

Dependency of photoluminescence from SiO₂ thin films containing Si_{1-x}Ge_x quantum dots on Ge/Si doping ratio

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SiO₂ thin films containing Si_{1-x}Ge_x quantum dots (QDs) are prepared by ion implantation and annealing treatment. The photoluminescence (PL) and microstructural properties of thin films are investigated. The samples exhibit strong PL in the wavelength range of 400–470 nm and relatively weak PL peaks at 730 and 780 nm at room temperature. Blue shift is found for the 400-nm PL peak, and the intensity increases initially and then decreases with the increase of Ge-doping dose. We propose that the 400–470 nm PL band originates from multiple luminescence centers, and the 730- and 780-nm PL peaks are ascribed to the Si=O and GeO luminescence centers.

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The group IV semiconductor quantum dots (QDs) have attracted much interest because the QDs exhibit efficient photoluminescence (PL) and thus have potential use in Si-based optoelectronic devices^[1,2]. Recently, many research groups have reported that nanocrystal-Si (nc-Si) or nanocrystal-Ge (nc-Ge) embedded in SiO₂ matrix exhibits PL and electroluminescence (EL) in the range of visible light at room temperature^[3,4]. The quantum confinement effectively breaks up the restriction of indirect gap-band, and strong visible luminescence has been observed. Therefore, it has been anticipated that optoelectronic devices with Si-QDs-contained materials will be manufactured^[4].

There are many methods for the preparation of silicon or germanium QDs, such as plasma enhanced chemical vapor deposition (PECVD), molecular beam epitaxy (MBE), and radio frequency (RF) sputtering^[1]. Ion implantation is a favorable technique for this purpose, because it offers the possibility of controlling the number and depth profile of atoms by changing the ion fluence and the acceleration energies^[3]. However, ion implantation also results in the creation of luminescent centers. Some ion-irradiated defects could be eliminated through annealing treatment of samples, although new ones appear, for example, ≡Si-Si≡, ≡Ge-Ge≡, and ≡Si-O-O-Si≡^[1]. Much effort has been devoted to elucidate the luminescence mechanism from Si- or Ge-doped SiO₂ thin films^[4–7]. However, studies on doubly Si/Ge-implanted SiO₂ thin films are scarce. In this letter, the Si_{1-x}Ge_x-QDs-contained SiO₂ thin films are prepared by Si and Ge ion implantation. The relationship between the PL spectra and Ge/Si doping ratio is investigated, and the PL mechanism is also discussed.

The Si_{1-x}Ge_x-QDs-contained SiO₂ thin films were prepared by ion implantation of the 300-nm-thick SiO₂ film grown on the n-type (100)-oriented Si substrate with a resistivity of 2–5 Ω·cm. Si ions were implanted into

SiO₂ films at 36 keV with doses of 0, 0.2, 0.5, 0.8, and 1.0×10¹⁷ cm⁻². Subsequently, Ge ions were implanted using doses of 1.0, 0.8, 0.5, 0.2, and 0×10¹⁷ cm⁻² at 70 keV. For any sample, the total dose of Si and Ge dopants was 1×10¹⁷ cm⁻². For convenience, we used the Ge-doping dose to represent the samples. According to SRIM2006 simulation, the projecting depths of both Si and Ge ions were about 50 nm. The as-implanted samples were furnace-annealed at 1000 °C for 1 h in N₂ ambient with water sealed at a fluence of 300 sccm. Before the heating treatment, the furnace was rinsed with N₂ gas for 10 min to remove air.

The PL spectra were measured using Fluorolog-Tau-3 photo-spectrometer with R928P photomultiplier at room temperature. The excitation wavelength was 250 nm. A high-resolution transmission electron microscope (HRTEM, JEM-2010) was used to determine the formation of QDs. X-ray photoelectron spectroscopy (XPS, PHI Quantera SXM) was carried to determine the chemical state of elements in the film. Before the XPS measurement, the sample surface was cleaned by Ar⁺ sputtering.

Figure 1 shows the HRTEM image of Si_{1-x}Ge_x-QDs-contained SiO₂ film with Ge doped at a dose of 0.5×10¹⁷ cm⁻² and annealed at 1000 °C for 1 h. The QDs are near spherical in shape and are dispersed in the SiO₂ matrix with a diameter range of 2–5 nm.

Figure 2 shows the XPS spectra of the films with different Ge doping doses. From Fig. 2(a), it can be seen that a prominent peak is observed at the binding energy of 28.6 eV and a weak peak at 30.8 eV. It has been reported that the binding energies of Si or Ge in Si_{1-x}Ge_x alloy have few changes with the Ge composition^[8]. The peak of 28.6 eV is related with the Ge3d electron of QDs. Ge oxide includes GeO, GeO₂, and Ge₂O₃; however, GeO₂ and Ge₂O₃ decompose easily during high temperature processing. GeO can be stable even at

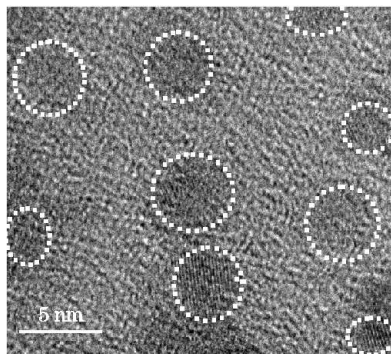


Fig. 1. HRTEM image of $\text{Si}_{1-x}\text{Ge}_x:\text{SiO}_2$ thin film with Ge doped at a dose of $0.5 \times 10^{17} \text{ cm}^{-2}$.

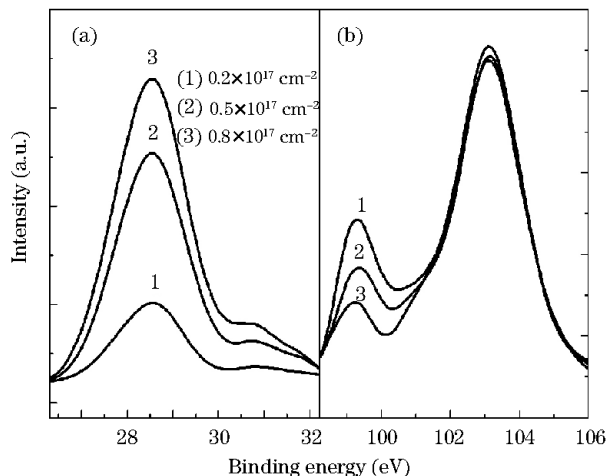


Fig. 2. XPS spectra of $\text{Si}_{1-x}\text{Ge}_x:\text{SiO}_2$ thin films with different Ge-doping doses. (a) $\text{Ge}3d$ spectra; (b) $\text{Si}2p$ spectra.

temperature as high as 1100°C , which means that the peak of 30.8 eV corresponds to $\text{GeO}^{[9]}$. For Si, two peaks are located at the binding energies of 99.5 and 103.3 eV (Fig. 2(b)), with the latter corresponding to the $\text{Si}2p$ electron of SiO_2 , and the 99.5-eV peak corresponding to the $\text{Si}2p$ electron of $\text{Si}_{1-x}\text{Ge}_x$ QDs.

Figure 3 shows the PL spectra of $\text{Si}_{1-x}\text{Ge}_x:\text{SiO}_2$ thin films with different Ge doping doses. In order to reduce the background noise in PL data, the smoothing process was carried out. Four PL peaks located at 295 , 400 , 470 , and 550 nm can be observed in the wavelength range from 295 to 700 nm . There are also two other PL peaks located at 730 and 780 nm in the wavelength range of $700\text{--}900 \text{ nm}$, as shown in Fig. 4. The second-order diffraction peaks around 500 nm from the 250-nm excitation light has been subtracted, thus the impact on the PL can be omitted by the PL excitation spectra. In order to understand both absorption and emission processes in these thin films, the PL excitation spectra were investigated with PL peaks at 295 , 400 , 470 , 550 , 730 , and 780 nm , respectively, as shown in Fig. 5. It is found that 250 nm is the optimal excitation wavelength except for a little excursion for the 730-nm PL peak. Similar PL excitation results were obtained for these PL peaks in the Si-doped or Ge-doped SiO_2 thin films^[8–10].

When the Si-doping dose is $1 \times 10^{17} \text{ cm}^{-2}$, the sample exhibits PL peaks at around $415\text{--}470 \text{ nm}$. After decomposing with multi-Gaussian function, two principal

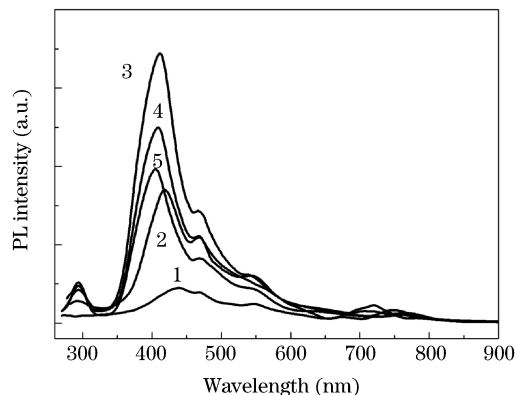


Fig. 3. PL spectra of $\text{Si}_{1-x}\text{Ge}_x:\text{SiO}_2$ thin films with different Ge-doping doses. Curves 1–5 Ge-doping doses of 0 , 0.2 , 0.5 , 0.8 , and $1.0 \times 10^{17} \text{ cm}^{-2}$.

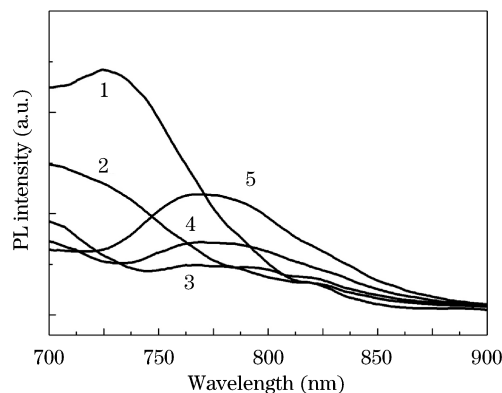


Fig. 4. PL spectra of $\text{Si}_{1-x}\text{Ge}_x:\text{SiO}_2$ thin films with different Ge-doping doses in the range of $700\text{--}900 \text{ nm}$. Curves 1–5 correspond to Ge-doping doses of 0 , 0.2 , 0.5 , 0.8 , and $1.0 \times 10^{17} \text{ cm}^{-2}$.

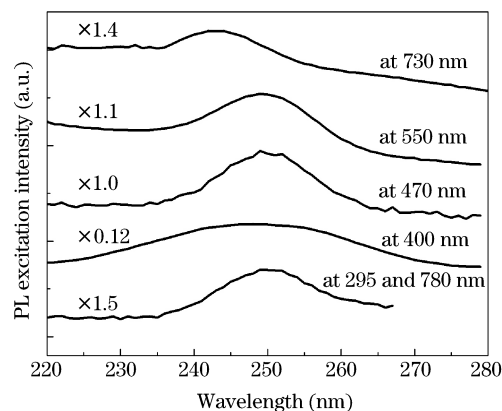


Fig. 5. PL excitation spectra of $\text{Si}_{1-x}\text{Ge}_x:\text{SiO}_2$ thin films monitored at different PL peaks.

luminescent centers at 420 and 470 nm can be identified. The result is similar to those obtained by Lin *et al.*^[10]

In principle, during the ion implantation process, the Si-related neutral oxygen vacancy center ($\equiv\text{Si}\text{--}\text{Si}\equiv$, NOV) and the oxygen interstitials are concurrently generated under the physical destruction process^[11]. This process can be described by the reaction rule of $\text{O}_3\equiv\text{Si}\text{--}\text{O}\text{--}\text{Si}\equiv\text{O}_3 \rightarrow \text{O}_3\equiv\text{Si}\text{--}\text{Si}\equiv\text{O}_3 + \text{O}_{\text{interstitial}}$ ^[12,13]. The weak-oxygen bond (O–O, WOB) defects can be formed and

activated after thermal annealing by the reaction rule of $O_{\text{interstitial}} + O_{\text{interstitial}} \rightarrow O-O$ ^[10]. Lin *et al.* have observed a stable blue emission (~ 415 -nm band)^[10], attributed to the WOB center, from the Si-ion-implanted SiO₂ films thermally grown on the Si substrate under ultraviolet excitation. We propose that the WOB center is responsible for the 420-nm PL. The formation of NOV center has been frequently reported in silica glass and in SiO₂ matrix by ion implantation^[1], and the defect can survive high-temperature annealing. The PL excitation peak was observed at 250 nm and the related PL peak at 470 nm was assigned to the NOV centers^[14].

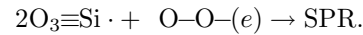
After the Ge doping, one (or both) Si atom(s) in the $\equiv\text{Si-Si}\equiv$ center might be replaced by a Ge atom, which forms a $\equiv\text{Ge-Si}\equiv$ (or $\equiv\text{Ge-Ge}\equiv$) center. From the molecular spectroscopy^[15], we know that when Ge ion replaced Si ion in the $\equiv\text{Si-Si}\equiv$ center, the transition energy will increase, and thus a blue shift of the PL peak from the ordered $\equiv\text{Ge-Si}\equiv$ or $\equiv\text{Ge-Ge}\equiv$ center can be expected, compared with the PL from the $\equiv\text{Si-Si}\equiv$ center. Rebohle *et al.* have also reported PL peaks at 366 and 407 nm, which are ascribed to the $\equiv\text{Ge-Ge}\equiv$ center and $\equiv\text{Ge-Si}\equiv$ center, respectively^[16]. Therefore, we tentatively interpret that the blue shift is due to the formation of $\equiv\text{Ge-Ge}\equiv$ and $\equiv\text{Ge-Si}\equiv$ defect centers in the Ge-doped SiO₂ thin films.

Shen *et al.* have reported that in GeO the 295-, 400-, and 780-nm PL peaks are induced by the $S_1 \rightarrow S_0$, $T_\Sigma \rightarrow S_0$, and $T'_\Pi \rightarrow S_0$ transitions, respectively^[17]. There is an absorption band at 250 nm, as can be seen from Fig. 5. This PL excitation spectrum corresponds to the higher energy level of the GeO center according to Huber's results^[18], and the XPS results suggest the existence of the GeO center. The transitions in the GeO center are intra-transition which will not be affected by the environment, and are only related with the amount of GeO. When the thin films contain Si composition, because the binding energy of Si-O bond is higher than that of Ge-O bond, the Si atom has a priority to bond with the O atom^[7]. The XPS result has verified that the composition of GeO is small, thus the GeO center-related PL peaks at 295 and 780 nm are weak. Further discussion on the 400-nm PL band will be given in the following.

With the Ge-doping dose increasing, the size of QDs is expected to grow^[19,20]. If the 400-nm PL is assigned to the quantum confinement effect, the related PL should red shift, which conflicts with the experimental result, thus the interpretation is unreasonable. Based on the above analysis, we think the 400-nm PL band originates from multiple luminescence centers such as the WOB center, GeO center, and Si- and Ge-related NOV centers. The PL excitation spectrum at 400-nm emission is a wide peak located at 250 nm owing to the existence of multiple luminescence centers. With the increase of Ge-doping dose, the XPS result suggests that the GeO composition increases. The change in intensity of the 400-nm PL is inconsistent with the change in GeO composition. When the Ge-doping dose is $0.5 \times 10^{17} \text{ cm}^{-2}$, the PL band intensity reaches the maximum value. From the change in intensity, we presume that Ge doped at a dose of $0.5 \times 10^{17} \text{ cm}^{-2}$ is beneficial to the formation of the $\equiv\text{Ge-Si}\equiv$ center, and the 400-nm PL band is mainly

due to the $\equiv\text{Ge-Si}\equiv$ center.

The PL excitation spectrum monitored at 550-nm emission is a sharp peak (full-width at half-maximum (FWHM) 20 nm), around 250 nm, as shown in Fig. 5. The position of this PL peak is stable with the Ge-doping dose. It implies that the luminescence also originates from the defect center. Sakurai *et al.* observed a PL band at about 2.24 eV (554 nm) in γ -irradiated SiO₂ glass samples containing substantial amounts of excess oxygen, and proposed that the PL band was associated with a surplus of oxygen defects formed by the small "peroxy radical" (SPR)^[21]. The silicon dangling bands (E' center, $O_3\equiv\text{Si}\cdot$) and the oxygen interstitials were formed in the Si- and Ge-doped SiO₂ matrix. A species of SPR can be created by a reaction of interstitial oxygen atom or O₂ molecule with an E' center^[22]:



We suggest that the 550-nm PL originates from the SPR center in the SiO₂ thin films.

In the PL spectra from red to near infrared range shown in Fig. 4, the samples exhibit PL peaks at 730 and 780 nm. When the thin films do not contain Ge composition, the PL peak at 730 nm is the strongest. With the Ge-doping dose increasing, both the amount of GeO and the PL intensity of 780 nm increase. The PL excitation spectrum for 780-nm PL is located at 250 nm. Combined with the discussion above, the 780-nm PL is ascribed to the GeO center. When the Ge-doping dose is above $0.5 \times 10^{17} \text{ cm}^{-2}$, the 730-nm PL nearly disappears. Thus, the 730-nm PL can only originate from the interface between the QDs and the disordered SiO₂. The Si=O defect is one type of defect on the surface of QDs, and its amount is related with the composition of QDs. The decrease of Si composition will lead to the decrease of Si=O defects and PL intensity. On the other hand, the PL excitation spectrum for 730-nm PL is located around 243 nm and related with the Ge-doping dose. Perhaps the optical-absorption takes place inside QDs and the emission process occurs at the interface. We think the 730-nm PL originates from the Si=O defects on the surface of QDs^[23].

In conclusion, Si_{1-x}Ge_x-QDs-contained SiO₂ thin films have been fabricated by ion implantation and annealing treatment. The samples exhibit PL peaks at 295, 400–470, 550, 730, and 780 nm. With the increase of Ge-doping dose, the blue shift of 400-nm PL band is observed. This PL band is ascribed to the multiple luminescence centers. The 550- and 730-nm PL peaks are attributed to the SPR center and Si=O defects, respectively. The 295- and 780-nm PL peaks originate from the different energy level transitions of the GeO center.

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