Visible photoluminescence related to Si precipitates in Si$^+$-implanted SiO$_2$

LETTER TO THE EDITOR

Visible photoluminescence related to Si precipitates in Si$^+$-implanted SiO$_2$

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Abstract. We have investigated visible photoluminescence from Si$^+$-implanted SiO$_2$. It is found that a luminescence band observed around 2.0 eV in as-implanted specimens disappears on annealing to 500 °C and then a band around 1.7 eV appears on annealing to 1100 °C. We discuss the origin of the luminescence bands in terms of the defects in SiO$_2$ and the Si nanocrystals grown in SiO$_2$.

Modification of the surface layers of materials and synthesis of new phases having novel optical, electrical and mechanical properties by ion implantation have been employed in a diverse range of modern technologies. The ion implantation technique has the advantage that a given number of ions can be placed in a controlled-depth distribution [1].

For insulators, many works have been carried out for implantation of non-metallic species for the purpose of the modification of surface properties [2]. Recently it has been found that implantation of metals into some insulators gives rise to highly non-linear optical properties [3, 4].

The present authors have carried out studies of the properties of Si$^+$-implanted SiO$_2$. It has been shown that radiation damage introduced by Si$^+$ implantation is drastically different from that introduced by non-Si ions, such as Ar$^+$: defects are generated not only in SiO$_2$ but also in Si and at the Si–SiO$_2$ interfaces [5–7]. It is also shown that the number of E$'$ centres produced by implantation is much less than that produced by Ar$^+$-implantation. These results indicate that the implanted Si atoms interact with defects produced by the implantation and even form precipitates. To date, no luminescence measurements of Si$^+$-implanted SiO$_2$ have been carried out and it is not yet clear whether the luminescence characteristic of the Si nanophase is emitted in Si$^+$-implanted SiO$_2$.

The purpose of this letter is to report the studies of photoluminescence and Raman scattering from Si$^+$-implanted SiO$_2$. We find two luminescence bands in Si$^+$-implanted SiO$_2$, having different characteristics, in the spectral region of the porous Si luminescence: one in as-implanted specimens and the other in specimens annealed to 1100 °C. We ascribe the former to defects in SiO$_2$ and the latter to nanophase Si in SiO$_2$.

Suprasil fused quartz specimens of dimensions 10 × 10 × 1 mm^3 were used in the present experiments. Si$^+$ implantation was carried out using a Tandem accelerator at an

energy of 1 MeV to fluences of $1-4 \times 10^{17}$ ions cm^{-2} at a constant current of about 5 μA. We estimated the depth profiles of implanted Si atoms using the TRIM code [8], to be distributed around a depth of 1.35 μm from the surface. Heat treatments of the implanted specimens were carried out in a vacuum using an electric oven.

Photoluminescence and Raman spectra of Si$^+$-implanted specimens before and after annealing were measured at room temperature in a conventional way. An Ar-ion laser (488 nm, 2.54 eV) was used as an excitation source and the luminescence and scattered light were detected by the photon counting technique.

Photoluminescence spectra of specimens Si$^+$-implanted at several fluences were obtained before heat treatments. The results for fluences of 1×10^{17} and 2×10^{17} ions cm^{-2} are shown in figure 1. A broad luminescence band is observed in each of these specimens. The peak position shifts to lower energy with increasing fluence of implanted Si ions. We found also that low-temperature implantation produces a peak at higher energies: implantation at liquid nitrogen temperatures to a fluence of 2×10^{17} ions cm^{-2} gives a peak at 2.2 eV. The luminescence band as observed in the present experiments is much stronger than that observed after implantation with other ions, such as Ar$^+$, B$^+$ and Al$^+$. We observed also that the luminescence band is eliminated by irradiation with a laser pulse, which is known to cause the emission of all implanted Si atoms [9].
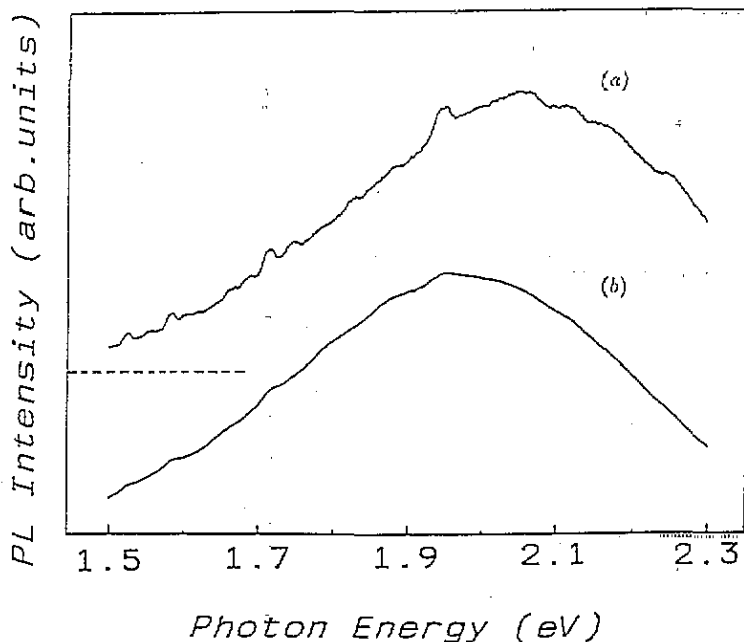

Figure 1. Photoluminescence spectra of Si$^+$-implanted SiO$_2$ at fluences of (a) 1×10^{17} and (b) 2×10^{17} ions cm^{-2} at an energy of 1 MeV, without annealing. The zero line of curve (a) is shifted vertically to the position of the horizontal dashed line.

The effects on the luminescence of isochronal annealing after implantation were also studied. The reduction of the luminescence band starts to be observed after annealing at temperatures higher than 300 °C. Figure 2 shows the luminescence spectra for a fluence of 2×10^{17} ions cm^{-2} before and after isochronal annealing for 30 minutes at several

temperatures. The luminescence band disappears after isochronal annealing above 500 °C, and a new luminescence band appears around 1.7 eV after annealing at 1100 °C, which corresponds to the phase decomposition temperature of SiO_x into Si and SiO_2 [10].
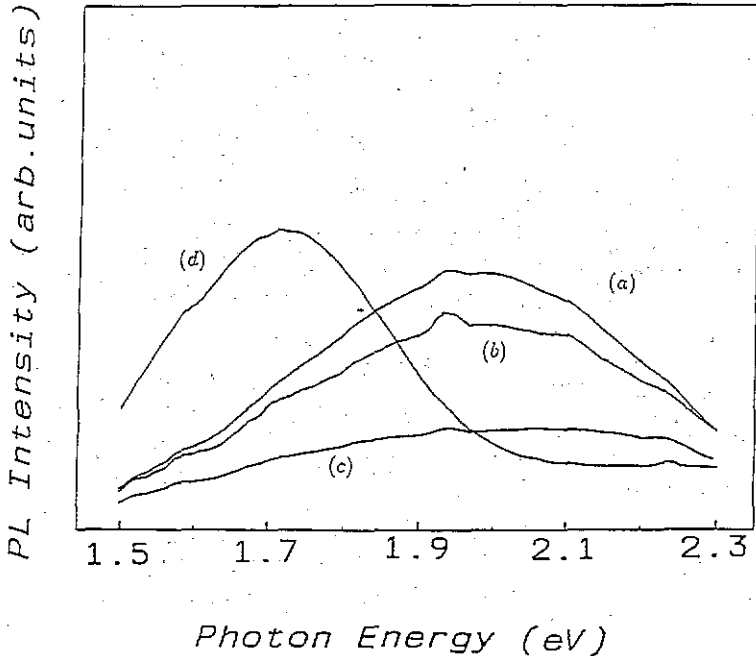

Figure 2. Photoluminescence spectra of Si^+-implanted SiO_2 at a fluence of 2×10^{17} ions cm^{-2} at an energy of 1 MeV. Curve (a), as-implanted; curves (b), (c) and (d), after isochronal annealing for 30 minutes at 400 °C, 500 °C, 1100 °C, respectively.

In order to observe the evolution of the new band in more detail, we investigated the effects of isothermal annealing. In figure 3, we show the change of the luminescence spectra as specimens irradiated at several fluences are annealed at 1100 °C for 60 minutes and 240 minutes. A peak shift to lower energies and broadening are observed as the annealing proceeds for an implantation fluence of 1×10^{17} ions cm^{-2}, while only broadening was observed for other fluences.

Raman spectra were also obtained for Si^+-implanted SiO_2 before and after annealing. Substantial changes in the Raman spectra were only observed in specimens implanted at a fluence above 2×10^{17} ions cm^{-2} after annealing above 1100 °C. Figure 4 shows the results for the specimens implanted to fluences of 2×10^{17} and 4×10^{17} ions cm^{-2} and subsequently annealed at 1100 °C for 240 minutes. Evidently the peak around 490 cm^{-1} due to Si–Si vibration in Si crystals grows after annealing.

In the present investigation, we observed two different luminescence bands in Si^+-implanted specimens: one induced as-implanted and the other induced after annealing at 1100 °C. These two luminescence bands are considered to be of different origin, although they appear in nearly the same energy range.

We first discuss the luminescence band that appears after ion implantation and anneals between 200 °C and 500 °C. The weakness of the luminescence band for implantation of ions other than Si at the same fluences, and the elimination of the band by laser-induced
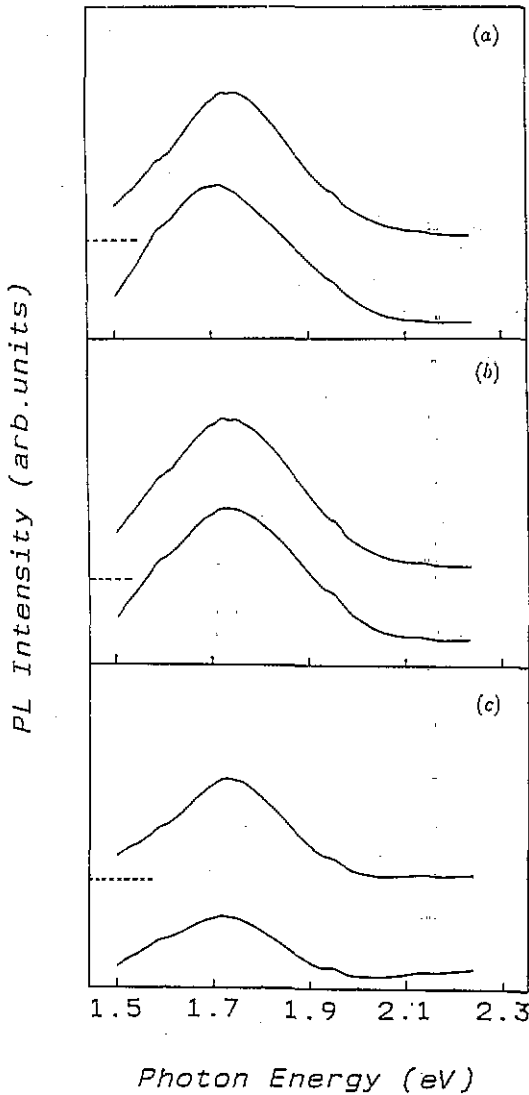
Figure 3. Photoluminescence spectra of Si^+-implanted SiO_2 at fluences of (a) 1×10^{17}, (b) 2×10^{17} and (c) 4×10^{17} ions cm^{-2} at an energy of 1 MeV after isothermal annealing at 1100 °C. In each frame, the upper curve is after annealing for 60 minutes and the lower curve after 240 minutes. The zero line of the upper curve is shifted to the position of the horizontal dashed line.

removal of Si atoms, indicates that the origin of the luminescence is related to the excess of Si atoms in SiO_2. On the other hand, the thermal stability of the luminescence band is approximately identical to that of the E' centres reported previously [7]. Moreover, a luminescence band at 2 eV has been reported in SiO_2 implanted with Ti^+, Bi^+, and Cu^+ [3], although we presume that the efficiency of the emission is lower than that in the Si^+-implanted specimen. According to these latter two experimental results, it appears that the luminescence band originates from defects in SiO_2 introduced by implantation. In view of the results of the enhancement of the luminescence by Si^+ implantation, we suggest that the luminescence band is due to the E'-type defects in a local SiO_x structure, which are generated only in small concentrations by implantation of ions other than Si. Such Si-excess defects will disappear, along with the E' centres, at the temperature where the oxygen interstitials in SiO_2 become mobile. The peak shift to lower photon energies with increasing fluence is in accordance with the model, since the decrease in x reduces the energy of the trapped
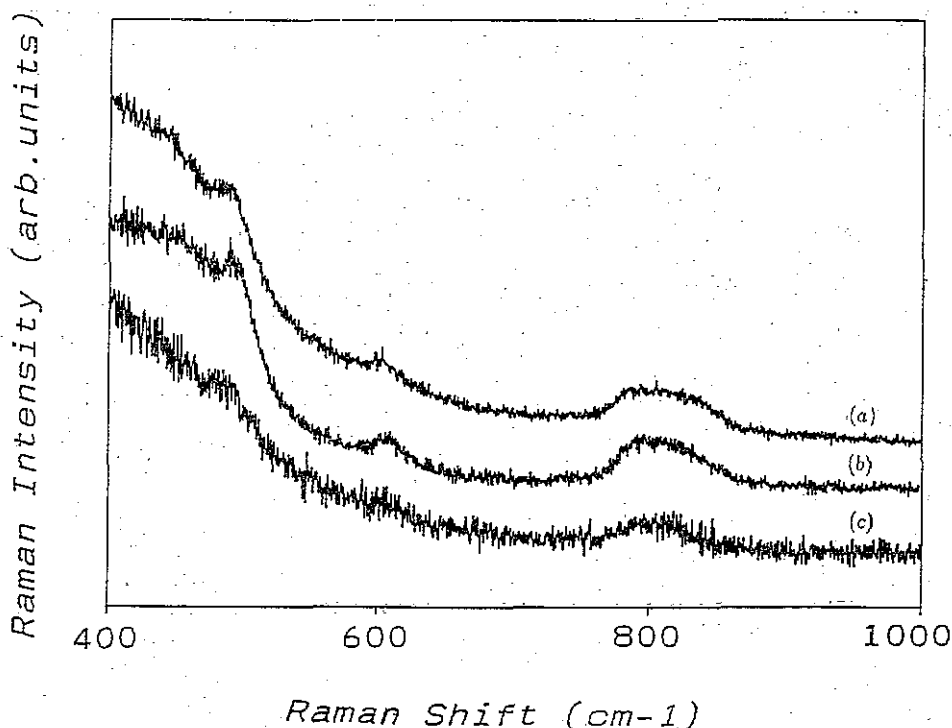
Figure 4. Raman spectra of Si^+-implanted SiO_2 at fluences of (a) 2×10^{17} and (b) 4×10^{17} ions cm^{-2} at an energy of 1 MeV after isothermal annealing at 1100 °C or 240 minutes. (c) shows the Raman spectra of the as-implanted specimen at a fluence of 2×10^{17} ions cm^{-2}.

electron in the E' centres in a local SiO_x structure. The optical absorption measurements of 2 MeV Si^+-implanted SiO_2 by Heidemann [11] favours the interpretation that SiO_x is formed.

Now we discuss the origin of the luminescence band that appears after annealing at 1100 °C. The growth of the Si Raman peak only by prolonged annealing above 1100°C indicates that Si precipitates of significant sizes do not exist in specimens annealed below this temperature; Si is either in the form of SiO_x or in extremely small clusters, for which the Raman spectrum is known to be broad [12]. The appearance of the 1.7 eV luminescence band after annealing at 1100 °C, at which temperature it is known that the Si phase is separated from SiO_x [10], suggests strongly that the 1.7 eV band is related to the Si nanocrystals. The luminescence band is intense after annealing for 60 minutes but its intensity decreases as the annealing proceeds to the stage where the Raman peak becomes sharp. We indeed observed that the sharp Raman peak due to the Si–Si vibration is observed after prolonged annealing of more heavily Si^+-implanted specimens [13]. According to the experimental observation by Okada *et al* [12], small Si particles of an average size of 20 nm give a sharp Raman peak, while those of 8 nm give only a small sharp shoulder on the lower-energy side of a broad Raman peak. Since the luminescence band is observed before the shoulder peak appears, we presume that it is emitted from Si nanocrystals of a size smaller than 8 nm.

The origin of the luminescence from Si nanocrystals is still controversial: several origins of the luminescence have been suggested besides quantum confinement: Si–H alloys

[14], amorphous Si:H [15], siloxene [16], defects or interface states [17]. The present investigation can exclude some possibilities, since the nanocrystals are grown in a SiO_2 environment after annealing at high temperatures. Further studies on the details of the peak shift and the growth of the Si clusters are in progress.

In conclusion, we observed two luminescence bands associated with Si^+-implanted SiO_2. The one observed around 2 eV after implantation and annealing at 500 °C was ascribed to defects in Si-rich SiO_2, and the other observed around 1.7 eV after annealing the implanted specimen at 1100 °C was ascribed to Si nanocrystals. The mechanism of the luminescence for the latter is under investigation. The present investigation provides a new technique of producing visible luminescence from Si crystals and may be of technical use, similarly to porous Si.

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