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Formation of Si nanocrystallites observed by in situ transmission electron microscopy and their effect on the enhancement of Er photoluminescence in Er-doped SiO₂

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I. INTRODUCTION

The sensitization of Er ion emission (λ = 1.54 μm) by host materials, such as crystalline Si (c-Si), amorphous Si (a-Si), and Si nanocrystallites (nc-Si), has been extensively investigated. In the case of c-Si, the nonradiative de-excitation process leads to thermal quenching of Er ion emission. The second a-Si case shows a weaker temperature dependence of Er ion emission than in the c-Si case; however, lifetime is a problem. On the other hand, the effective excitation cross section of nc-Si is much higher than that of resonant excitation for Er ion in SiO₂ and the decay time of the Er ion emission is close to being temperature independent. Hence, nc-Si is regarded as one of the most promising sensitizers. More recently, we have synthesized Er-doped SiO₂ including nc-Si by laser ablation and investigated the hydrogen passivation effect of interfacial defects between nc-Si and the SiO₂ matrix in enhancing energy transfer from nc-Si to Er ions, resulting in enhanced Er ion emission.

To maximize the effectiveness of nc-Si, it is necessary to further investigate the formation process of nc-Si within an SiO₂ matrix. In the present study, we investigated this by in situ annealing while taking transmission electron microscopy (TEM) measurements and ex situ annealing in an electronic furnace. The correlation between the formation of nc-Si and the Er ion was also comprehensively investigated by photoluminescence (PL) and electron spin resonance (ESR) measurements.

II. EXPERIMENT

Erbium-dispersed SiO₂ films containing nc-Si were prepared by laser ablation: Er thin films were deposited on Si substrates in a vacuum by ablating Er metal plates, after which the Si substrates with Er thin films were laser ablated in O₂ gas at a pressure of 40 mTorr to deposit Er-dispersed SiO₂ films. The laser light used was a 532 nm Nd:YAG (YAG denotes yttrium aluminum garnet) laser light with a pulse duration of 7 ns and a fluence of about 4 J/cm². After the pulsed laser deposition, in situ annealing was performed to directly investigate the formation process of nc-Si in the Er-dispersed SiO₂ films. This in situ annealing was performed using a TEM grid holder with a heater. After the specimens had been annealed for about 30 min at each temperature, TEM images were taken at four areas (an area: 40×40 μm²). These procedures were repeated from 200 to 900 °C. To observe the effect of heating by electron beam irradiation during the TEM observations, some of the Er-dispersed SiO₂ films were annealed in an electronic furnace under an Ar gas flow for 30 min at 400–900 °C. The Er concentration was estimated to be about 2 × 10²⁰ cm⁻³ by Rutherford backscattering spectroscopy using 1.5 MeV protons at a backscattering angle of 150°. The mean Si and O compositions of the film were also estimated to be about 40 and 60 at. %, respectively.

III. RESULTS AND DISCUSSION

PL spectra of Er ions and nc-Si were detected using an InGaAs detector employing a lock-in amplifier system and Si photodiode, respectively, at RT. The excitation source was a
cw He–Cd laser light at 325 nm. ESR measurements were carried out at RT using an X-band ESR spectrometer. The derivative of resonant microwave absorption with respect to the magnetic field was measured using a lock-in amplifier and magnetic field modulation with a frequency of 100 kHz. The microwave power was set at 1 mW. An external ESR standard signal of Mn$^{2+}$ in MgO was used to take into account possible changes in the quality factor of the microwave resonator among separate measurements. TEM (JEOL, JEM-3100F) measurements at various temperatures were performed to make direct observations of the formation of nc-Si in the SiO$_2$ films.

Figures 1(a) and 1(b) show the ex situ annealing temperature dependence of the PL spectra observed in two regions, and Fig. 1(d) that of the ESR signal of defects in an Er-dispersed SiO$_2$ film. This annealing was performed in a furnace to investigate the formation of nc-Si in Er-dispersed SiO$_2$ films. Before the ex situ annealing, no PL spectra of Er ions or nc-Si were observed, indicating that nc-Si was not included in the film and the film was defective. Figure 1(a) shows the PL spectrum of Er ions with increasing annealing temperature. A broad PL spectrum was also observed at around 700 nm after annealing at 400 °C; the peak showed a redshift with increasing annealing temperature, as shown in Fig. 1(b). The results are summarized in Fig. 1(c). The broad PL spectra are probably due to PL from nc-Si or amorphous Si nanograins composed of few Si atoms. The assignments will be explained later based on the TEM results. Hereinafter, we call these broad PL spectra nano-Si PL.

The ESR signals in Fig. 1(d) are due to defects in the Er-dispersed SiO$_2$ films. Before ex situ annealing, the $g$ value of the ESR signal was about 2.0028. The ESR signals showed a shift to a lower magnetic field with increasing annealing temperature, finally reaching a position with a $g$ value of 2.005. The $g$ values of oxygen-deficient defects ($\text{Si}_x\text{O}_{3−x}\equiv\text{Si}·; \ x=1−3$) in SiO$_2$ are in the range of 2.002–2.004, depending on the structures, i.e., $g$ values increase on decreasing the number of oxygen atoms. With increasing annealing temperature, the SiO$_2$ film is transformed into perfect SiO$_2$, resulting in the precipitation of nc-Si. Finally, defects are present only in the interface between the SiO$_2$ matrix and nc-Si. This defect is a kind of interfacial defect, a so-called $P_b$ center ($\text{Si}_x\equiv\text{Si}·$). The ESR signals with $g$ value of 2.002–2.004 are thus probably due to oxygen-deficient defects in the SiO$_2$ film and that of 2.005 due to $P_b$ centers.

The intensity of the ESR signal increased with increasing annealing temperature. It also indicates that the formation of nc-Si proceeds with increasing annealing temperature.

TEM measurements were performed for specimens annealed in the furnace at 500, 700, and 900 °C. The ex situ annealing at 500 and 700 °C showed no nc-Si formation, while the results of PL in Fig. 1(b) show the maximum intensity after ex situ annealing at 500 °C. These results suggest that the annealing temperatures at 500 and 700 °C are not sufficiently high for the formation of nc-Si or that the size of nc-Si is below 1 nm, since the detection limit of nc-Si is around 1 nm in our TEM system. In the case of the latter, nc-Si with diameters below 1 nm is considered as the origin of the nano-Si PL, while in the former case, amorphous Si nanograins may be the origin of the PL. On the other hand, nc-Si with diameters ranging from 3 to 5 nm were observed in the specimen after the ex situ annealing at 900 °C. The diameter distribution of nc-Si after ex situ annealing is shown in Fig. 3. The result is explained later in addition to results of in situ annealing.

To further investigate the formation process of nc-Si in the Er-dispersed SiO$_2$ film over a wide temperature range, in situ annealing was performed during TEM observations. Typical TEM images are shown in Fig. 2. The dependences of the diameter and the density of nc-Si on the annealing temperature are summarized in Fig. 3. The data in Figs. 3(a)–3(f) correspond to in situ annealing cases, while those in Figs. 3(g) and 3(h) correspond to ex situ annealing cases. Here, the counts in the vertical axis in Fig. 3 indicate the number of nc-Si observed in a region of 6400 $\mu$m$^2$. The lattice fringes of Si crystal were clearly observed in the films.
marked by dotted circles after \textit{in situ} annealing at 400–900 °C. The diameter of nc-Si was about 3 nm after \textit{in situ} annealing at 400 °C and it reached about 10 nm after \textit{in situ} annealing at 900 °C. These results clearly show that the diameter and the density of nc-Si increase with increasing annealing temperature.

The formation temperatures of nc-Si shown in Fig. 2 are significantly different from those for the specimens annealed in the furnace. The formation of nc-Si could not be observed, even for the specimen after \textit{ex situ} annealing at 700 °C, as shown in Fig. 3(g). Electron beam-assisted annealing during TEM observations is the one of the reasons, since electron beam irradiation increases the local temperature of the irradiated part of the specimen depending on the electron beam current. Considering the beam current density, the temperature rise is probably less than 300 °C, indicating that another additional effect has to be considered, since the formation of nc-Si was observed from 400 °C in the case of \textit{in situ} annealing, but not even for the specimen after \textit{ex situ} annealing at 700 °C in the furnace. Electron-nuclear collision by electron beam irradiation may be a factor. It often induces defects, resulting in atomic displacement by the subsequent diffusion of defects. This probably promotes the precipitation of amorphous Si nanograins and finally their crystallization. The role of the electron beam-assisted annealing is to increase the temperature in the irradiated part of the specimen and to cause the precipitation of nc-Si, while that of the electron-nuclear collision causes the further enhancement of the precipitation of nc-Si by using defects introduced. The result of \textit{ex situ} annealing at 900 °C in Fig. 3(h) shows the similar tendency to that for the case of \textit{in situ} annealing at 500–600 °C in Figs. 3(a)–3(c). However, the density of nc-Si for the \textit{ex situ} annealing case is lower than that for the \textit{in situ} annealing cases. Considering these results, we think that the electron-nuclear collision corresponds to the tem-
temperature rise of about 100 °C. We also investigated the effect on temperature during electron beam irradiation. A sample was annealed at 700 °C for 30 min in TEM chamber without electron beam irradiation and then investigated by TEM at RT. No trace of crystallization was observed by TEM at RT. This result indicates that irradiation temperature is important for the formation of nc-Si, namely, the electronic and collisional effects by the electron beam are thermally activated.

Figure 4 shows a summary of the results of Fig. 1, namely, the results of ex situ annealing. There is a clear inverse correlation between the intensity of nano-Si PL and that of the ESR defect signal. This means that the interfacial defects formed between nano-Si and the surrounding SiO$_2$ matrix act as nonradiative defects. The decrease in the intensity of nano-Si PL can thus be mainly explained by the increase in the size of nc-Si, and thereby the formation of interfacial defects. There is another reason for the decrease in the intensity of nano-Si PL, namely, the energy transfer from nano-Si to Er ions. In fact, an inverse correlation between Er PL and nano-Si PL was also observed in the specimen annealed at below 700 °C. This result shows that nc-Si with a diameter less than 1 nm or amorphous Si nanograins are effective for enhancing Er PL.

IV. CONCLUSION

The formation of nc-Si in Er-dispersed SiO$_2$ (x ≤ 2) films was investigated by performing TEM measurements during in situ annealing. The correlation between the formation of nc-Si and Er ion emission was also comprehensively investigated by PL and ESR measurements. The results show that the formation of nano-Si region with the suitable size is important for the enhancement of Er ion emission.

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