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LETTER TO THE EDITOR

Photoluminescence from nanoparticles of silicon embedded in an amorphous silicon dioxide matrix

Tsutomu Shimizu-Iwayama†, Setsuo Nakao‡, Kazuo Saitoh‡ and Noriaki Itoh§

† Department of Materials Science, Aichi University of Education, Igaya-cho, Kariya-shi, Aichi 448, Japan
‡ National Industrial Research Institute of Nagoya, Hirate-cho, Kita-ku, Nagoya 462, Japan
§ Department of Physics, Faculty of Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan

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Abstract. We have investigated visible photoluminescence related to nanometre-sized Si crystals in thermal oxide films grown on a crystalline Si wafer, created by Si^+-implantation and subsequent annealing in a vacuum at 1100 °C (the temperature at which SiO_x decomposes into Si and SiO_2). Evidence for the formation of Si nanocrystals by annealing at 1100 °C is presented by transmission electron microscopy. The shape of the emission spectrum of the photoluminescence is found to be independent of both excitation energy and annealing time, while the excitation spectrum of the photoluminescence increases as the photon energy increases and its shape depends on annealing time. The results indicate that the photons are absorbed by nanometre-sized Si crystals, for which the band gap is modified by the quantum confinement, and that the emission of photons is not due to direct electron–hole recombination inside Si nanocrystals but is related to defects probably at the interface between Si nanocrystals and SiO_2.

Ion implantation has been employed extensively to modify surface layers of materials and to synthesize new phases having novel properties. The ion implantation technique has the advantage that a given number of ions can be placed in a controlled depth distribution [1]. For insulating materials, many ion implantations have been carried out for the purpose of modifying the optical properties [2–4], for which further treatments, such as thermal annealing, are often employed [5–7]. Recently, it has been found that implantation of metals into some insulating glasses gives rise to highly non-linear optical properties due to metallic colloid formation [8–10].

Currently there is also much interest in semiconductor nanostructures, especially porous Si [11, 12] and Si ultrafine particles [13–16], which exhibit strong visible photoluminescence even at room temperature. Electroluminescence (EL) devices of porous Si have also been achieved by a number of research groups [17, 18]. Although many models of the light emission from these nanostructures have been proposed, the mechanism is still controversial. The complexity of the structure and of the composition of Si nanoparticles fabricated so far may be a cause of the controversy.

The present authors have carried out studies on the properties of Si^+-implanted silica glasses [19–21] and thermal oxide films grown on crystalline Si wafers [22, 23]. We have shown that silica glasses and thermal oxide films implanted with Si ions exhibit luminescence bands in the visible range. Two kinds of luminescence band having different natures have

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been observed: one peaked around 2.0 eV observed in as-implanted specimens and annealed at about 600 °C, and the other peaked around 1.7 eV observed in the specimens heated to 1100 °C after Si ion implantation. Since heating the Si^+-implanted specimens at higher temperatures induces decomposition of SiO_x leading to crystalline Si precipitation, the 1.7 eV band has been ascribed to electron–hole recombination in the interface between Si nanocrystals and SiO_2 formed by segregation of crystalline Si from SiO_x. On the other hand, the 2.0 eV band has been ascribed to electron–hole recombination in Si-rich SiO_2. However, the detailed mechanism of the photoemission is not yet clear. Ion beam synthesis of Si nanocrystals in a SiO_2 matrix, if it occurs, is a potential candidate for manufacturing well defined Si nanocrystals not only for basic research but also for applications. The purpose of this letter is to report further evidence for the growth of Si nanocrystals in Si^+-implanted thermal oxide films grown on crystalline Si wafers.

In the present experiments, boron-doped p-type Si(100) wafers with a resistance of 0.01–0.02 Ω cm were used. A thermal oxide layer was grown on the crystalline Si wafer to a thickness of about 1.75 μm through oxidation at 1050 °C for 10 h in an atmosphere of 60% H_2 and 40% O_2. Si^+-implantation into the thermal oxide films was carried out in vacuum at an energy of 1 MeV to a fluence of 2×10^{17} ions cm^{-2} at a constant current of about 1 μA. The temperature of the substrates during ion implantation was kept at room temperature. Heat treatments of the implanted specimens were carried out in vacuum using an electric oven.

Photoluminescence spectra, under excitation with an Ar-ion laser (2.41, 2.54, 2.71 eV), were detected with a cooled photomultiplier tube employing the photon counting technique. The photoluminescence excitation spectroscopy was carried out using monochromatized light beams from a Xe-lamp as an excitation source and by detecting the luminescence through appropriate sharp-cut filters. In order to investigate the microstructures of the ion-implanted specimens, transmission electron micrographs of cross-sectioned specimens were obtained by using a 300 keV electron microscope (H-90000NAR, Hitachi). For the cross-sectioning, the specimens were first mechanically thinned down and then ion-milled to electron transparency using Ar^+-ion bombardment.

As reported previously [20, 23], visible luminescence at around 2.0 eV is observed in as-implanted specimens. This luminescence, which is annealed after heating to about 600 °C, has been ascribed to the Si excess defects formed in SiO_2 or defects in SiO_x ($x < 2$). In this letter we are concerned with the luminescence that is observed after annealing at 1100 °C. In the specimen annealed at 1100 °C a periodic interference pattern in the optical absorption spectra was observed [20], indicating the growth of a high-dielectric-constant substance in the Si^+-implanted area. No luminescence or periodic pattern was observed after annealing between 600 °C and 1100 °C.

The spectra of the luminescence induced after annealing at 1100 °C for 90 min of the specimens implanted to a fluence of 2×10^{17} ions cm^{-2} at room temperature obtained by excitation at several photon energies are shown in figure 1. Since the luminescence intensity grows and then decreases as the annealing time increases, an annealing time of 90 min was chosen, where the maximum luminescence intensity was obtained. The spectra are normalized by the peak heights and excitation photon energies are shown in the figure. As reported previously [22, 23], the shapes of the photoluminescence spectra obtained in the present experiments are complex because of interference: the shape is altered by changing the thickness of the oxide layer. From the analysis of the interference effects, we found that the primary luminescence band peaks around 1.7 eV, as shown by the dashed line in the figure. This band shape is almost the same as observed in Si^+-implanted silica glasses after annealing at 1100 °C. It is clear from the figure that the luminescence spectra are

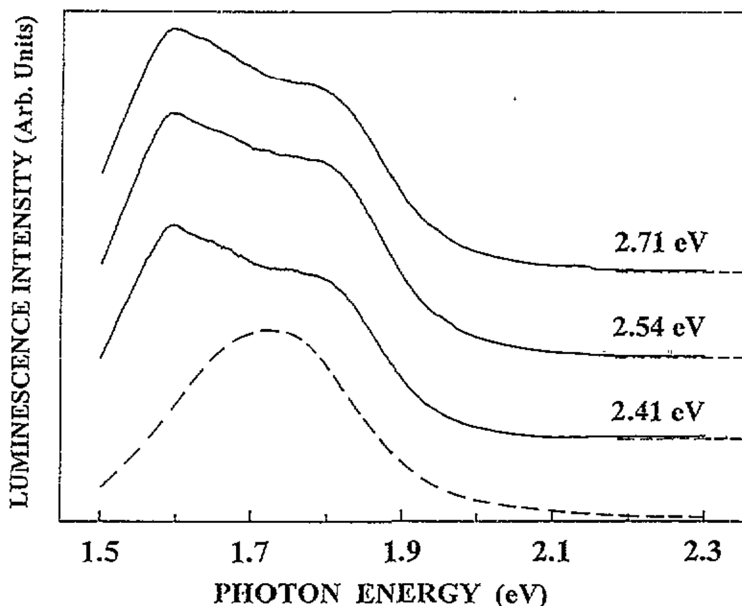

Figure 1. Photoluminescence spectra of 1 MeV Si^+-implanted thermal oxide films grown on crystalline Si wafers to fluences of 2×10^{17} ions cm^{-2} at room temperature, after subsequent annealing at 1100 °C for 90 min. The excitation energy is indicated in the figure. The primary luminescence band is also shown by a dashed line. The zero lines of the curves are shifted vertically to the position of the horizontal dashed lines.

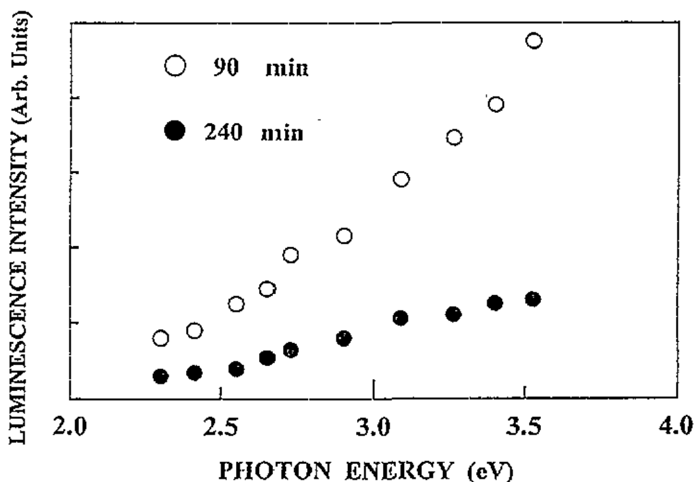

Figure 2. Excitation spectra for the photoluminescence of 1 MeV Si^+-implanted thermal oxide films grown on crystalline Si wafers to fluences of 2×10^{17} ions cm^{-2} at room temperature, after subsequent annealing at 1100 °C for 90 min and 240 min.

not affected by the excitation photon energies. Although it is not shown in the figure, no changes of the luminescence spectra were observed by changing the annealing time for any

of the excitation energies investigated.

The excitation spectra for the photoluminescence of the specimens implanted with Si ions were obtained after heat treatments at 1100 °C for 90 min and 240 min. The results are shown in figure 2. It is clear that the emission intensities increase with increasing incident photon energy in both specimens, although the increase is more significant in the specimen annealed for 90 min.

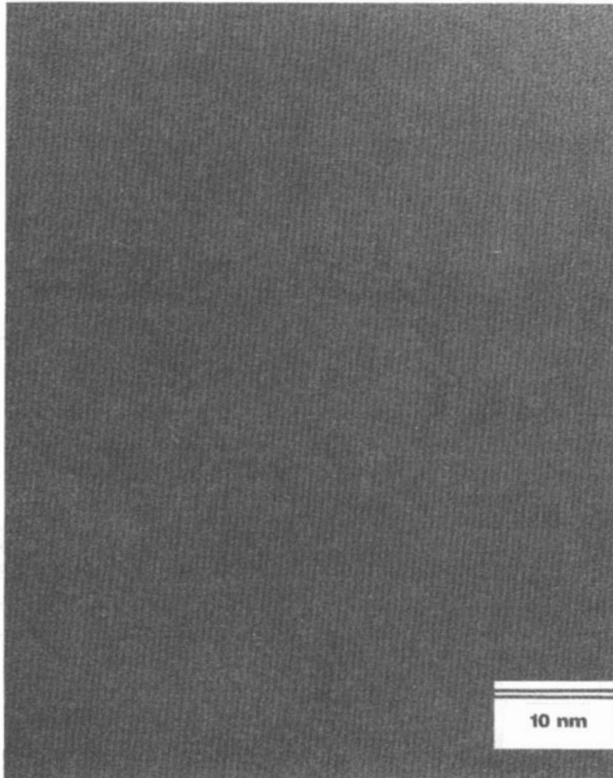

Figure 3. Cross-section transmission electron micrograph of the specimen implanted with 1 MeV Si ions to a fluence of 2×10^{17} ions cm^{-2} at room temperature and annealed at 1100 °C for 90 min.

The cross-section transmission electron micrographs for the Si^{+}-implanted specimens before the heat treatment at 1100 °C indicate no trace of the formation of nanocrystals. However, those for the specimens after the heat treatments at 1100 °C for 90 min indicate nanocrystals of sizes of about a few nanometres in the amorphous silicon oxide matrix, as shown in figure 3. These nanocrystals were distributed in the depth of implanted Si ions calculated using the TRIM (transport of ions in matter) code [24]. Although we carried out the transmission electron diffraction measurements, we cannot identify the Si diffraction pattern, probably because of the smallness of the nanocrystals. However, we have observed a growth of the Si–Si Raman line at around 520 cm^{-1} in a specimen implanted at room temperature with 150 keV Si ions to higher fluence after annealing at 1100 °C, as previously reported [20]. We note that no luminescence was observed in these specimens in which the Si–Si Raman line is observed.

The 1.7 eV luminescence band in Si^+-implanted SiO_2 is observed only after annealing the specimens at 1100 °C. As has been shown elsewhere [20, 23], after annealing Si^+-implanted SiO_2 at 600 °C, most defects (as well as the defect-related luminescence) are annihilated. It is most likely that most of the implanted Si ions are stabilized in the form of SiO_x in the Si^+-implanted SiO_2 annealed between 600 °C and 1100 °C. Thus it appears that SiO_x embedded in SiO_2 does not luminesce. On the other hand, evidence has been accumulated that annealing at 1100 °C produces Si segregates; this has been observed using transmission electron microscopy and Raman spectroscopy. According to Okada *et al* [25], the Raman line due to the Si–Si bond can be observed only for nanocrystals of sizes larger than about 10 nm. The 1.7 eV luminescence band is not observed in these specimens.

The 1.7 eV luminescence band is observed strongly in the specimens at the initial stage of annealing at 1100 °C. Since prolonged annealing at this temperature is shown to produce Si crystals, it is most reasonable to consider that the 1.7 eV luminescence band originates from Si nanocrystals grown in the amorphous SiO_2 matrix. According to the theoretical calculation by Takagahara and Takeda [26], the exciton energy strongly depends on the size of the Si particle, in the order of a few nanometres. Obviously the size of the Si crystals grows as the annealing time increases. The absence of the dependence of the luminescence peak energy on the annealing time excludes the possibility that the luminescence is due to recombination between electrons and holes confined in the Si nanocrystals.

On the other hand, the excitation spectrum is consistent with the presumption that the optical absorption is induced by the generation of electron–hole pairs confined in the Si nanocrystals. As the average size is smaller, photons of higher energies can make a contribution to the luminescence and hence the excitation spectrum increases as the photon energy increases. Moreover, as the annealing time increases the average size increases and hence the optical absorption coefficient at higher photon energies will be diminished. Furthermore, the energy of the photon imparted to the kinetic energy of electrons and holes is considered to be dissipated by interaction with phonons. Thus, only the Si nanocrystals having a band-gap energy of equivalent to the luminescence energy can cause luminescence. This explains why there is no luminescence in the specimens with large-sized Si crystals, in which the Si–Si Raman line is observed.

In conclusion, the present experimental results give the most conclusive evidence that Si nanocrystals in SiO_2 can be the source of the absorption of photons of energies above the band-gap energy and are capable of emitting photons of 1.7 eV, if the size is sufficiently small. The emission, however, does not originate from quantum effects but is probably due to defects at the interface between Si nanocrystals and SiO_2. The system developed in this study, Si nanocrystals embedded in amorphous SiO_2, is the cleanest among the nanostructures developed so far. The system can be used to reveal the mechanisms of visible luminescence of Si nanocrystals, the process of optical absorption, the energy transfer process to the luminsecent centre and the nature of the luminescent centres. The application of the present system for optical devices is considered to be promising.

References

[1] Perez A 1984 *Nucl. Instrum. Methods* B **1** 621
[2] Townsend P D 1977 *J. Phys. E: Sci. Instrum.* **10** 197
[3] Townsend P D 1987 *Rep. Prog. Phys.* **50** 501
[4] Magruder R H III, Weeks R A, Zuhr R A and Whichard G 1991 *J. Non-Cryst. Solids* **129** 46
[5] van Ommen A H 1984 *J. Appl. Phys.* **56** 2790
[6] Devine R A B 1984 *J. Appl. Phys.* **56** 563

[7] Hosono H, Suzuki Y, Abe Y, Oyoshi K and Tanaka S 1992 *J. Non-Cryst. Solids* **142** 287
[8] Becker K, Yang L, Haglund R F Jr, Magruder R H, Weeks R A and Zuhr R A 1991 *Nucl. Instrum. Methods* B **59/60** 1304
[9] Hosono H, Abe Y, Lee Y L, Tokizaki T and Nakamura A 1992 *Appl. Phys. Lett.* **61** 2747
[10] Takeda Y, Hioki T, Motoshiro T and Noda S 1993 *Appl. Phys. Lett* **63** 3420
[11] Canham L T 1990 *Appl. Phys. Lett.* **57** 1046
[12] Lehmann V and Gösele U 1991 *Appl. Phys. Lett.* **58** 856
[13] DiMaria D J, Kirtley J R, Pakulis E J, Dong D W, Kuan T S, Pesavento F L, Theis T N and Cutro J A 1984 *J. Appl. Phys.* **56** 401
[14] Furukawa S and Miyasato T 1988 *Japan. J. Appl. Phys.* **27** L2207
[15] Takagi H, Ogawa H, Yamazaki Y, Ishizaki A and Nakagiri T 1990 *Appl. Phys. Lett.* **56** 2379
[16] Morisaki H, Ping F W, Ono H and Yazawa K 1991 *J. Appl. Phys.* **70** 1869
[17] Richter A, Steiner P, Kozlowski F and Lang W 1991 *IEEE Trans. Electron Device Lett.* **EDL-12** 691
[18] Koshida N and Koyama H 1992 *Appl. Phys. Lett.* **60** 347
[19] Shimizu-Iwayama T, Ohshima M, Niimi T, Nakao S, Saitoh K, Fujita T and Itoh N 1993 *J. Phys.: Condens. Matter* **5** L375
[20] Shimizu-Iwayama T, Fujita K, Nakao S, Saitoh K, Fujita T and Itoh N 1994 *J. Appl. Phys.* **75** 7779
[21] Fujita T, Fukui M, Okada S, Shimizu-Iwayama T, Hioki T and Itoh N 1994 *Nucl. Instrum. Methods* B **91** 418
[22] Shimizu-Iwayama T, Fujita K, Akai M, Nakao S and Saitoh K 1994 *J. Non-Cryst. Solids* submitted
[23] Shimizu-Iwayama T, Nakao S and Saitoh K 1994 *Appl. Phys. Lett.* submitted
[24] Ziegler J F, Biersack J P and Littmark U 1985 *The Stopping and Range of Ions in Solids* vol 1 (New York: Pergamon)
[25] Okada T, Iwaki T, Yamamoto K, Kasahara H and Abe K 1984 *Solid State Commun.* **49** 809
[26] Takagahara T and Takeda K 1992 *Phys. Rev.* B **46** 15578