Visible photoluminescence induced in Si/SiO_2 samples by Si implantation

Visible photoluminescence induced in Si/SiO$_2$ samples by Si implantation

A D Lan, B X Liu and X D Bai

Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, People's Republic of China

Abstract. Implantation-induced visible light emission was studied using 120 and 160 keV Si-ion implantation into Si single crystals covered with thin SiO$_2$ layers of various thicknesses. A visible band centred at around 2.0 eV was observed from the samples implanted to a dose range of $(0.5-1) \times 10^{17}$ cm^{-2}. After post-annealing at 1100 °C in flowing N$_2$ gas, another visible band located at 1.7 eV was detected for all of the samples. The photoluminescence intensity was found to correlate with the oxygen concentration in the implantation region, which was estimated using the program TRIM-92 (from 'transport of ions in matter'). A mechanism that may be responsible for the observed light emission was discussed in terms of the so-called three-region model.

1. Introduction

Currently, intensive studies are being made of the optical and electronic properties of nanocrystalline silicon (nc-Si), on the basis of the interest in the fundamental physics, as well as because of the industrial interest in its application in Si-based optoelectronic devices [1–3]. Most previous research work was focused on electrochemically etched Si, i.e., porous Si (por-Si), from which strong visible photoluminescence (PL) was observed at room temperature. Despite the significant quantity of theoretical and experimental data concerning por-Si obtained in the last few years, there still remains basic confusion as regards the origin of the luminescence [4, 5]. Also, the solution-based (wet) methods used for the synthesis of por-Si led to poor mechanical properties and unstable luminescence properties, and hence made it quite difficult to integrate this material into the current very-large-scale integrated-circuit manufacturing technology. Thus several alternative methods for preparing nanocrystalline Si have recently been attempted, but none of them has so far been developed to a stage of practical application [6, 7].

Recent reports on a strong red PL from SiO$_2$ treated by Si-ion implantation and subjected to a high-temperature post-annealing [8–11] demonstrated that ion implantation was a potential candidate as a technique for manufacturing Si-based luminescent materials which exhibit a better mechanical and chemical stability than por-Si. Also, the lack of any involvement of hydrogen in the ion implantation process offered an opportunity for promoting an understanding of the physics of PL. Up to now, however, there has still been no sound interpretation of the origin of the implantation-induced photoemission [8–11]. It is noted that most researchers have so far studied silica or thick thermally grown SiO$_2$ on Si, and thus the observed light emission was strongly related to the SiO$_2$. It is thought that if the starting material is Si covered with a thin SiO$_2$ overlayer, enabling the implanting

ions to penetrate through the Si/SiO_2 interface, one may acquire some revealing results; this was the objective of this study. We report, in this article, our experimental results, and give a discussion of the possible influence of the oxygen content on the photoemission.
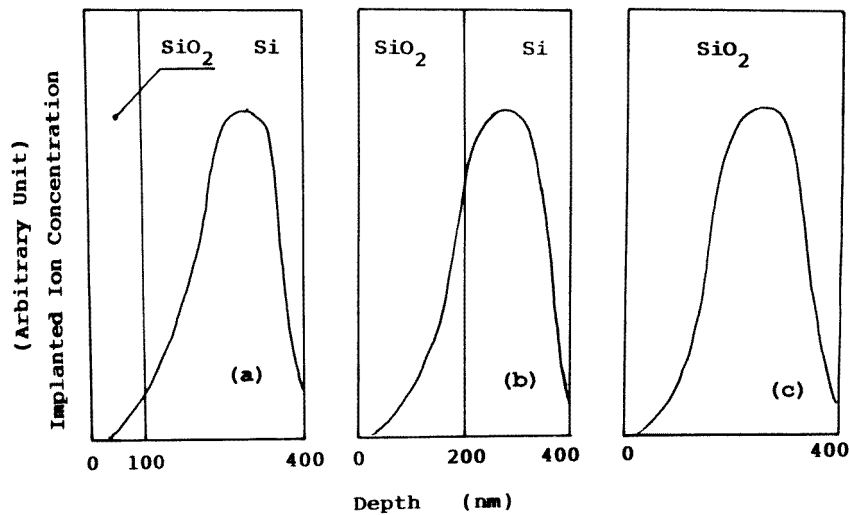
Figure 1. A schematic illustration of the distribution of implanted Si atoms in samples after 160 keV implantation (a) for sample A, (b) for sample B, and (c) for sample C.

2. Experimental procedure

Boron-doped p-type (111)-orientated Si wafers, 0.35 mm thick, with a resistivity of 0.01–0.02 Ω cm were used in this study. SiO_2 overlayer films were grown on Si wafers at high temperature ($T > 1000\,^\circ$C) in flowing dry O_2 gas. Three sets of samples with various SiO_2 layer thicknesses were prepared, and they are called samples A, B, and C, corresponding to oxide layer thicknesses of 1000 Å, 2000 Å, and 6000 Å, respectively, as measured by an ellipsometer with an uncertainty of less than 100 Å. Two energies, 120 keV and 160 keV, for the ^{28}Si-ion implantation to doses in the range $(0.5–1) \times 10^{17}$ cm^{-2} were used, with a current density of about 2.5 μA cm^{-2}. The TRIM-92 (from 'transport of ions in matter') program was employed to estimate the depth profiles of the implanted Si atoms in the samples. In our experiment, it was apparent that the distributions of the implanted Si ions in the three sets of samples were quite different. For the 160 keV implantation, the implanted region was estimated to be at a depth of between 1700 Å and 3200 Å below the surface (concentration maximum: 2500 Å; standard deviation: ±700 Å), while for 120 keV implantation, the implanted region was at a depth between 1200 Å and 2400 Å (concentration maximum: 1800 Å; standard deviation: ±600 Å). Obviously, for sample C (covered with a 6000 Å SiO_2 layer; abbreviated as 6000 Å later, and similarly for other samples), all of the implanted ions were distributed in the SiO_2 layer. For sample B (2000 Å), the concentration maximum was near the SiO_2/Si interface. For the samples B implanted at 120 keV, the concentration maximum was in the SiO_2 layer, while for the samples B implanted at 160 keV, it was in the Si substrate. As for sample A (1000 Å), the implanted Si ions were almost entirely stopped in the Si substrate for both 120 and 160 keV implantation. Figure 1 shows a schematic distribution of the implanted Si ions in samples

A, B, and C at the energy of 160 keV.

Post-annealing of the as-implanted samples was conducted in a furnace using flowing N_2 gas of high purity. A Raman spectrometer was employed to measure the room temperature photoluminescence spectra of the as-implanted and post-annealed samples. A Spectra-Physics 2000 Ar^+-ion laser was employed as the excitation source. The 514.5 nm line and the 488 nm line of the argon laser were both used as excitation sources, and it was found that the choice of line did not make any appreciable difference to the observed PL spectra. The luminescence was detected using a Spex 1403 spectrometer.

3. Results and discussion

The PL measurements of the as-implanted samples showed that an emission band peaked at around 2.0 eV was visible in the PL spectra of all of the samples. In our case, the ion implantation treatment for samples C was very close to that reported by Shimizu-Iwayama *et al*, and we therefore ascribed the 2.0 eV luminescence band to the E′ defects in local SiO_x structures created by Si-ion implantation into the SiO_2 layers [8–10]. The same 2.0 eV PL bands as were observed for the as-implanted samples A and B can also be attributed to the E′ defects. In fact, in a measurement for samples A and B implanted to low doses, we obtained experimental evidence for the E′ centre line from the electron spin-resonance (ESR) spectra [12].

Table 1. A list of PL results (peak energy and relative intensity). The PL intensity data listed were obtained under the same measurement conditions. The annealing was conducted at 1100 °C in flowing pure N_2 gas for either 5 h or 90 min.

Implantation parameters (cm⁻²)	Annealing time	Thickness of SiO₂		
		1000 Å	2000 Å	6000 Å
0.5×10^{17}	90 min	1.71 eV, 1.0	1.71 eV, 5.5	1.71 eV, 36.8
160 keV	300 min	No light	1.71 eV, 2.1	1.72 eV, 250.0
1×10^{17}	90 min	1.70 eV, 4.9	1.70 eV, 4.9	1.67 eV, 55.3
160 keV	300 min	No light	1.72 eV, 57.9	1.67 eV, 447.4
1×10^{17}	90 min	1.70 eV, 3.2	1.67 eV, 71.1	1.65 eV, 89.5
120 keV	300 min	No light	1.70 eV, 234.2	1.65 eV, 315.8

We now turn to the luminescence that was observed after high-temperature (1100 °C) post-annealing, and the results of the PL measurement are listed in table 1. As shown in the table, a PL band peaked at around 1.7 eV with a half-width (full width at half-maximum) of about 0.32 eV was detected from all of the samples after annealing for 90 minutes. On prolonging the annealing time up to five hours, the band disappeared from sample A (1000 Å), while for samples B and C the band remained and the intensity varied. For sample C (6000 Å) the intensity increased with increasing annealing time. For sample B, the situation was a little complicated, i.e. the intensity of the 1.7 eV band exhibited a dependence on the implantation energy as well as the ion dose, as shown in figure 2. For samples implanted with 160 keV Si to a dose of 0.5×10^{17} ions cm⁻², prolonged annealing led to a reduced PL intensity, while for a sample implanted to a dose of up to 1×10^{17} ions cm⁻², the PL intensity increased with increasing annealing time. When the implantation energy was 120 keV and the dose was of 1×10^{17} ions cm⁻², the PL intensity became stronger
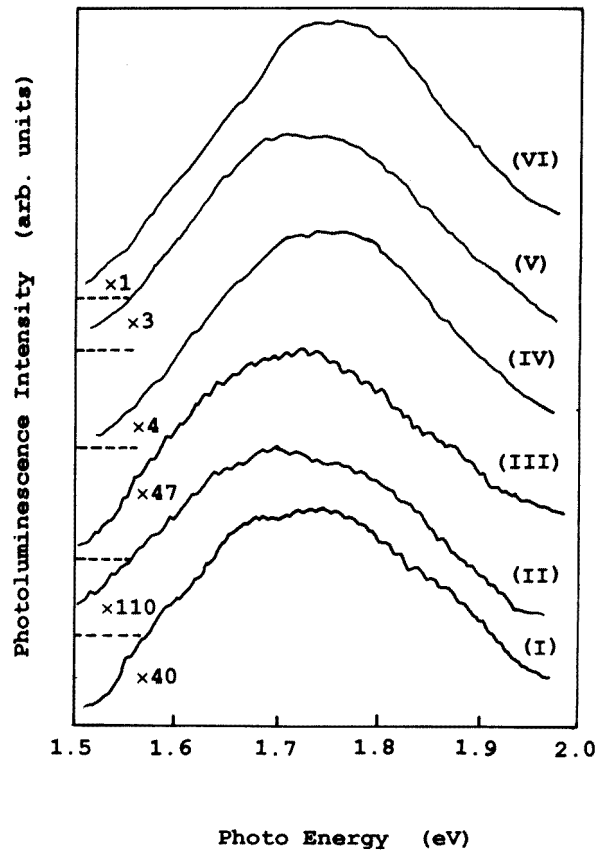
Figure 2. PL spectra of samples B after 120 and 160 keV implantation to doses of (0.5–1) $\times 10^{17}$ cm^{-2}, and post-annealing for various times: (I) after 160 keV implantation to a dose of 0.5 $\times 10^{17}$ cm^{-2}, and post-annealing for 90 min; (II) after 160 keV implantation to a dose of 0.5 $\times 10^{17}$ cm^{-2}, and post-annealing for 300 min; (III) after 160 keV implantation to a dose of 1 $\times 10^{17}$ cm^{-2}, and post-annealing for 90 min; (IV) after 160 keV implantation to a dose of 1 $\times 10^{17}$ cm^{-2}, and post-annealing for 300 min; (V) after 120 keV implantation to a dose of 1 $\times 10^{17}$ cm^{-2}, and post-annealing for 90 min; and (VI) after 120 keV implantation to a dose of 1 $\times 10^{17}$ cm^{-2}, and post-annealing for 300 min. The zero lines for curves (II)–(VI) are shifted vertically and shown by the dashed line. Relative intensity factors are also shown for each curve.

than that for implantation at 160 keV, and increased with increasing annealing time.

Since the annealing of the samples implanted with Si ions at 1100 °C would induce a decomposition of SiO$_x$ resulting in the precipitation of crystalline Si, the 1.7 eV band was ascribed to electron–hole recombination in the interfaces between Si nanocrystals and SiO$_2$ [8–10]. For sample C with a SiO$_2$ layer 6000 Å thick, Si implantation would induce much SiO$_x$ structure, and it was reasonable to consider the 1.7 eV photoemission band observed in this study as originating from the Si/SiO$_2$ interfaces, which were formed by the segregation of the crystalline Si from SiO$_x$. On the other hand, for the samples A (1000 Å), the 1.7 eV band was more or less unexpected: as most of the implanted Si ions stopped in the crystalline Si substrate, only a little SiO$_x$ structure could have been involved. Nevertheless, the 1.7 eV band observed from the samples A featured a remarkable similarity as regards peak energy

and FWHM (full width at half-maximum) to those observed for samples B and C; its origin was thus considered to be the same as that for samples B and C. After inspection of the intensity variation among the samples, we found that under the same treatment conditions, the PL intensity increased with increase of the SiO_2 layer thickness of the samples, and that for the same sample configuration, lower-energy implantation resulted in more intense light emission. These features are clearly shown by table 1, and suggest that the PL intensity is closely related to the oxygen/silicon ratio (O/Si ratio $= X, 0 < X < 2$) in the implanted region. The bigger the value of X, the greater the PL intensity. In our experiments, after implantation, there is a considerable difference in the oxygen concentration, or a different average ratio of O to Si, in the implanted regions of the three sets of samples, according to the TRIM-92 simulation. Since most of the luminescence centres were thought to be situated in the implanted region, then, as a deduction, the variation of the PL intensity in the different samples could be attributed to the variation in the O/Si ratio induced by implantation and post-annealing. At this stage, a quantitative correlation is still lacking, and this merits further extensive studies.
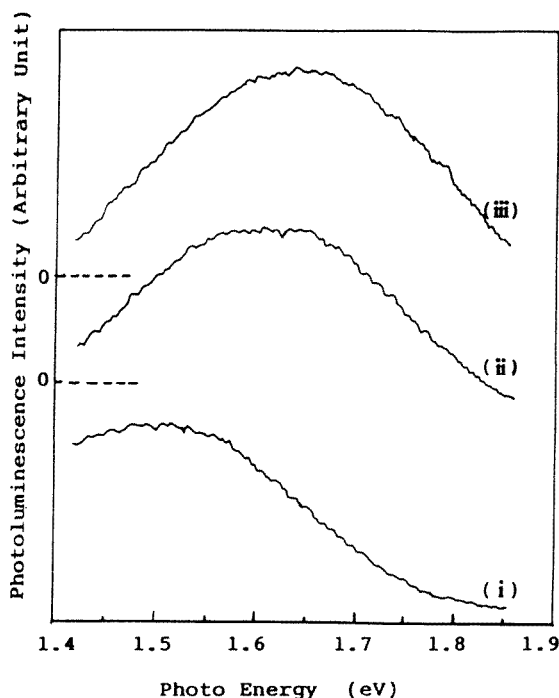
Figure 3. PL spectra of samples implanted with 160 keV Si ions to a high dose of 3×10^{17} cm^{-2} after post-annealing: (i) sample C (6000 Å); (ii) sample B (2000 Å); and (iii) sample A (1000 Å). The zero levels for curves (ii) and (iii) are shifted vertically and shown by dashed lines.

For sample A, the oxygen atoms in the Si matrix might be either recoil atoms produced by ballistic collision, or mobile oxygen atoms produced through radiation-enhanced diffusion. Simulation (the TRIM-92 code was used) of the implantation process for samples A showed that the recoiled oxygen atoms induced by the implantation from the SiO_2 overlayer could transport through the SiO_2/Si interface and stop in the Si substrate, and the concentration of oxygen atoms in the substrate would certainly increase with increase of the Si-ion dose. In an effort to obtain experimental evidence in support of this possible

explanation, we conducted a 160 keV Si-ion implantation into sample A, together with one into samples B and C to a high dose of 3×10^{17} ions cm^{-2} for comparison. Some new results were obtained after post-annealing at 1100 °C for five hours. For samples A and B, a PL band peaked at around 1.64 eV—which was roughly similar to 1.7 eV—was probed, while for sample C, a new band centred at 1.5 eV was observed, as shown in figure 3.

Among several proposed mechanisms for interpreting the observed PL bands, the three-region model proposed by Kanemitsu *et al* [13, 14] may serve as a relevant explanation for the observed 1.64 eV band, which was considered to have the same origin as the 1.7 eV band. Firstly, a high-dose ion implantation could drive the damaged Si region amorphous, and the Si was either in the form of SiO$_x$ or in the form of extremely small clusters. And annealing at 1100 °C would lead the SiO$_x$ to decompose into amorphous SiO$_2$ (a-SiO$_2$) and nanocrystalline Si (nc-Si) [15]. The a-SiO$_2$ could serve as the interfaces among the Si nanocrystals in the samples. Although the a-SiO$_2$ itself could not contribute to the visible PL, it could induce the quantum confinement of photogenerated carriers within the nc-Si core due to the large band gap of a-SiO$_2$. Naturally, the size of the nc-Si core was correlated with the implantation dose and post-annealing time. The interfacial region between a-SiO$_2$ and the nc-Si core, which contained nonstoichiometric amounts of oxygen atoms, was thought to play an important role in the PL process. For simplicity, this surface region can be considered as a one-sided oxidized planar Si sheet. The band-gap energy of the oxygen-terminated Si sheet was calculated to be about 1.7 eV [16], which was approximately equal to the peak energy of the band observed in this study. The radiative recombination process was thought to proceed as follows. The photogeneration of carriers occurred within the core state. When the band-gap energy of the interfacial layer was lower than that of the nc-Si core, the excitons were subjected to a confinement potential, and were confined within the interfacial region until they recombined radiatively.

As far as we are aware, the 1.5 eV band has not been reported before, and its origin is not yet understood. Of course, further clarification of the origin of all of the above observed PL bands needs much more study, e.g. cross sectional transmission electron microscopy examination, and some investigations are currently under way.

In summary, Si-ion implantation into SiO$_2$/Si can induce characteristic photoluminescence. The observed 2.0 eV band was ascribed to the E$'$ defects, while the 1.7 eV band could probably be attributed to the recombination of electrons and holes confined in the interfacial region between the Si nanocrystals and SiO$_2$.

Acknowledgments

References

[1] Canham L T 1990 *Appl. Phys. Lett.* **57** 1046
[2] Lehmann V and Gosele U 1991 *Appl. Phys. Lett.* **58** 856
[3] Kanemitsu Y, Uto H, Masumoto Y, Matsumoto T, Futagi T and Mimura H 1993 *Phys. Rev.* B **48** 2827
[4] Brus L E 1991 *Appl. Phys.* A **53**
    Brus L E 1994 *J. Phys. Chem.* **98** 3575
[5] Koch F, Koch V P, Muschik T, Nikolov A and Enko V G 1993 *Mater. Res. Soc. Symp. Proc.* **283** 197
[6] Kawaguchi T and Miyamiza S 1993 *Japan. J. Appl. Phys.* **32** L215

[7] Risbud S H, Liu L C and Shackelford J F 1993 *Appl. Phys. Lett.* **63** 1648

[8] Shimizu-Iwayama T, Ohshima M, Niimi T, Nakao S, Saitoh K, Fujita T and Itoh N 1993 *J. Phys.: Condens. Matter* **5** L375

[9] Shimizu-Iwayama T, Fujita K, Nakao S, Saitoh K, Fujita T and Itoh N 1994 *J. Appl. Phys.* **75** 7779

[10] Shimizu-Iwayama T, Nakao S and Saitoh K 1994 *Appl. Phys. Lett.* **65** 1814

[11] Mutti P, Ghisiotti G, Berroni S, Bonoldi L, Cerofolini G F, Meda L, Grilli E and Guzzi M 1995 *Appl. Phys. Lett.* **66** 851

[12] Lan A D, Bai X D and Liu B X 1996 *Tsinghua University Internal Report*

[13] Kanemitsu Y, Ogawa T, Shiraishi K and Takeda K 1993 *Phys. Rev.* B **48** 4883

[14] Kanemitsu Y 1994 *Phys. Rev.* B **49** 16 845

[15] Matsushita T, Aoki T, Ohtsu T, Yamoto H, Hayashi H, Okayama M and Kawana Y 1976 *Japan. J. Appl. Phys. Suppl.* **15** 35

[16] Takeda K and Shiraishi K 1993 *Solid State Commun.* **85** 301