Visible photoluminescence in Si^+-implanted thermal oxide films on crystalline Si

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We have investigated visible photoluminescence excited by Ar ion laser (488 nm, 2.54 eV) at room temperature from Si^+-implanted thermal oxide films grown on crystalline Si wafer, as-implanted and after subsequent annealing in vacuum. We found two types of visible luminescence bands similar to those of silica glasses; one band is observed in as-implanted specimens and disappears after heating to about 600 °C, and the other band is observed only after heating the specimens to about 1100 °C. Though the shapes of these luminescence spectra are different from those having been observed in Si^+-implanted silica glass, the origins of these bands are the same as in silica glass. We discuss the similarities and the differences of luminescence bands in Si^+-implanted silica glasses and thermal oxide films grown on crystalline Si. © *1994 American Institute of Physics.*

Ion implantation has been extensively employed to modify surface layers of materials and to synthesize new phases having novel properties. The ion implantation technique has the advantage that given numbers of ions can be placed in a controlled depth distribution.[1] For insulating materials, many works of ion implantation 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.[5–8] Recently, it has been found that implantation of metals into some insulating glasses gives rise to highly nonlinear optical properties, due to metallic colloid formation.[9,10]

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. The 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 present authors have carried out studies on the properties of Si^+-implanted silica glass.[19–21] We have shown that silica glass implanted with Si ions exhibits luminescence bands in the visible range; two luminescence bands of different nature have been observed. One band with a peak at around 2.0 eV is observed in as-implanted specimens and anneals out at about 600 °C and the other one with a peak at around 1.7 eV develops by heating the specimen to 1100 °C. Moreover, the heating of the Si^+-implanted specimens at higher temperatures induces decomposition of SiO_x leading to crystalline Si precipitation. Based on these studies, we ascribed the 2.0-eV band to the electron-hole recombination in Si-rich SiO_2 and the 1.7-eV band to the electron-hole recombination in the interface between the Si nanocrystal and the SiO_2 formed by segregation of crystalline Si from SiO_x. Thus implantation of Si ions into silica glass and subsequent annealing is a potential candidate for the method of manufacturing Si nanocrystal of a pure condition.

Silicon oxide films are widely used in silicon and other semiconductor based technologies as gate oxides in metal–oxide semiconductor field effect transistors and as electrical insulation. The purpose of this letter is to report the studies of photoluminescence from Si^+-implanted thermal oxide films grown on crystalline Si wafer, as the first step for EL device applications. We discuss the similarities and the differences of the luminescence bands in silica glasses and thermal oxide films on crystalline Si.

In the present experiments, boron-doped *p*-type 0.6-mm-thick Si wafer with a resistivity of 0.01–0.02 Ω cm were used. The orientation of the wafers was (100). Thermal oxide films on crystalline Si wafer were obtained by oxidation of the wafers at 1050 °C for 10 h in 60% H_2 and 40% O_2 ambient. The oxide thickness was about 1.75 μm. Si^+ implantation into thermal oxide films was carried out in a vacuum at an energy of 1 MeV to fluences of $(1–4)\times 10^{17}$ ions/cm^2 at a constant current of about 1 μA. The temperature of the substrates during ion implantation was kept at room temperature or liquid-nitrogen temperature. Heat treatments of the implanted specimens were carried out in a vacuum using an electric oven.

Photoluminescence spectra of Si^+-implanted specimens before and after annealing were measured at room temperature using a conventional method. An Ar ion laser (488 nm, 2.54 eV) was used as an excitation source and the luminescence was detected by a cooled photomultiplier tube, employing the photon counting technique.

We estimated the depth profiles of implanted Si atoms in thermal oxide films grown on crystalline Si, using the TRIM (transport of ions in matter) code,[22] to be distributed around a depth of 1.35 μm from the surface of oxide film for 1−MeV Si ions. Photoluminescence spectra of specimens Si^+-implanted at room temperature and liquid-nitrogen temperature to several fluences were obtained before heat treatments. The results are shown in Figs. 1 and 2, and the spectrum of Si^+-implanted silica glass is also shown in Fig. 2 for comparison. A broad luminescence band around 2.0 eV is

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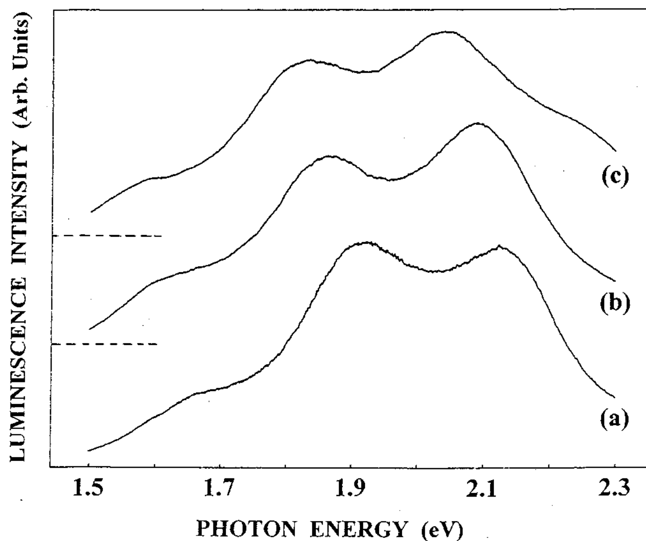

FIG. 1. Photoluminescence spectra of 1-MeV Si^+-implanted thermal oxide films grown on crystalline Si to fluence of (a) 1×10^{17}, (b) 2×10^{17}, and (c) 4×10^{17} ions/cm^2 at room temperature, without annealing. The zero line of curve (b) and (c) are shifted vertically to the position of the horizontal dashed line.

observed in each of these specimens. The peak energy shifts to the lower energy with increasing fluence of Si ions. It is also clear from Fig. 2 that the peak energy in the specimen implanted at liquid-nitrogen temperature is higher compared to the specimen implanted to the same fluences at room temperature. Moreover, the periodic pattern with a constant interval is observed in all of these figures except for silica glass specimen. This luminescence band starts to decrease around 300 °C and disappears after isochronal annealing around 600 °C for 30 min. No peak shift and no change of the interval of the pattern were accompanied with the reduction of the height of the luminescence band.

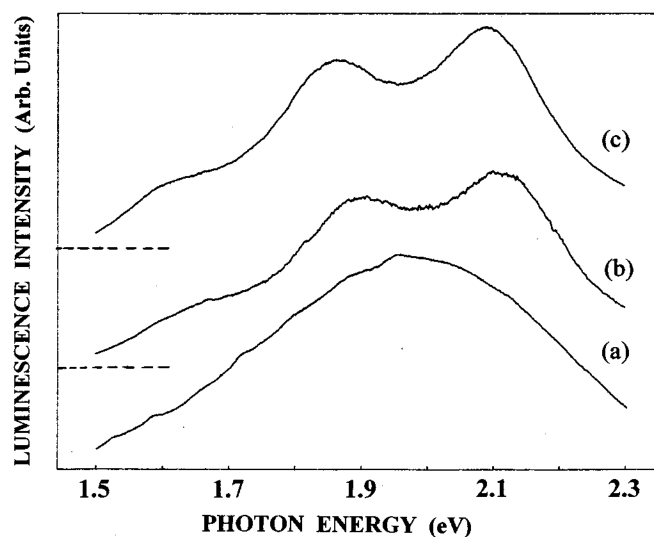

FIG. 2. Photoluminescence spectra of 1-MeV Si^+-implanted (a) silica glass to fluence of 2×10^{17} ions/cm^2 at room temperature, and thermal oxide films grown on crystalline Si to fluence of 2×10^{17} ions/cm^2 at (b) liquid-nitrogen temperature and (c) room temperature, without annealing. The zero line of curve (b) and (c) ar shifted vertically to the position of the horizontal dashed line.

The origin of the luminescence is related to the excess Si atoms implanted into thermal oxide films as previously reported in case for silica glasses.[20] The luminescence is emitted by the presence of either Si-excess centers or oxygen interstitials stabilized by SiO_x phase in SiO_2. It appears that electron-hole pairs are produced in the SiO_x phase and emission is induced at the defect sites. The peak energy of the luminescence band decreases as the Si segregation becomes dominant. Thus we consider that Si excess defects formed near SiO_x is responsible for the luminescence. The periodic patterns appears in the photoluminescence spectra as shown in Figs. 1 and 2 originate from the interference of the reflected light at the surface and the interface, not at the implanted Si layer. This is justified from the result that no interference is observed in photoluminescence spectrum of Si^+-implanted silica glass, as shown in Fig. 2. Moreover, it is important to note that the implanted Si ions form SiO_x before annealing at 1100 °C and the refractive index is not so different from that of pure SiO_2 as was already reported elsewhere.[20]

The interval of the interference pattern due to multiple reflection is interpreted by using the following equation:[23]

$$2nd=(1/\lambda_2-1/\lambda_1)^{-1},$$

where n is the refractive index, d is the thickness of the oxide film, and λ_1 and λ_2 ($\lambda_1>\lambda_2$) are the maximum peak wavelengths which appeared in the spectra. Using the value of $d=1.75$ μm (thickness of the thermal oxide film), we obtain $n=1.58$. This value n is little larger than that of SiO_2 ($n=1.46$). Since implanted Si ions form SiO_x ($x<2$),[24,25] the average value of the refractive index in Si-implanted thermal oxide layer differs little from that of SiO_2 as noted above.

The spectrum of the luminescence induced after annealing at 1100 °C for 90 min of the specimen implanted to a fluence of 2×10^{17} ions/cm^2 at room temperature is shown in Fig. 3. In Fig. 3, the spectrum of the specimen of silica glass is also shown for comparison. It is clear in Fig. 3, the additive peak is observed in the low-energy side of the spectrum for the Si-implanted thermal oxide specimen. A similar luminescence band is also observed in the specimens of thermal oxide films implanted with Si ions to other fluences at room temperature and at liquid-nitrogen temperature and annealed at 1100 °C. We also found that the shapes of these curves are almost the same and independent of annealing time, and that only the intensities depend on these conditions. Though the luminescence intensity grows and then decreases with prolonged annealing similar to silica glass, the growth rate of the luminescence is faster for thermal oxide films compare to silica glass.

We emphasize that the Si phase is separated from SiO_x at this temperature range.[20,26] Thus it is most likely that the luminescence band around 1.7 eV is formed as a result of crystalline Si precipitation and hence of formation of Si nanoparticles. This luminescence band around 1.7 eV arises from the electron-hole recombination at Si nanocrystal-SiO_2 interfacial layers similar to silica glass.[20] Though the origin of the lower energy band observed only in thermal oxide

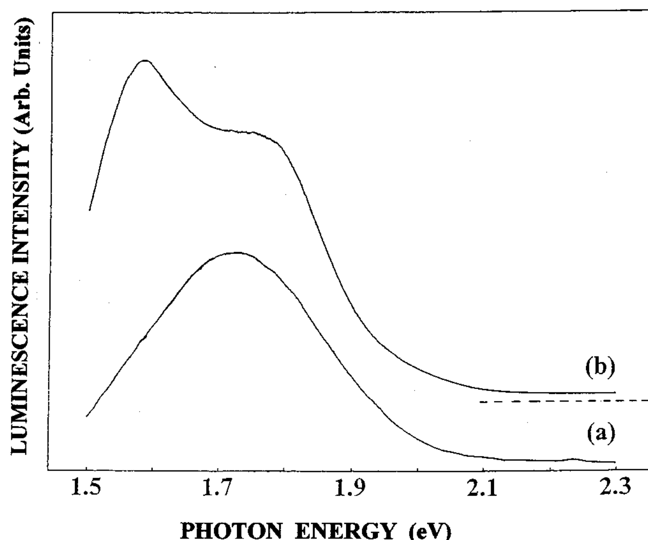

FIG. 3. Photoluminescence spectra of 1-MeV Si^{+}-implanted (a) silica glass and (b) thermal oxide film on crystalline Si to fluences of 2×10^{17} ions/cm^2 at room temperature, after subsequent annealing at 1100 °C for 90 min. The zero line of curve (b) is shifted vertically to the position of the horizontal dashed line.

films is not yet clear in the present experiments, it probably originates from some interference effect as previously discussed. The difference in the growth rate of the luminescence band arises from the difference in thermal conductivities during annealing of these materials.

In conclusion, we have shown that the implantation of Si ions into thermal oxide films on crystalline Si produces characteristic bands from 1.5 to 2.3 eV similar to those having been observed in silica glass: The one that is observed in as-implanted specimen can be attributed to Si excess defects formed in SiO_x environment. The one that is observed after annealing 1100 °C is related to the formation of Si nanocrystals by precipitation from SiO_x. Further studies on the direct observation of Si nanocrystals and the possibilities of EL are now in progress.

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