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Photoluminescence characteristics of rare earth ion-implanted SiO_2/Si

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Abstract

The photoluminescence (PL) characteristics were studied for the ion-implanted Tb, Eu and Dy ions with the accelerated voltage 180 kV into SiO_2/Si, changing the annealing temperatures every 100 °C up to 1200 °C for an hour. Then, the thickness of thermally oxidized SiO_2 film was determined as 400 nm from TRIM simulation and SIMS atom analysis. At first from PL spectra, we found that the ion-implanted rare earth ions as mass-filtered monovalent states actually were both embedded as the trivalent states: Tb^{3+} and Eu^{3+}, respectively. This suggested that accelerated RE ions had lost their own electrons generating lattice defects through colliding with SiO_2 atoms. With increasing annealing temperatures, the intensities of PL lines at 544 nm of Tb^{3+} ion increased more, reaching the maximum at 600 °C to disappear at 1000 °C. A peak at 280 nm observed commonly through all the specimens was identified as a hole-trapped O-vacancy defect or E′ center created in SiO_2 because the PL intensity decreased in response to the intensity of electron spin resonance (ESR) spectrum measured in parallel with the increasing annealing temperatures.

Keywords: Photoluminescence; Tb; Eu; Ion-implantation; SiO_2/Si; ESR

1. Introduction

The rare earth (RE) elements such as terbium (Tb) and europium (Eu) have recently attracted more interest for application to especially high-potential visible luminescence sources [1]. Among various application of RE opt-devices, an interesting approach is to the improvement of conversion efficiencies of solar cells, in which our group has firstly developed [2]. The RE ions can transform the absorption energy in shorter wavelength region into the luminescence energy in the longer wavelength region with high-luminosity. If this wavelength shifts were applied to solar cells, the cells could produce larger electric power than current solar cells in use which have spectroscopic sensitivity peaks at longer wavelengths [3,4].

In the present study, we have paid attention Tb, Eu and dysprosium (Dy) as strong luminescence active centers doped into the thermally oxide film of Si substrate; SiO_2 that is one of the highly applicable host materials. For the doping of RE ions, the ion-implantation method was adopted because this method was most popular to fabricate semiconductor devices. After heat treatments or high temperature annealings of the doped SiO_2/Si, the intensity variations of the luminescence were investigated. The distribution of atoms including doped atoms against the depth close to the surface layer of the specimen were measured with an ion micro analyser or secondary ion mass analysis (SIMS). Usually, ion-implantation procedures may create various lattice defects in target semiconductors owing to ion bombardments under high accelerated voltages. A created defect, well-known E′ center, in SiO_2 film [5] was found by using electron spin resonance (ESR) analyses, and its relationship to the observed luminescence was discussed.

The PL studies on the ion-implanted Tb [6] and Eu [7] in SiO_2/Si have been reported, but not yet investigated on the relationship of them to the E′ center.

2. Experimental methods

Fundamental n-type ⟨100⟩ Si substrates (Furuuchi Chem. Co.) have $380 \pm 20\,\mu m$ in thickness, and their resistivities

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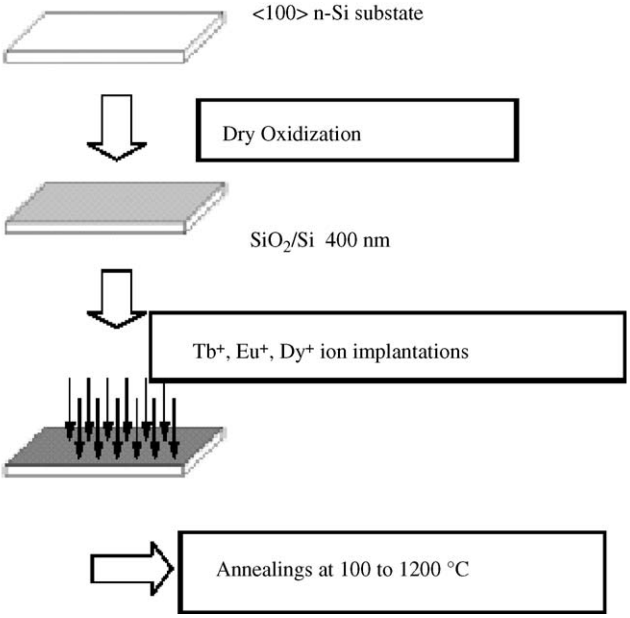

Fig. 1. The processes of making the rare earth doped SiO_2/Si specimens.

are below 1000 Ωcm. Thermally oxidized SiO_2 films were obtained by flowing dried oxygen gas at 1200 °C for 5 h into the oxidization furnace (Asahi Rikagaku Co.), in which several Si substrates were arranged. The thickness was determined as 400 nm whose value was settled from TRIM simulator, ion-implantation simulation software, and SIMS (ATOMIKA, SIMS4000), so as for implanted rare earth ions not to reach at the surface Si substrate, mentioned later in the detail. For these SiO_2/Si specimens, ion implantations (Nissin Electric Co., NHV-1014A, Kyoto) were performed by the dose quantities of $1.0 \times 10^{16}\,cm^{-2}$ for Eu and $1.0 \times 10^{15}\,cm^{-2}$ for Tb, Dy, respectively.

These vaporized RE metals were selected as monovalent states and implanted under the implantation energy of 180 keV. For the purpose of removing lattice defects, making diffuse doped ions and investigating the variations of luminescence intensities of doped RE ions, the annealing temperature of specimen was changed every 100 °C up to 1200 °C for an hour by the furnace mentioned above. The processes of making rare earth doped SiO_2/Si specimens are shown in Fig. 1.

The PL and PLE spectra were measured with a spectrophotometer (JASCO, FP-6500, Japan) in the wavelength region of 220–750 nm. The ESR experiments were carried out with a X-band spectrometer (Bruker ESP300E, Germany).

3. Results and discussion

The PL spectra for SiO_2/Si with Tb is shown in Fig. 2, in which seven sharp line spectra are observed, and were assigned as the transitions from ^5D_J to ^7F_J in the trivalent Tb ion, as written in a text [8]. This suggested that accelerated RE ions had lost their own two electrons generating lattice defects through colliding with SiO_2 atoms. For the purpose of removing the second diffraction light for the exciting light at 245 nm in Fig. 2, the result with a 350 nm cut filter is given together the one without the filter. By using the cut filter, a strong peak at 280 nm was observed commonly through the spectra for all the present RE ion-implanted specimens.

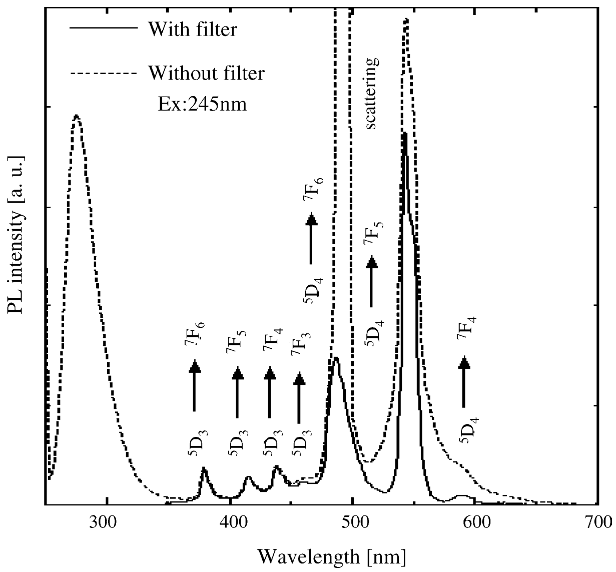

Fig. 2. PL spectra with and without a cut filter below 350 nm of Tb^{3+} ion-implanted SiO_2/Si annealed at 200 °C.

Also for Eu, the observed spectra were originated from the trivalent Eu ion. The ion-implanted RE ions as mass-filtered monovalent states actually were both embedded as the trivalent states: Tb^{3+} and Eu^{3+}, respectively. For Dy, no any PL spectra were observed except for the 280 nm line in the region of measured wavelengths.

With increasing annealing temperatures, the three main lines at 544, 488 and 380 nm for Tb^{3+} ion, as shown in Fig. 3, increased the intensities more, reaching over 2.5 times in maximum at 600 °C to disappear at 1000 °C.

The measurement result of ESR for SiO_2/Si with Tb is shown in Fig. 4. The spectrum is of a sharp resonance line ($g = 2.0062$, $\Delta H_{p\text{–}p} = 5$ gauss) associated with a small side band in the lower field. This signal was commonly observed for all the Tb, Eu and Dy ion-implanted specimens. Considering from a lot of reports by researchers including ourselves [9–12], this center was identified as a hole-trapped O-vacancy defect or E′ center, created into SiO_2. The E′ center is often observed for also LSI, MPU and other semiconductor devices that the lattice defects are created during their fabrication processes.

The annealing temperature dependences of PL intensity of a strong peak at 280 nm were investigated in parallel with the dependences of ESR spectra of E′ centers for all the Tb, Eu and Dy ion-implanted specimens. The results are shown in Fig. 5, in which we can notice that their decreasing behaviours are very similar each other with increasing the temperatures.

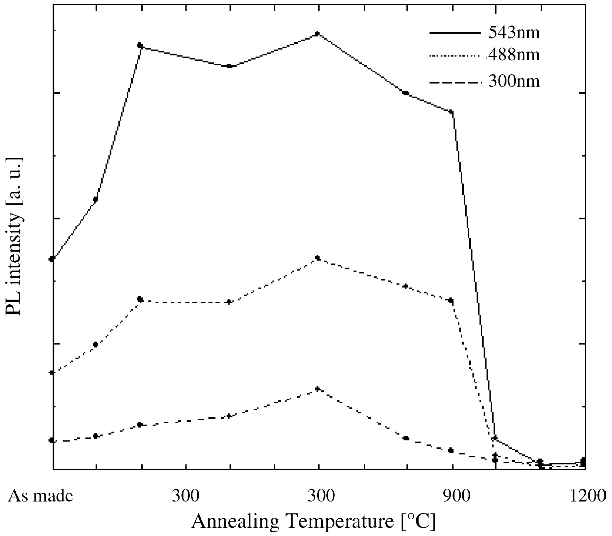

Fig. 3. Annealing temperature dependences of the intensities of three main lines at 544, 488 and 380 nm for Tb^{3+} ion.

Accordingly, we found that a strong peak at 280 nm was just identified as E′ center

By using the TRIM92 ion-implantation simulation software, it was estimated that implanted RE ions in SiO_2 at 180 keV energy would be located in the depth range until 200 nm from the surface.

Following this prediction, Eu ion was implanted into SiO_2 film of the thickness of 200 nm which was formed under the thermal oxidization for 2 h at 1100 °C. The SIMS results are shown in Fig. 6 for the non-annealed Eu implanted SiO_2/Si. The Eu ion reaches at the Si substrate beyond the SiO_2 layer of 200 nm. Actually, no PL was observed in this film thickness, and so resettled as 400 nm, as mentioned in Section 2.

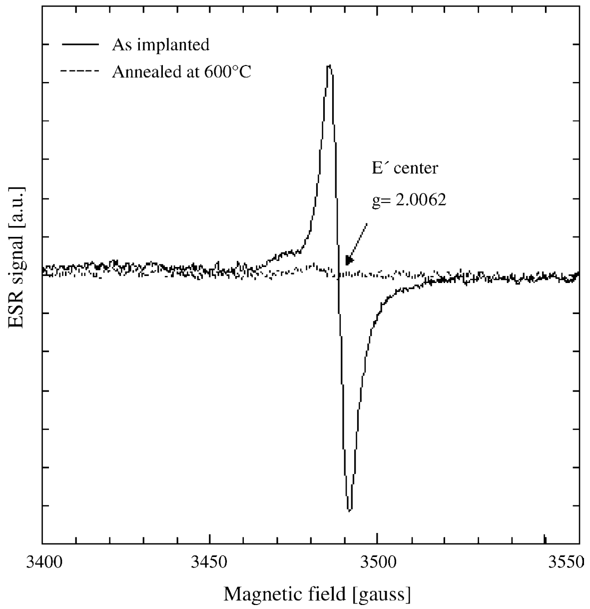

Fig. 4. The ESR spectra for as-implanted and annealed at 600 °C specimens in Tb ion-implanted SiO_2/Si.

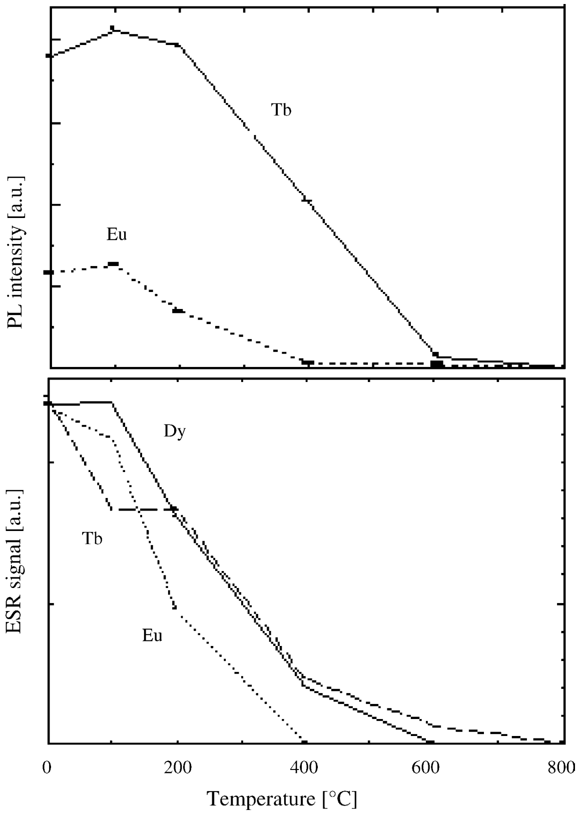

Fig. 5. The annealing temperature dependences of PL intensity of a strong peak at 280 nm for Tb, Eu and the intensity of E′ center in ESR spectrum for Tb, Eu, Dy.

Finally, we will summarize the obtained results in the present study, and propose a model on this implantation processes, as shown in Fig. 7. The ion-implanted RE ions as monovalent states actually are both embedded as the trivalent

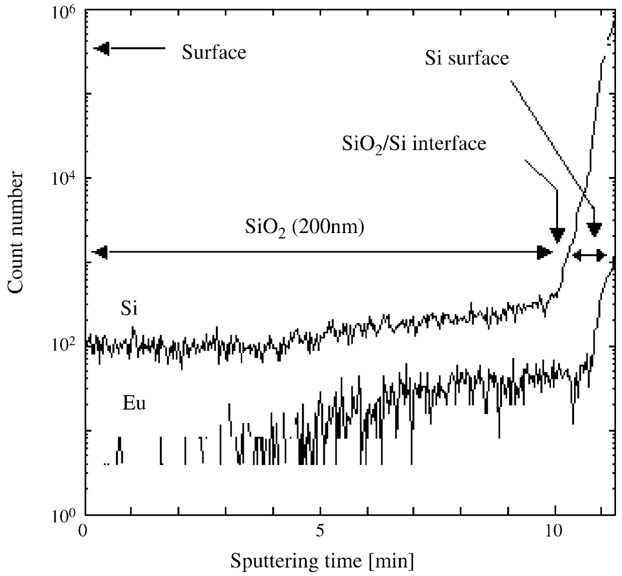

Fig. 6. The SIMS results showing the quantities or count number of implanted Eu and substrate Si against the spattering time corresponding to the depth from the surface of specimen.

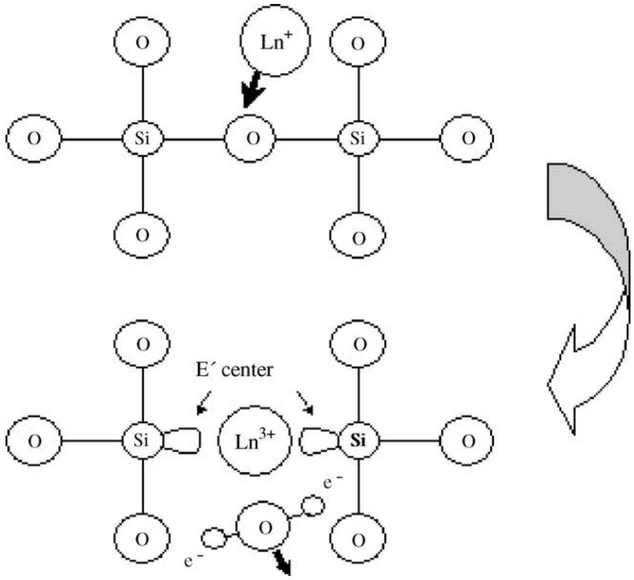

Fig. 7. Schematic diagram of a model on the implantation processes. The ion-implanted monovalent rare earth (Ln^+) ion changes into the trivalent (Ln^{3+}) ion to create two hole-trapped vacancies or two E′ center.

states. The accelerated monovalent RE or Ln^+ ions with high energies go into SiO_2 inside colliding violently with Si and O atoms on the surface. The collision cuts off O–O bonds, and Ln^+ changes into Ln^{3+} ions to give the two own electrons. Then, two O atoms associated with each one electron are interstitially flied in the lattice to leave two O-vacancies as bond partners of Si. Eventually, two hole-trapped vacancies or two E′ centers are supposed to be created.

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