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## Blue and red photoluminescence from Ge<sup>+</sup> implanted SiO<sub>2</sub> films and its multiple mechanism

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Under violet excitation, a strong blue band and a broad red band are emitted simultaneously from the Ge nanocrystal embedded  $SiO_2$  films fabricated by  $Ge^+$  implantation and annealing. The blue band exhibits a complex annealing behavior, and the photoluminescence excitation spectral analysis indicates that it results from a combination of several implantation-induced deficient centers. The peak position of the red band shifts from 600 to 640 nm when the mean size of Ge nanocrystals increases from 4.3 to 6.7 nm, suggesting that the red band comes from the radiative recombination of excitons confined in Ge nanocrystals. © 1998 American Institute of Physics. [S0003-6951(98)02739-9]

Since the observation of efficient room-temperature photoluminescence (PL) in porous silicon,<sup>1</sup> much research has been done to the luminescence of group IV semiconductor nanocrystals in order to develop integrated optoelectronic devices on silicon substrates.<sup>2</sup> Many methods, such as cosputtering,<sup>3</sup> oxidation of SiGe alloys,<sup>4</sup> hydrothermal reduction of  $Si_xGe_{1-x}O_2$ ,<sup>5</sup> and Ge ion implantation,<sup>6,7</sup> have been employed to fabricate luminescent Ge nanocrystals (nc-Ge) in a SiO<sub>2</sub> matrix. Ion implantation is, undoubtedly, a favorable method because it is compatible with the conventional silicon integrated circuit process technology. The usual PL spectrum of Ge nanocrystal embedded SiO<sub>2</sub> films fabricated by ion implantation is a broad red band round 600-800 nm.<sup>8-10</sup> On the other hand, it is well known that SiO<sub>2</sub>:Ge glasses with some kinds of defects exhibit violet and blue PL,<sup>11,12</sup> and blue PL has also been obtained from Ge nanocrystal embedded SiO<sub>2</sub> films fabricated by dc magnetron sputtering.<sup>13</sup> Recently, results pertinent to blue PL from Ge<sup>+</sup>-implanted SiO<sub>2</sub> layers have been reported by Rebohle et al.<sup>14</sup> A complete investigation of the kinetics of formation of the two emission bands has not been conducted so far. In this letter, we report experimental results on thermal SiO<sub>2</sub> films implanted with a high Ge<sup>+</sup> dose. Under violet excitation, a broad red band and a strong blue band emit simultaneously from the annealed films.

200 nm thick  $SiO_2$  films were thermally grown on (100) oriented p-type Si substrates. Ge ions were implanted into the SiO<sub>2</sub> films at an energy of 120 keV with a dose of 1  $\times 10^{17}$  cm<sup>-2</sup>. The substrates were kept at room temperature during implanting. The implantation energy was selected so that the implanted Ge concentration profile is completely within the oxide film, with the peak concentration lying at 70 nm from the surface. The Ge peak concentration is 16 at. %, as determined by Rutherford backscattering spectrometry (RBS) measurements. Subsequently, the implanted films were annealed in a quartz tube under N2 atmosphere for 30 min. The annealing temperature  $(T_{an})$  is in the range of 300-1100 °C. The PL spectra and PLE spectra were taken using a Hitachi 820 fluorescence photospectrometer at room temperature. The light source of the spectrometer was a xenon lamp, and the resolution of the monochromators was 2 nm. X-ray diffraction (XRD) measurements were carried out with a D/max- $\gamma$ A rotating anode diffractometer. The anode was rotated at a step of 0.02°. The wavelength of the x ray (Cu  $K\alpha$ ) is 0.1542 nm.

Figure 1 shows the XRD pattern from selected annealed films. The clearly visible Ge(111), (220), and (311) Bragg reflection peaks indicate the Ge crystallization. With increasing  $T_{an}$ , the full width at half maximum (FWHM) of the XRD peaks decreases, which indicates that the size of Ge particles in the annealed films increases with increasing  $T_{an}$ . A Gaussian curve fitting program has been used to obtain the FWHM value and centroidal peak position of the XRD peaks. For the (111) peak, at  $T_{an}$  of 600, 900, and 1100 °C, its FWHM is 1.9°, 1.6°, and 1.2°, respectively. The mean nc-Ge size estimated from the FWHM is 4.3, 5.1, and 6.7 nm, respectively. The centroidal peak position of the (111) peak is  $2\theta = 27.32^{\circ}$ ,  $27.39^{\circ}$ , and  $27.54^{\circ} (\pm 0.05^{\circ})$ , respectively. The lattice constants of nc-Ge determined from the centroidal peak position are 0.565, 0.564, and 0.561 nm  $(\pm 0.001 \text{ nm})$ , respectively. The lattice constants for  $T_{an}$  of 900 and 1100 °C are smaller than the value of bulk Ge (0.566 nm), which may result from the strain field between the nc-Ge and the surrounding matrix.<sup>15</sup> As a matter of record, the Bragg reflection peaks are not clear in the XRD pattern of the as-implanted film. For comparison, Ge<sup>+</sup>-implanted films with a low dose  $(1 \times 10^{15} \text{ cm}^{-2})$  were also done. There is no nc-Ge in the annealed films, as determined by XRD measurements.

The facts shown in Fig. 1 reveal that the Ge+ dose and the annealing process control the growth of nc-Ge. Thermal annealing can synthesize nc-Ge in SiO<sub>2</sub> films implanted with higher Ge<sup>+</sup> doses. The higher the annealing temperature, the larger the nanocrystals. Why does thermal annealing synthesize nc-Ge in the films with a dose of  $1 \times 10^{17}$  cm<sup>-2</sup>, but not in those with a dose of  $1 \times 10^{15}$  cm<sup>-2</sup>? For the doses of 1



FIG. 1. The XRD pattern from the annealed films, where curve A, B, and C correspond to the films annealed at 600, 900, and 1100 °C, respectively.

 $\times 10^{15}$  and  $1 \times 10^{17}$  cm<sup>-2</sup>, the peak Ge concentrations are 0.2 and 16 at %, respectively. According to the phase diagrams, a small amount of elemental Ge (less than 1 at %) can dissolve in SiO<sub>2</sub>. The as-implanted film with a dose of 1  $\times 10^{17}$  cm<sup>-2</sup> is therefore a supersaturated solid solution containing a large amount of excess Ge. Thermal annealing induces phase separation, which results in nc-Ge. On the other hand, due to low Ge concentration, nc-Ge cannot be synthesized in the  $1 \times 10^{15}$  cm<sup>-2</sup> Ge<sup>+</sup>-implanted films.

Under 250 nm (5 eV) excitation, the  $1 \times 10^{17}$  cm<sup>-2</sup> Ge<sup>+</sup>-implanted films emit a strong blue PL band and a red PL band simultaneously. Figure 2(a) shows the PL spectra for the as-implanted film and the film annealed at different  $T_{\rm an}$ . The as-implanted film exhibits a broad blue PL band peaked at 460 nm (2.7 eV). The annealing process causes apparent changes in the shape of the blue band. After annealing at 400 °C, a peak around 400 nm (3.1 eV) becomes dominant, and a shoulder around 425 nm (2.9 eV) appears. For  $T_{an}$  in the range of 400–900 °C the bi-modal behavior is retained, but the intensity ratio of these two peaks changes in favor of the 425 nm peak. For  $T_{an}$ >900, the 425 nm peak is dominant in the blue band. With increasing  $T_{an}$ , the integrated intensity of the blue band increases and reaches its maximum at 700 °C, then decreases dramatically. On the other hand, the red PL band of the as-implanted film and the films annealed at low  $T_{an}(<500 \text{ °C})$  is around 600–800 nm. It is weak, broad and shapeless. With increasing  $T_{an}$ , the red band becomes sharper, and its peak position shifts towards longer wavelength. For T<sub>an</sub> of 600, 900, and 1100 °C, the peak position is at 600 nm (2.07 eV), 630 nm (1.97 eV), and 640 nm (1.94 eV), respectively. The integrated intensity of the red band increases with increasing  $T_{an}$ , and reaches its maximum at 1100 °C. Its maximum is much weaker than that of the blue band.

Figure 2(b) shows the PLE spectra of the above films, which is monitored at the emission wavelength of 425 nm. These PLE spectra exhibit three excitation bands peaked at 230 nm (5.4 eV), 242 nm (5.1 eV), and 250 nm (5.0 eV), respectively. The 250 nm band is dominant in the asimplanted film, and becomes weaker when the film is annealed. The 230 and 242 nm bands become stronger and



FIG. 2. The PL and PLE spectra for the  $1 \times 10^{17}$  cm<sup>-2</sup> Ge<sup>+</sup>-implanted films. (a) The PL spectra for the as-implanted film and the annealed films. (b) The PLE spectra for the above films.

reach their maximums at 600 and 700 °C, respectively, then decrease significantly. The annealing behaviors of the 250, 242, and 230 nm PLE bands are similar to those of the 460, 425, and 400 nm blue PL subbands, respectively. The PLE multi peaks with different annealing behaviors indicate that there are several kinds of implantation-induced luminescent centers, which contribute to the blue band.

The PL spectra of the  $1 \times 10^{15}$  cm<sup>-2</sup> Ge<sup>+</sup>-implanted films differ distinctly from those of the  $1 \times 10^{17}$  cm<sup>-2</sup> Ge<sup>+</sup>-implanted films. The annealed films do not exhibit the red PL band. Typical PL and PLE spectra of the annealed films are shown in Fig. 3. The annealed films exhibit a sharp blue PL band peaking at 425 nm, with an excitation at 242 nm. These PL and PLE spectra reveal that the films have one kind of implantation-induced luminescent center contained in the  $1 \times 10^{17}$  cm<sup>-2</sup> Ge<sup>+</sup>-implanted films. The inset shows the PL integrated intensity depending on  $T_{an}$ . With increasing  $T_{an}$ , the integrated intensity of the blue band increases and reaches its maximum at 800 °C, then decreases dramatically. Its maximum is weaker than that of the 1  $\times 10^{17}$  cm<sup>-2</sup> Ge<sup>+</sup>-implanted film by a factor of  $\sim 20$ .

The red PL band is absent in the films containing no nc-Ge (as shown in Fig. 3), whereas it appears in the films containing nc-Ge [as shown in Fig. 2(a)], and its peak posi-



FIG. 3. The PL and PLE spectra for the  $1 \times 10^{15}$  cm<sup>-2</sup> Ge<sup>+</sup>-implanted films annealed at 600 °C for 30 min. The PL spectrum is under 5.0 eV excitation, and the PLE spectrum is monitored at the emission wavelength of 425 nm. The inset shows the PL integrated intensity depending on  $T_{an}$ .

tion shifts systematically with the nc-Ge size. The observed results reveal that the red PL band is correlated to the presence of nc-Ge, and it is produced by the radiative recombination of quantum-confined excitons in nc-Ge. The PL peak redshift in our experiment is smaller than what has been predicted for radiative recombination of quantum-confined excitons.<sup>16</sup> [The calculated PL peak position from Ref. 16 should shift from 610 nm (2 eV) to 950 nm (1.3 eV) when the nc-Ge size increases from 4.3 to 6.7 nm.] This difference may result from two factors. One factor is the shortening of the lattice constant of nc-Ge, as determined by XRD measurement. The change in the lattice constant would cause some change in energy band structure of nc-Ge,<sup>17</sup> so the energy of the  $1S_e \rightarrow 1S_h$  transition is different from that of Ref. 16. The other factor is the inhomogeneity of the nc-Ge size. Maeda<sup>17</sup> pointed out that besides the radiative recombination inside nc-Ge, excitons might recombine nonradiatively also. The nonradiative relaxation procedure takes place at the surface dangling bonds of nc-Ge or the interface between nc-Ge and the SiO<sub>2</sub> matrix. The PL efficiency of nc-Ge depends on the exciton decay rates of the radiative recombination and the nonradiative one. According to the size dependence of the radiative decay rate,<sup>16</sup> the smaller the nc-Ge size, the higher the PL efficiency. The nc-Ge fabricated by implantation and annealing exhibits a Gaussian size distribution.<sup>9</sup> The red luminescence is contributed by the combination of nanocrystals with different sizes. Due to the size dependence of PL efficiency, the PL peak energy should be higher than the value calculated with the mean nc-Ge size, as is observed in this study.

As shown in Figs. 2(a) and 3, both the  $1 \times 10^{15}$  cm<sup>-2</sup> Ge<sup>+</sup>-implanted films and the  $1 \times 10^{17}$  cm<sup>-2</sup> Ge<sup>+</sup>-implanted films exhibit the blue band, with excitation bands around 5 eV. This fact suggests that the blue band is out of relation to nc-Ge. Due to the Ge<sup>+</sup> implantation into SiO<sub>2</sub>, the ratio of O atoms to the addition of Si and Ge is less than 2, which indicate that Ge<sup>+</sup> implantation creates oxygen-deficient defects in the SiO<sub>2</sub>. Therefore, we assume that the blue PL band results from the implantation-induced oxygen-deficient

luminescent centers. The subpeaks in the PL blue band and the PLE multi peaks indicate that different luminescent centers are formed during the annealing process. We have previously used x-ray photoelectron spectrometry (XPS) measurements to analyze the Ge chemical bonding in the films implanted with high Ge<sup>+</sup> fluences.<sup>18</sup> Due to Ge<sup>+</sup> implantation, some Ge oxides are produced, and the matrix becomes nonstoichiometric SiO<sub>x</sub>. Ge atoms in the matrix are in several chemical states such as Ge<sup>2+</sup>, Ge<sup>3+</sup>, and Ge<sup>4+</sup>. The annealing process induces some thermodynamical reactions between Ge oxides and the nonstoichiometric SiO<sub>x</sub>, which results in nc-Ge and stoichiometric SiO<sub>2</sub>. Since the matrix becomes nonstoichiometric due to Ge<sup>+</sup> implantation, a Si atom has a possibility of connecting with another Si atom, which forms a Si-Si bond in the matrix network, i.e., neutral oxygen vacancy (it is denoted hereafter as  $O_3 \equiv Si = Si \equiv O_3$ ). Due to the thermodynamical reactions during annealing, one or both Si atoms of the O3=Si-Si=O3 center are substituted by Ge atoms, which form a O<sub>3</sub>=Ge-Si=O<sub>3</sub> or  $O_3 \equiv Ge = Ge \equiv O_3$  center. As is known from the molecule spectroscopy,<sup>19</sup> these substitutes will result in increasing of the energy of the  $T_1 \rightarrow S_0$  transition. Therefore, it is assumed that the blue subbands at 400, 425, and 460 nm (and the PLE peaks at 230, 242, and 250 nm) correspond to the

 $O_3 \equiv Ge - Ge \equiv O_3, O_3 \equiv Ge - Si \equiv O_3, and O_3 \equiv Si - Si \equiv O_3$ centers, respectively.

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