Shift in room-temperature photoluminescence of low-fluence Si\(^{+}\)-implanted SiO\(_{2}\) films subjected to rapid thermal annealing

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Abstract

We experimentally demonstrate the effect of the rapid thermal annealing (RTA) in nitrogen flow on photoluminescence (PL) of SiO\(_{2}\) films implanted by different doses of Si\(^{+}\) ions. Room-temperature PL from 400-nm-thick SiO\(_{2}\) films implanted to a dose of 3 \times 10^{16} \text{ cm}^{-2} shifted from 2.1 to 1.7 eV upon increasing RTA temperature (950–1150 °C) and duration (5–20 s). The reported approach of implanting silicon into SiO\(_{2}\) films followed by RTA may be effective for tuning Si-based photonic devices.

Keywords: rapid thermal annealing (RTA), Si\(^{+}\) implantation, photoluminescence, SiO\(_{2}\) films

1. Introduction

Given the advantages of Si technology in electronic integrated circuits and its potential applications in photonics and optoelectronics, silicon nanocrystals embedded in SiO\(_{2}\) have attracted much attention [1]. Room-temperature visible photoluminescence (PL) was first observed from porous silicon, but many practical problems have been encountered in exploiting this property [2, 3]. Plasma-enhanced chemical vapor deposition [4], evaporation and the termination of the glass-melt reactions [5] have been used to produce silicon nanocrystals emitting visible light, but none of those techniques was found suitable for manufacturing integrated devices. Silicon implantation into SiO\(_{2}\) film grown on crystalline Si, followed by annealing, is another method of fabricating Si-based luminescent structures. Many research groups have observed emission bands between 1.5 and 2.0 eV after implanting Si\(^{+}\) into SiO\(_{2}\) films and conventional annealing above 1000 °C in vacuum, Ar or N\(_{2}\) [6–11]. However, the implantation doses were relatively high (>10^{17} \text{ cm}^{-2}) and the annealing process took several hours. Spectral shift of PL upon short annealing (seconds) has not been studied much.

In this study, we applied rapid thermal annealing (RTA) to 400-nm-thick Si\(^{+}\)-implanted SiO\(_{2}\) films. Increasing RTA temperature (950–1150 °C) or duration (5–20 s) shifts the PL maximum from 2.1 to 1.7 eV. This approach can reduce the doses of Si\(^{+}\) implantation and shorten the
Figure 1. PL spectra of 400-nm-thick wet SiO$_2$ films implanted by Si$^+$ ions to doses of (a) $4 \times 10^{15}$ cm$^{-2}$, (b) $1 \times 10^{16}$ cm$^{-2}$, and (c) $3 \times 10^{16}$ cm$^{-2}$ after dry-N$_2$RTA for 20 s at 1150 °C.

Figure 2. PL spectra of 400-nm-thick $3 \times 10^{16}$ cm$^{-2}$ Si$^+$-implanted SiO$_2$ film after dry-N$_2$RTA at 1150 °C for 20 s, without (a) and with (b, c) subsequent HF etching. The etching reduced the SiO$_2$ thickness from 400 nm (a) to 260 nm (b), and 160 nm (c).

Figure 3. PL spectra of 400-nm-thick $3 \times 10^{16}$ cm$^{-2}$ Si$^+$-implanted SiO$_2$ film after dry-N$_2$RTA for 20 s at 950 °C (a), 1050 °C (b), and 1150 °C (c).

2. Experimental procedure

Samples were prepared by implanting Si$^+$ into a 400-nm-thick SiO$_2$ layer thermally grown on (100)-oriented p-doped Si substrates. The doses of the implanted Si$^+$ were $4 \times 10^{15}$, $1 \times 10^{16}$ and $3 \times 10^{16}$ cm$^{-2}$. During the implantation, the samples were kept at liquid nitrogen temperature. Acceleration energy of 160 keV resulted in the estimated implanted depth of 250 nm with the standard deviation of ±60 nm. The samples were subjected to RTA in N$_2$ flow. Gas pressure of 50 mbar was applied to the furnace entrance; heating rate was ∼100 °C s$^{-1}$ and cooling rate was ∼100 °C min$^{-1}$. The annealed films were etched with a 10% aqueous HF solution to reduce the SiO$_2$ thickness to 260, 160 and 100 nm. The average SiO$_2$ layer thickness was determined using atomic force microscopy.

Luminescence was excited with a He–Cd laser (3.8 eV, 5 mW) and detected using a monochromator, cooled photomultiplier tube and lock-in detection which improved the signal-to-noise ratio. No PL could be detected from $3 \times 10^{16}$ cm$^{-2}$ Si$^+$-implanted SiO$_2$ films without annealing.

Hydrogen-related species in the oxide films were studied by FTIR transmittance. Spectra were recorded at room temperature in N$_2$ atmosphere with a 2 cm$^{-1}$ resolution and 200-scan averaging.

3. Results and discussion

Figure 1 demonstrates the effect of Si$^+$ dose ($4 \times 10^{15}$, $1 \times 10^{16}$ or $3 \times 10^{16}$ cm$^{-2}$) on PL spectra from SiO$_2$ films subjected to RTA at 1150 °C for 20 s. A shift from ∼2.2 eV to 1.7 eV with increasing dose is observed, thus revealing that the Si$^+$ dose determines the PL peak position. PL intensity decreases with the dose, but the decrease is minor.
Figure 4. PL spectra of 400-nm-thick $3 \times 10^{16}$ cm$^{-2}$ Si$^+$-implanted SiO$_2$ film after dry-N$_2$ RTA at 1150 °C for 5 s (a), 10 s (b), and 20 s (c). Curve (d) corresponds to the Si$^+$ dose of $1 \times 10^{17}$ cm$^{-2}$ and slow annealing in dry N$_2$ at 1150 °C for 8 h.

Figure 5. FTIR spectra of 100 nm (a), 200 nm (b) and 400 nm thick (c) SiO$_2$ films without Si$^+$ implantation or annealing, and of 400-nm-thick film Si$^+$ implanted to doses of $1 \times 10^{16}$ cm$^{-2}$ (d) and $3 \times 10^{16}$ cm$^{-2}$ (e) after RTA at 1150 °C for 20 s.

Figure 6. FTIR spectra of 400-nm-thick SiO$_2$ films without implantation or RTA (a), Si$^+$-implanted to doses of $4 \times 10^{15}$ cm$^{-2}$ (b) and $1 \times 10^{16}$ cm$^{-2}$ (c) and subjected to wet-N$_2$ RTA at 1150 °C for 20 s, Si$^+$-implanted to doses of $1 \times 10^{16}$ cm$^{-2}$ (d) and $3 \times 10^{16}$ cm$^{-2}$ (e) and subjected to dry-N$_2$RTA at 1150 °C for 20 s.

down to 100 nm. These results confirm our estimate of the implantation depth (250 ± 60 nm). They also suggest that larger implanted Si$^+$ density results in bigger Si clusters and thus and lower-energy PL.

We have further analyzed the effects of the temperature and duration of RTA on the PL shift. As the temperature of isochronal (20 s) dry-N$_2$ RTA is increased from 950 to 1150 °C, luminescence shifts from 2.1 to 1.7 eV, as shown in figure 3. Similar shift is observed when the duration of isothermal (1150 °C) RTA is increased from 5 to 20 s (figure 4). Figure 4 also shows PL spectrum of the $1 \times 10^{17}$ cm$^{-2}$ Si$^+$-implanted SiO$_2$ film after 8 h of conventional, slow annealing (curve d). Slow annealing also shifts PL peak to 1.7 eV, but PL intensity is reduced as compared to RTA. Similar PL peak at 1.7 eV was observed by Fernandez et al in the 800-nm-thick Si$^+$-implanted (150 keV, $1 \times 10^{17}$ cm$^{-2}$) SiO$_2$ films after slow annealing at 1100 °C for 8 h [10] and by Mutti et al in 430-nm-thick Si$^+$-implanted (160 keV, $3 \times 10^{17}$ cm$^{-2}$) SiO$_2$ films annealed at 1000 °C for 5 h [7].

We have analyzed the effect of implantation and annealing on the density of Si–H$_x$ ($x = 1, 3$) and Si–O–H bonds via FTIR absorption at ~2100 cm$^{-1}$ (figure 5) and ~3750 cm$^{-1}$ (figures 6 and 7), respectively [13, 14–16]. We could not detect absorption peaks at ~1450 or ~2900 cm$^{-1}$ corresponding to C–H$_x$ bonds [14, 17]. Figure 5 reveals that Si–H$_x$ absorption depends on the SiO$_2$ thickness; this absorption is weak for the studied 400 nm films and it is not affected by Si$^+$ implantation and dry-N$_2$ RTA. Similar conclusion can be made regarding the Si–O–H bonds (curves...
reveal that such annealing does induce higher Si$^+$ implantation doses. Luminescence spectra from those samples (inset in figure 7) showed intensity decrease in wet-N$_2$ annealed samples as compared to SiO$_2$ films annealed in dry N$_2$ [18, 19]. The PL peak shift in figure 7 is due to different implantation doses. This intensity decrease suggests that Si–O–H groups are not the origin, but perhaps a quencher of the observed PL; neither Si–O–H nor Si–H$_x$ or C–H$_x$ bonds seem to affect the PL from SiO$_2$ films annealed in dry N$_2$.

Figure 8 shows the PL peak intensities for temperatures of additional RTA for 10 min in dry N$_2$. It reveals similar annealing behavior for different implantation doses and annealing procedures (rapid or slow annealing), thus suggesting similar mechanism of PL induced at those conditions. Comparison of curves $d$ and $e$ also confirms much weaker PL intensity in Si$^+$ implanted SiO$_2$ annealed in wet nitrogen than annealed in dry nitrogen.

4. Conclusions

We have experimentally demonstrated the effect of RTA on the shift of room-temperature photoluminescence in Si$^+$-implanted SiO$_2$ film. The PL shift increases with the Si$^+$ dose, RTA temperature and duration. Infrared absorption suggests that the PL is not related to C–H, Si–H or Si–O–H groups. Comparison of PL between rapid and slow annealing suggests similar origin of PL, namely Si nanocrystals in the oxide matrix [6–11, 20]. The PL peak position can be tuned between 1.7 and 2.1 eV by varying RTA temperature (950–1150°C) and RTA duration (5–20 s); the processing time is significantly shorter for RTA than for conventional annealing. Those attractive features of RTA appear useful for manufacturing of optoelectronic devices.

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