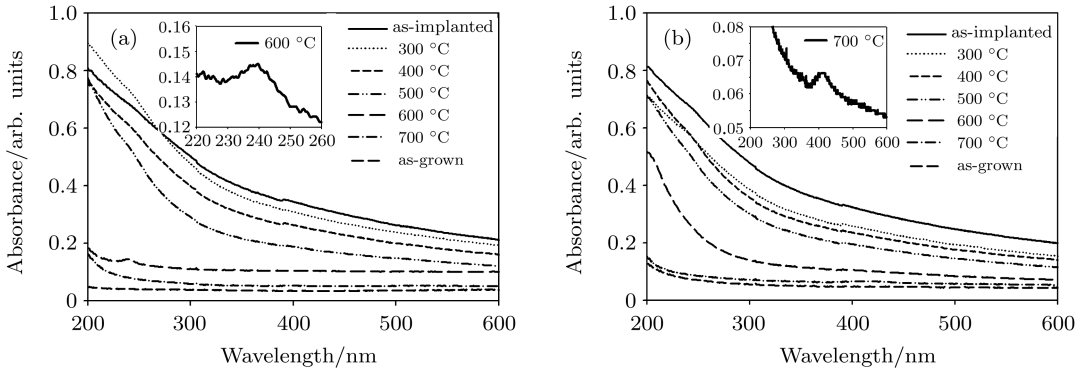


Fig. 5. Optical absorption spectra of as-grown, as-implanted and annealed samples in O_2 (a) and N_2 (b) atmospheres.

After annealing at 700 °C in N_2 atmosphere, a new absorption peak at 418 nm appears which may be attributed to the Si–N composite according to the XPS results. There is no change in the absorption spectra of the samples annealed at temperatures above 700 °C in O_2 and N_2 atmospheres. There is no absorption peak appearing after annealing up to 1000 °C in Ar atmosphere (not shown).

The photoluminescence spectra of as-grown, as-implanted and annealed samples in O_2 (a) and N_2 (b) atmospheres are shown in Fig. 6. The PL spectra of the sample annealed in Ar atmosphere (not shown) are similar to those in N_2 atmosphere. There is a clear emission peak at around 370 nm in the as-grown sample. Three PL emission bands peaked at 290, 385, and 415 nm (4.28, 3.21, and 2.99 eV) appear after ion implantation. These PL bands become strong with the increase of annealing temperature and then re-

cover to those of the as-grown sample after annealing at 700 °C for the three samples annealed in different atmospheres. Differently, the sample annealed in O_2 atmosphere has the strongest PL after annealing at 400 °C, and the other two occur after annealing at 500 °C. This is because maximum values of GeO content occur at different temperatures for the annealed samples in different atmospheres.

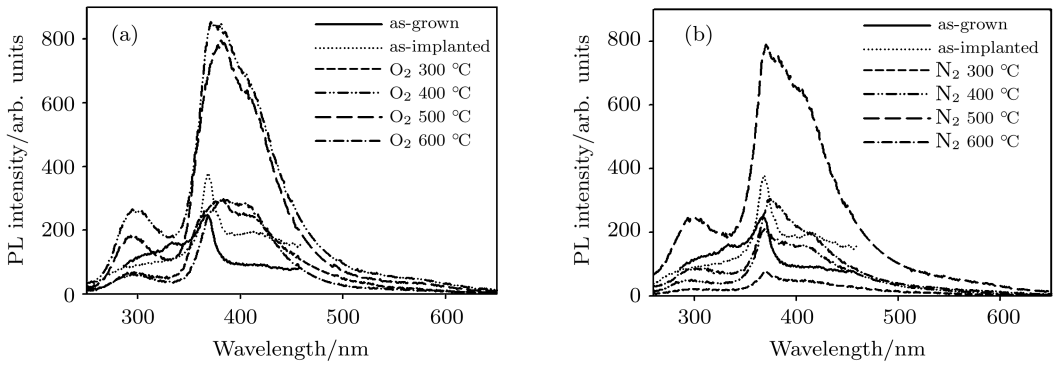


Fig. 6. Photoluminescence spectra of as-grown, as-implanted and annealed samples in O_2 (a) and N_2 (b) atmospheres.

The NOV is a consequence of ≡Si–Si≡ bond formation after removing one oxygen atom, which can be extended to ≡Ge–Si≡ and ≡Ge–Ge≡ bond formation in the case of Ge^+-implanted SiO_2.[8] The as-grown SiO_2 substrate has a small number of ≡Si–Si≡ NOVs although it cannot be observed from the absorption spectra in Fig. 5. These NOVs result in an emission peak at around 370 nm in the as-grown sample. After ion implantation and annealing, the ≡Si–Si≡ NOVs are replaced partly by ≡Ge–Si≡ and ≡Ge–Ge≡ NOVs. Therefore, the three different types of NOVs result in the absorption peak at 245 nm and the emission band at 370 nm in Fig. 6.

In addition to the PL band at 370 nm, oxygen deficient defect centres in silica are known to have two PL bands at 4.4 eV and 3.0 eV, separately. The PL band at 4.4 eV has been suggested to consist of PL bands at ∼4.4 and ∼4.3 eV, the α_a and α_b respectively.[17,18] Therefore, the PL bands at 290 nm and 415 nm in Fig. 6 could be ascribed to the Ge-associated NOV, and their intensities are dependent on the annealing temperature and atmosphere.

After annealing at 300 °C in O_2 atmosphere, the PL peak at 370 nm shifts to 385 nm due to the increasing GeO content. Actually, this PL band is composed of two PL bands peaked at 370 and 385 nm respectively. The 370 nm PL band is due to the NOV as discussed above. The 385 nm PL band is related to optical transition in the GeO colour centres,[6−10,15] i.e. the absorption band at 240 nm in Fig. 5. For the annealed samples in N_2 atmosphere, the PL peak wavelength shift from 370 to 385 nm is not so clear as those of the samples in O_2 atmosphere. This indicates that the annealing in O_2 atmosphere is good for the PL of GeO colour centres. As for the PL mechanism of GeO colour centres, the transition from ground singlet state to excited singlet state ($S_0 \rightarrow S_1$) is responsible for the absorption band at 240 nm in Fig. 5. Some of the excited electrons directly relax to the singlet state ($S_1 \rightarrow S_0$), thereby producing the PL band at 290 nm. Other excited electrons relax to the triplet states without photon radiation, and then return to ground singlet states ($T_1 \rightarrow S_0$) and emit 385 nm photons. Therefore, the absorption band at 240 nm and two PL bands at 290 nm and 385 nm could be ascribed to the same colour centres, i.e. GeO centres.

It can be concluded that the photoluminescences at 370 and 415 nm are caused by NOVs (≡Si–Si≡, ≡Ge–Si≡ and ≡Ge–Ge≡). The 385 nm PL band arises from the GeO colour centres. The PL band at 290 nm is probably due to both NOVs and GeO colour centres.

4. Conclusions

Ge, GeO and GeO_2 coexist in the Ge^+ ion implanted and annealed SiO_2. Ge nanoparticles dominate in the as-implanted sample. Regardless of out-diffusion, the GeO content and the GeO_2 content depend on the

annealing temperature and atmosphere. GeO colour centres result in an optical absorption band at 240 nm and two photoluminescence bands at 385 and 290 nm. NOVs are related to the photoluminescence bands at 290, 370, and 415 nm respectively.

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