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Effect of Hydrostatic Pressure on Photoluminescence Spectra from Structures with Si Nanocrystals Fabricated in SiO_2 Matrix

K.S. Zhuravlev[a,*], I.E. Tyschenko[a], E.N. Vandyshev[a], N.V. Bulytova[a], A. Misiuk[b], L. Rebohle[c] and W. Skorupa[c]

[a]Institute of Semiconductor Physics
Pr. Lavrentieva, 13, Novosibirsk, 630090, Russia
[b]Institute of Electron Technology, al. Lotników 32/46, 02-668 Warsaw, Poland
[c]Institute of Ion Beam Physics and Materials Research
Research Center Rossendorf, Inc., POB 510119, 01314 Dresden, Germany

The effect of hydrostatic pressure applied at high temperature on photoluminescence of Si-implanted SiO_2 films was studied. A "blue"-shift of PL spectrum from the SiO_2 films implanted with Si^+ ions to total dose of 1.2×10^{17} cm^{-2} with an increase in hydrostatic pressure was observed. For the films implanted with Si^+ ions to a total dose of 4.8×10^{16} cm^{-2} high temperature annealing under high hydrostatic pressure (12 kbar) causes a "red"-shift of photoluminescence spectrum. The "red" photoluminescence bands are attributed to Si nanocrystals while the "blue" ones are related to Si nanocrystals of reduced size or chains of silicon atoms or ≡Si–Si≡ defects. A decrease in size of Si nanocluster size occurs in result of the pressure-induced decrease in the diffusion of silicon atoms.

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1. Introduction

Silicon nanocrystals fabricated by Si^+ ion implantation into silicon oxide with subsequent thermal annealing are promising candidates as light emitters [1]; they show the near-infrared photoluminescence (PL) in the 700–900 nm range. Different

*corresponding author; e-mail: zhur@thermo.isp.nsc.ru

mechanisms of radiative recombination in silicon nanocrystals were discussed in the literature [2–4], but the nature of this behavior is not well understood until now.

The fabrication technique of silicon nanocrystals which we use gives a unique opportunity to control with a high accuracy the concentration and distribution of Si atoms introduced into the matrix. The content and distribution of Si atoms define the size of nanocrystals and their luminescence properties. By now the effects of the implanted dose, the temperature, duration and atmosphere of the annealing on the luminescence properties of the structures with silicon nanocrystals were studied in detail [5–10].

In the present paper the effect of a high hydrostatic pressure applied during annealing at high temperature on PL of Si-implanted SiO_2 films was investigated. It was found that the PL band from the films is shifted due to this treatment. The direction of the shift depends on the dose of the implanted Si^+ ions. Based on present results a tentative explanation of the origin of luminescence centers formed in the Si-rich SiO_2 film is given.

2. Experimental details

The samples were prepared from 500 nm thick layers of SiO_2 thermally grown at 1000°C on Si wafer which were implanted subsequently with 200 and 100 keV Si^+ ions. The implantation doses are of $6.3 \times 10^{16} + 3.9 \times 10^{16}$ cm^{-2} (high dose or HD) and $3.0 \times 10^{16} + 1.8 \times 10^{16}$ cm^{-2} (low dose or LD). The energy of ions was chosen so that maximum of their distribution was placed near the middle of the films. The substrate temperature during implantation was kept at –60 to −20°C. The density of Si^+ ions current was kept at 0.5–1.0 μA/nm^2. Subsequently, the samples were annealed for 5 hours at different temperatures in the range of $T_a = 600 \div 1130$°C under atmospheric pressure and also argon pressure of $P = 1$ kbar, 6 kbar, 9 kbar and 12 kbar (denoted below as the high pressure–high temperature (HP–HT) treatment). A more detailed description of the sample preparation is given in [11].

A pulsed N_2 laser ($\lambda = 337$ nm) with a pulse duration of 7 ns and peak power density of 4 kW·cm^{-2} was used for PL excitation. The PL signal was spectrally resolved and detected by a double diffraction grating monochromator equipped with a cooled S-20 photomultiplier operating in the photon counting mode. The PL measurements were conducted at room temperature.

3. Experimental results

Figure 1 shows PL spectra from HD Si-implanted SiO_2 films measured before and after high temperature annealing. The films were annealed at $T_a = 1130$°C at different pressure of $P = 1$ bar, 6 kbar, 9 kbar or 12 kbar during 5 hours. It

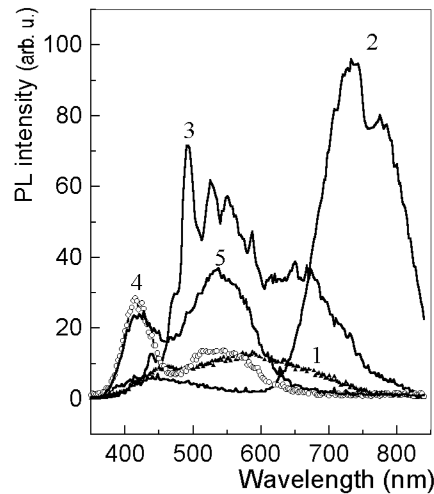

Fig. 1. PL spectra of the SiO_2 films implanted with Si^+ ions to total dose of 1.2×10^{17} cm^{-2} (HD): (1) as-implanted specimen; specimens treated at $T_a = 1130°C$ for 5 hours at hydrostatic pressure of: (2) $P = 1$ bar, (3) $P = 6$ kbar, (4) $P = 9$ kbar, (5) $P = 12$ kbar.

is seen from the figure that in the spectrum of the as-implanted specimen a weak broad PL band with a maximum near 600 nm was observed. The sample annealed at atmospheric pressure shows a pronounced near-infrared ($700 \div 850$ nm) PL band. The annealings at higher pressures lead to a strong shift of the PL band towards the shorter wavelengths and to the decrease in the PL intensity. The PL spectrum from the sample HP–HT treated at $P = 6$ kbar exhibits few peaks in the wavelength region of $550 \div 700$ nm. Further increase in the argon pressure up to $P = 9$ kbar applied during annealing causes an appearance of a peak at about 420 nm. In the spectrum of the sample annealed at the argon pressure of $P = 12$ kbar two peaks at 420 nm and 550 nm are clearly seen.

A distinct dependence of PL on hydrostatic pressure was observed for the LD films. A wide band with maximum at 650 nm was recorded for the as-implanted specimen (Fig. 2). The maximum of the PL spectrum shifts to 550 nm in the specimen annealed at $T_a = 1000°C$ at atmospheric pressure and then to 420 nm after annealing at the same temperature under 6 kbar argon pressure. As seen in Fig. 2, PL of the as-synthesized, LD specimens annealed at atmospheric pressure and argon pressure of $P = 6$ kbar is very weak. The PL intensity considerably increases and the PL band shifts towards longer wavelength after annealing at $P = 12$ kbar. In order to find the reason for these phenomena we studied the effect of the annealing temperature under $P = 12$ kbar argon pressure on the PL spectra. The result of this investigation is presented in Fig. 3. It is seen that the PL intensity of the specimen annealed at $T_a = 800°C$ is doubled in comparison

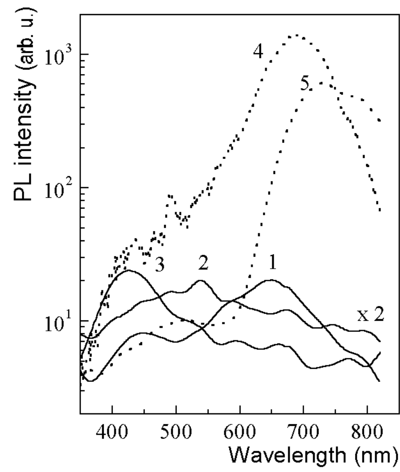

Fig. 2. PL spectra of the SiO_2 films implanted with Si^+ ions to total dose of 4.8×10^{16} cm^{-2} (LD): (1) as-implanted specimen; ($2 \div 4$) the specimens annealing at T_a = 1000°C for 5 hours at different hydrostatic pressures: (2) P = 1 kbar, (3) P = 6 kbar, (4) P = 12 kbar. The curve #5 is the spectrum of the HD specimen HP–HT treated at P = 1 kbar, T_a = 1130°C. The curves #1, 2, 3 are mathematically smoothed.

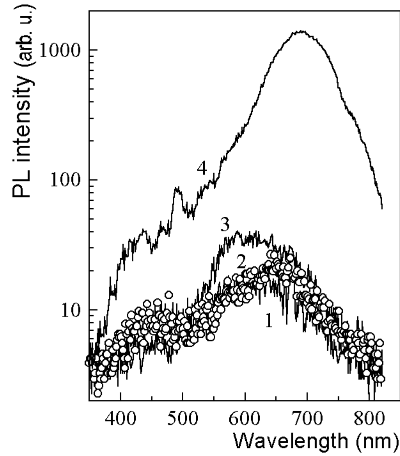

Fig. 3. PL spectra of LD specimens: (1) as-implanted; ($2 \div 4$) the samples annealed at P = 12 kbar at different temperatures: (2) T_a = 600°C, (3) T_a = 800°C, (4) T_a = 1000°C. For convenience the curve #2 is depicted in circles.

with the PL intensity from the as-implanted specimen. A sharp increase in the PL intensity together with a "red" shift of the PL peak position takes place at T_a = 1000°C.

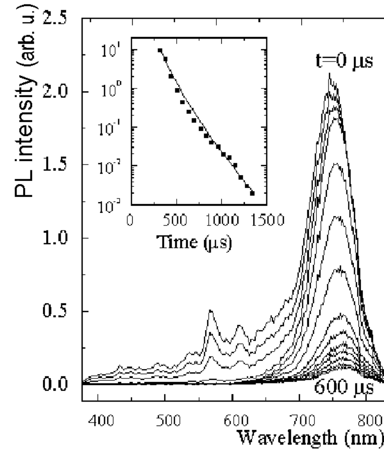

Fig. 4. Evolution of the transient PL spectrum from the LD specimen HP–HT treated at $P = 12$ kbar, $T_a = 1000°$C as a function of the annealing time. The inset shows the experimental curve (circles) integrated over the band spectrum and calculated decay curve according to formula 1 (straight line).

In Fig. 4 a set of time-resolved PL spectra from the LD specimen HP–HT treated at $P = 12$ kbar, $T_a = 1000°$C is presented as a function of delay time for the measurements done after the excitation pulse. The decrease in the intensity together with a "red"-shift of the peak position with the delay time is seen in the figure. This kind of behavior has been observed previously for Si nanoclusters [12]. The inset to Fig. 4 shows the decay curve integrated over the spectrum. The PL intensity decay is nonexponential, and can be fitted by a "stretch-exponential" function

$$I(t) = I_0 \exp\left[-(t/\tau)^{\beta}\right], \qquad (1)$$

where τ is thedecay time and β is the dispersion factor. The approximation of the decay curve gives a value of $\tau = 12$ μs and $\beta = 0.57$ for the decay time and dispersion factor, respectively. Similar results were obtained for the HD specimen HP–HT treated at $P = 1$ bar, $T_a = 1130°$C, though the value of decay time was $\tau = 20$ μs at $\beta = 0.57$.

4. Discussion

A single wide emission band peaking at near 800 nm is related to the radiative recombination of carriers in Si nanocrystals formed in Si-implanted SiO_2 films during a high temperature annealing ($T_a > 900°$C) [13]. Since the LD specimen treated at $P = 12$ kbar, $T_a = 1000°$C demonstrates the PL features (peak position and decay time) similar to the PL characteristics of the HD specimen annealed at atmospheric pressure at $T_a = 1130°$C we conclude that Si nanocrystals were

formed in this LD specimen. A "blue" shift of the PL peak from the LD specimen in comparison with the PL peak position for the HD specimen may be due to a smaller size of Si nanocrystals in the former specimen. No unique interpretation of the PL bands observed in a shorter wavelength region of the spectra (400–600 nm) has been found so far. Tentative explanation could be a quantum confinement of excitons in very small Si nanocrystals or excitonic recombination in chains of silicon atoms [14–16]. It was also suggested that the blue-light emission may be attributed also to a ≡Si–Si≡ defect [15]. It should be noted that the low intensity of the "blue" PL bands might be due to a low energy of photon of the exciting light, because an optimal excitation of PL from the ≡Si–Si≡ defects takes place at 250 nm [17].

Enhanced hydrostatic pressure at high temperature slows down diffusion of silicon atoms in the SiO_2 matrix [18] and therefore hampers the process of formation of Si nanoclusters. With an increase in the applied pressure the Si nanocrystals become smaller. At the even higher hydrostatic pressure only chains of silicon atoms are formed and the number of ≡Si–Si≡ defects increases. We suggest that this is a reason for the "blue" shift of the PL band with an increase in hydrostatic pressure. This effect is clearly apparent for the HD specimens in which the diffusion length of Si atoms $L = (Dt)^{1/2}$ exceeds a mean distance between the implanted silicon atoms $r = (1/N)^{1/3}$, where D is a diffusion coefficient of Si atoms in SiO_2, t is time of annealing, N is concentration of Si atoms. In our experimental conditions we have got a value of $L = 2.5$ nm and $r = 0.6$ nm for the diffusion length and the mean distance, respectively. For this estimation we used the expression for the diffusion coefficient of Si atoms in SiO_2 from [19].

There is no unique explanation of the "red" shift of the PL band and the increase in its intensity for the LD specimen annealed of $T_a = 1000$°C under pressure of $P = 12$ kbar. For this specimen $L = 0.8$ nm and $r = 0.8$ nm, therefore formation of the nanocrystals should be hampered even at atmospheric pressure. A possible explanation of the enhanced formation of light-emitting recombination centers during the annealing at high pressure has been given in [20]. It has been done in terms of the concept of an enhanced structural transformation [21] taking place within a metastable region such as non-stoichiometric region of Si-enriched SiO_2. The activation energy corresponding to changes in a short-range order may be substantially reduced in the case when atoms of the matrix are very far from the equilibrium state. It seems that a difference in the structure of HD and LD Si implanted films is much enhanced under hydrostatic pressure. The high pressure–high temperature treatment accelerates formation of Si nanocrystals in the LD Si-implanted SiO_2 films while it slows down the formation of Si nanocrystals in the HD Si-implanted SiO_2 films. Further work in this field is needed to reveal the physics of this process.

5. Summary

In the present paper the effect of application of hydrostatic pressure at high temperatures on photoluminescence spectra of SiO_2 films implanted with silicon ions has been examined. Basing on the identification of the PL bands the process of formation of silicon nanocrystals in the SiO_2 matrix has been studied. It is suggested that high hydrostatic pressure hampers the process of formation of Si nanoclusters in SiO_2 films if the diffusion length of Si atoms exceeds the mean distance between the implanted Si atoms. This can be explained as an effect of decreased diffusivity of silicon atoms at enhanced hydrostatic pressure.

Acknowledgments

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