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Infrared photoluminescence from Ge^+-implanted SiO_2 film

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Abstract

Ge ions were implanted into SiO_2 films thermally grown on crystalline Si at an energy of 60 KeV and with a dose of 1×10^{16} cm^{-2}, followed by annealing at different temperatures. Under an excitation of the 514.5 nm line of an Ar^+ laser, the implanted films exhibit a broad infrared photoluminescence (PL) at room temperature. The PL peak displays a redshift with increasing annealing temperature. The experimental results from Raman scattering, Rutherford backscattering and X-ray photoelectron spectroscopy were utilized to analysis the structure of the films. The PL mechanism is discussed in the light of the results of structural analyses. © 1999 Published by Elsevier Science B.V.

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Since the discovery of its visible room-temperature photoluminescence (PL), optical and electronic properties of porous Si (PS) have been widely investigated because of their potential use as new photoelectronic materials and devices. The quantum size effect (QSE) has been mainly proposed to be responsible for the visible PL. However, the fragile structure and instability of light-emission have limited its applications. Recently, Hirschman et al. [1] reported the successful integration of Si-based light emitters with Si electronics. This work has greatly stimulated further study of PS. On the other hand, much attention has recently been paid to other Si-based light-emitting materials, which are more robust in various thermal and chemical surroundings and thus have a greater potential in optoelectronics [2,3]. SiO_2 films have been widely used as passivation and electrical insulation layer in Si devices and integrated circuits due to their excellent compatibility with Si. Its wide energy bandgap can provide a high barrier for embedded nanocrystals. Therefore, efficient light emission can be obtained by embedding semiconductor nanocrystals in an SiO_2 matrix [4]. Studies on SiO_2 films embedded with Si nanocrystallites have been carried out for a long time, and red, green and blue PL have been observed due to QSE or some color centers [5]. Since bulk Ge has a larger dielectric constant and smaller carrier masses compared with bulk Si, QSE will be more prominent in Ge than in Si [4,6]. Recently, Kanemitsu et al. [7] fabricated a SiO_2 matrix embedded with Ge nanocrystals with size less than 4 nm by magnetic co-sputtering. They obtained 550 nm light emission from this material and

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ascribed it to QSE. Scheglov et al. [8] observed light emission from Ge-implanted SiO_2 films, and the PL spectra show a broad band peaked at 500–900 nm. They attributed the PL observed to the quantum confinement on Ge nanocrystals.

In this Letter, we report for the first time a near infrared PL from Ge^+-implanted SiO_2 films. Spectral analysis seems to indicate that the infrared PL also originates from the QSE of Ge nanocrystals.

A layer of SiO_2 films with thickness of 360 nm was formed on p-type ⟨100⟩ oriented crystal Si by thermal oxidation. Ge ions were implanted into this SiO_2 layer with a dose of 1×10^{16} cm^{-2} and at an energy of 60 KeV. The implanted samples were annealed at various temperatures (Ta) in N_2 for 30 min. PL and Raman spectra were obtained on a 44 W monochrome meter and SPEX 1403 Raman spectrometer, respectively.

Fig. 1 shows the PL spectra of three samples annealed at 400, 600 and 1100°C, measured at 77 K and under an excitation of the 514.5 nm line of an Ar^+ laser. The three spectra all exhibit a broad infrared PL peaked at ~ 800 (400°C), ~ 850 (600°C) and ~ 900 nm (1100°C), respectively. The PL peak position clearly shows a redshift with increasing Ta. Moreover, it was found that the PL intensity decreases with increasing Ta. The intensity of the sample with Ta = 1100°C is only half of that of the sample with Ta = 400°C. No similar emission was obtained from both pure SiO_2 film and the Ge^+-implanted SiO_2 film without annealing, so it is reasonable to infer that the PL depends on annealing of our samples.

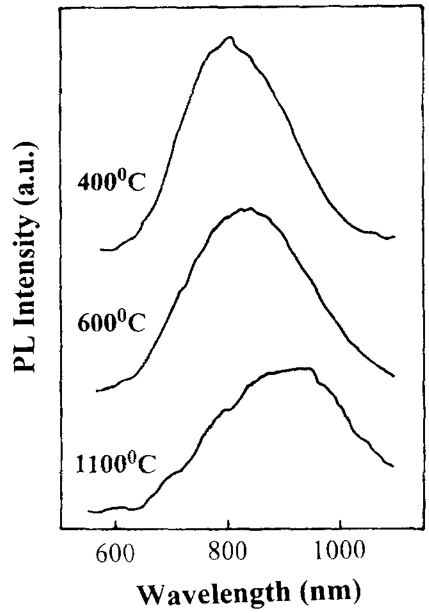

Fig. 1. PL spectra of samples with Ta = 400, 600 and 1100°C. An obvious redshift can be observed with increasing Ta.

To identify the origin of the infrared PL, we investigated the annealing behavior of implanted films and estimated the average crystallite sizes by means of Raman scattering. In Fig. 2, curves (a)–(d) are the Raman spectra of Ge^+-implanted samples annealed at 400, 600, 800 and 1100°C, respectively, measured under the same initial experimental conditions. A spectrum of bulk c-Ge is also shown for comparison. Although the spectra of the samples are noisy, they clearly show a sharp peak at ~ 300 cm^{-1}. Its position hardly changes but its full width at half maximum (FWHM) obviously decreases as Ta increases. Further comparing its integrated intensity relative to the 521 cm^{-1} peak from Si substrate, it is found that the integrated intensity also changes with Ta (3.2% for 400°C, 2.7% for 600°C 5.8% for 800°C and 2.3% for 1100°C). The result indicates that the 300 cm^{-1} peak cannot originate from one-phonon Raman scattering of Si substrate from transverse acoustic phonons at X[2TA(X)] [9–11]. Thus, we assign the ~ 300 cm^{-1} peak to the scattering of Ge nanocrystals formed during annealing. According to the phonon confinement model adopted by Fujii et al. [12], we can obtain the average crystallite sizes to be 3.6, 5.3, 5.7, and 6.4 nm for the samples with Ta = 400, 600, 800 and 1100°C, respectively. Obviously, the average size increases with Ta. Figs. 2a–d also show another two features:

(i) A broad band structure appears between 220 and 280 cm^{-1}. Its intensity changes with Ta and shows a maximum on the sample with low Ta (400°C). This band has been identified in the past and associated with some relatively small Ge nanocrystallites (< 2 nm) [6]. The reduction of its intensity with increasing Ta reflects an increase of Ge nanocrystal size.

(ii) Another band structure appears at ~ 400 cm^{-1}. The band can be assigned to the localization of Si–Si optical phonons (phonon confinement) in the Ge neighborhood as a result of the random introduction of Ge ions into the SiO_2 film [13]. Its appearance is a signature for compositional disorder and localization. The above results indicate that the PL may arise from the Ge nanocrystals and its redshift be related to the

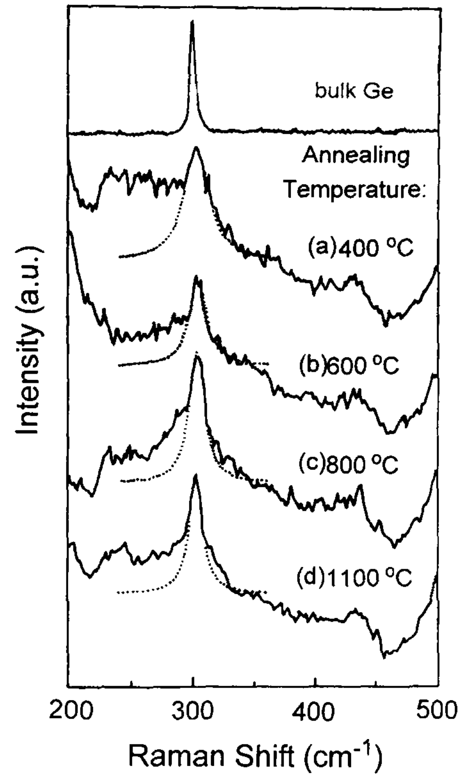

Fig. 2. Raman spectra of samples with Ta = 400, 600, 800 and 1100°C in the frequency range of 200-500 cm^{-1}.

growth of Ge nanocrystals.

According to our results from X-ray photoelectron spectroscopy [14], it has been shown that when Ge ions are implanted into SiO_2 films, many Si-O bonds are destroyed and a great deal of Ge, Si and O ions are produced. Upon annealing at low Ta, Ge-O bonds (GeO and Ge_2O_3) can be formed and Ge nanocrystals appear. Increasing Ta leads to dissolution of GeO and precipitation of Ge nanocrystals. However, increasing Ta also leads to outdiffusion of Ge atoms and the decrease of Ge content. Since the formation of Ge nanocrystals is a diffusion-controlled process and the diffusion coefficient increases with Ta, the higher the Ta, the larger the crystallite size. If the infrared PL originates from the QSE of the Ge nanocrystals, its redshift with increasing Ta can be easily understood, for, as indicated by the Raman data, the crystallite sizes increase with increasing Ta. Rutherford backscattering (RBS) was applied to detect the distribution of Ge before and after annealing at different temperatures. In the RBS spectra, besides the peak at the implantation depth, labeled peak A in Table 1, there is another peak at the interface between the Si substrate and SiO_2 film for these annealed samples labeled peak B. The data indicate that there is a loss of Ge upon annealing, which is due to Ge diffusion to the SiO_2 surface and subsequent evaporation. This causes a 24% loss in atoms of Ge after annealing at 1100°C. We should point out that although damaged SiO_2 is known to evaporate at 1100°C, we did not observe a significant decrease in SiO_2 content. Therefore, the decrease (24%) in Ge atoms content is mainly due to the outdiffusion.

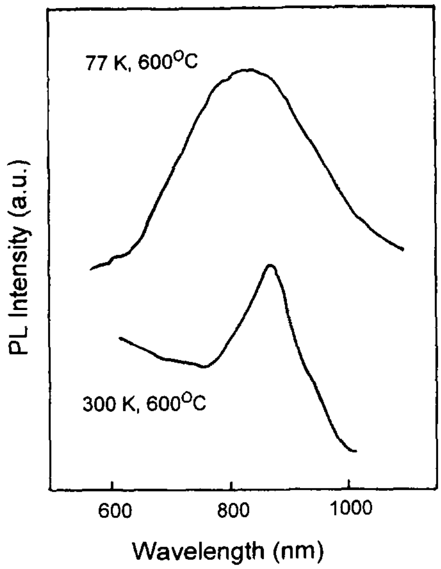

Fig. 3. PL spectra of sample with Ta = 600°C, measured at 300 and 77 K.

Though the results above have suggested that the infrared PL may come from QSE of Ge nanocrystals, the Bohr model cannot predict the PL peak position [15]. For Ge nanocrystals, the theoretical bandgap from the Bohr model can be calculated to be 4.9, 2.7 and 2.0 eV for the samples with Ta = 400, 600, and 1100°C, respectively. These results are quite different from our experimental values of 1.6, 1.5, 1.4 eV under corresponding Ta. In addition, although an apparent blueshift of 0.07 eV can be obtained from 870 (300 K) to 830 nm (77 K) (see Fig. 3) and explained in analogy to bulk Ge [16], an increase in FWHM by more than a factor of two at 77 K cannot be explained simply by analogy to bulk effects. Recently, Takaga-

Table 1
The amount of Ge atoms deduced from RBS results

Annealing temperature (°C)	Ge 10^{16} cm^{-2} (peak A)	Ge 10^{16} cm^{-2} (peak B)	Ge 10^{16} cm^{-2} (total amount)	Ge 10^{16} cm^{-2} (escaped amount)
0	1.38	0	1.38	0
600	1.18	0	1.18	0.20
900	1.21	0.01	1.21	0.17
1100	0.98	0.07	1.05	0.33

hara et al. [17] have proposed a model of the quantum confinement effect on excitons in Ge and Si quantum dots. According to this model, the bandgaps of Ge nanocrystals with sizes of 3.6, 5.3 and 6.4 nm are 2.1, 1.5 and 1.4 eV, respectively. These values are consistent with our experimental results. Thus, the PL can still be explained by QSE. Here, we should stress that the defects produced during Ge$^+$-implantation are not responsible for the infrared PL based on the following reasons.

Firstly, the redshift of the PL energy is closely related to an increase of Ge nanocrystal sizes. Thus, it shows a strong annealing temperature dependence. The defects (even structural stable up to the temperature as high as 1000°C) cannot cause the clear redshift [5,18]. Secondly, the blueshift of 0.07 eV at 77 K cannot be explained on the basis of the defects. For the disagreement between the Bohr model and our results, we note that in PS the radiative recombination often occurs through intermediate states or surface states on the passivated Si crystallite surfaces [19]. Thus, for our samples, the luminescence centers at interface between the Ge nanocrystals and SiO$_2$ matrix may be responsible for the obtained PL [5]. It should be pointed out that besides QSE, strain effects and alloying effects leading to the formation, for instance, of Ge$_{1-x}$Si$_x$ compounds can also be responsible for luminescence blue or red shift. Further investigation is required to clarify this problem.

In conclusion, for the annealed Ge$^+$-implanted SiO$_2$ films, a near infrared PL can be observed. The PL obviously displays a redshift from 800 to 900 nm with increasing Ta from 400 to 1100°C. The results from Raman scattering, Rutherford backscattering and XPS indicate that the obtained infrared PL comes from QSE of Ge nanocrystals embedded in SiO$_2$ film. The theoretical values from Takagahara's model are consistent with our experimental results.

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