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Photoluminescence from Eu ions implanted SiO_2 thin films

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Abstract

Photoluminescence (PL) and PL excitation spectra from Eu^{3+} implanted thermal growth SiO_2 thin films have been investigated at room temperature. After annealing at 1000°C in N_2, the red light emission from Eu ions doped SiO_2 film, corresponding to the $^5D_0$–^7F_J transition of Eu^{3+}, was observed. With increasing the annealing temperature (T_a) to 1200°C, a strong blue light emission band centered at around 450 nm appears. The conversion of Eu^{3+} to Eu^{2+} is discussed.

Keywords: Photoluminescence; Eu ions; SiO_2 thin films

1. Introduction

A great deal of interest in silicon based luminescent materials has been generated all over the world since the discovery of visible light emission from porous silicon [1], which would make silicon a promising material for optoelectronics applications. Rare-earth ions are effective luminescent centers that have been widely used in the industry. The 1.547 μm luminescence from erbium-doped crystalline and amorphous silicon has been observed at room temperature and has been applied to light amplifier [2,3]. The red and blue light emissions with high intensity from Eu^{3+} and Eu^{2+} doped SiO_2 prepared by the sol–gel method were observed [4]. It is important to prepare the SiO_2:Eu^{3+} thin film by silicon integrated technique. This paper presents the photoluminescence and its annealing behavior from the Eu^{3+} implanted silicon based thin films. The conversion of Eu^{3+} to Eu^{2+} in N_2 atmosphere at high temperature is discussed.

2. Experimental

The SiO_2 film with thickness of 0.25 μm was prepared by the thermal oxidation on the (100) crystalline Si substrate. The refractive index of the SiO_2 film is 1.39. Eu ions were introduced by ion implantation at 200 keV in energy with the doses of 1×10^{15} and $1\times10^{14}/cm^2$. After ion-implantation, the SiO_2:Eu^{3+} films were annealed in N_2 for 30 min in the temperature range of 1000–1200°C. The PL spectra and PL excitation spectra were measured with ELMER LS501 spectrophotometer.

3. Results and discussions

The PL spectra of SiO_2:Eu^{3+} films with an implantation dose of $1\times10^{15}/cm^2$ for as-implanted film and films annealed at different temperatures are shown in Fig. 1. The excitation wavelength is 464 nm. For comparison, the PL spectrum of thermal growth SiO_2 is concluded. It is found that there is no light emission from SiO_2 film. A broad light emission band with peak position at around 604 nm for as-implanted SiO_2:Eu^{3+} film was observed. After annealing above 1000°C, the 604 nm PL intensity increases dramatically then slightly decreases as the temperature rises to 1200°C. However, the shapes of the PL spectra do not change.

The 604 nm (2.0 eV) light emission from SiO_x films was often observed and has been explained by the Si–O related defects [5]. The PL intensity originated from such defects in SiO_2 films should decrease by about one or two orders of magnitude after annealing [6] Fig. l shows that with increasing T_a, the intensity of the 604 nm PL band increases. So, we consider that the 604 nm PL band is not related to the defects in the SiO_2 films. Fig. 2 shows the

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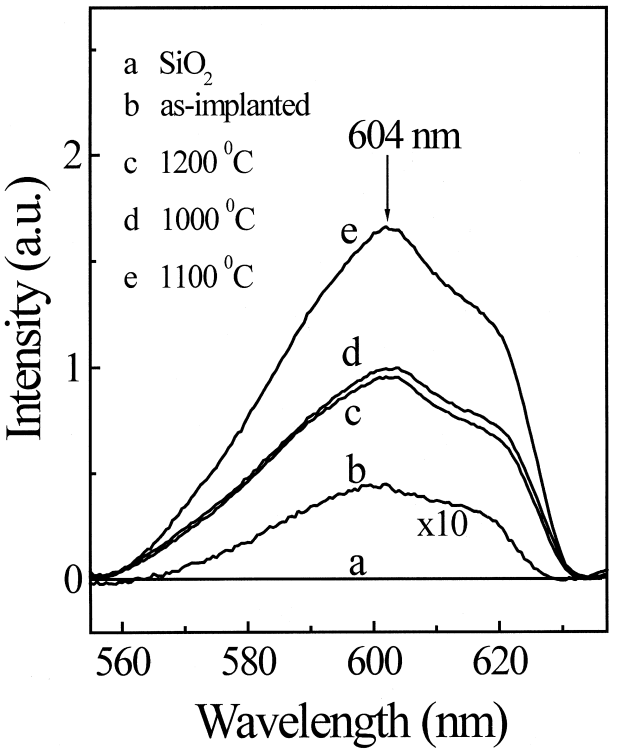


Fig. 1. The PL spectra of SiO_2:Eu^{3+} films with implantation dose of $1\times10^{15}/cm^2$ for as-implanted film and films annealed at different temperatures. The excitation wavelength is 464 nm. The PL spectrum of thermal growth SiO_2 is concluded.

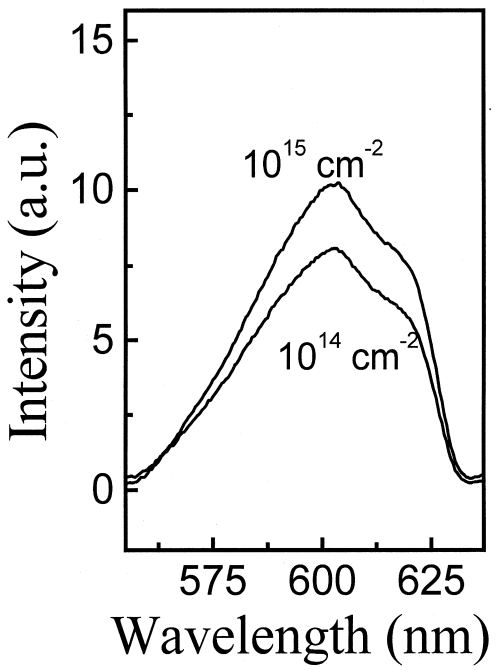
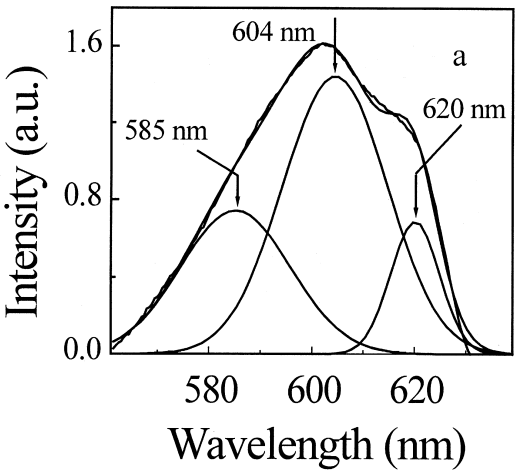


Fig. 2. The PL spectra of SiO_2:Eu^{3+} films annealed at 1100°C with different implantation doses.

PL spectra from SiO_2:Eu^{3+} films with implantation doses of 1×10^{14} and $1\times10^{15}/cm^2$ annealed at 1100°C. It is clear that the PL intensity increases with the implanted dose and the shape of the PL bands does not change. This shows that the 604 nm light emission is related to Eu^{3+} ions.

It is known that the sharp lines located at around 580 nm, 590–596 nm, 610–620 nm, 650 nm and 687–703 nm are corresponding to the standard $^5D_0$–^7F_J transitions of Eu^{3+} for J=0, 1, 2, 3 and 4, respectively [7]. Among them, the intensity of the 610–620 nm light emission is the strongest one. However, Figs. 1 and 2 show a broad PL band centered at around 604 nm. It seems different from the typical PL spectrum of Eu^{3+}. To find the further correlation between Fig. 1 and the $^5D_0$–^7F_J transition of Eu^{3+}, the deconvolution of the 604 nm PL band was performed in terms of Gaussian functions. The Gaussian fit



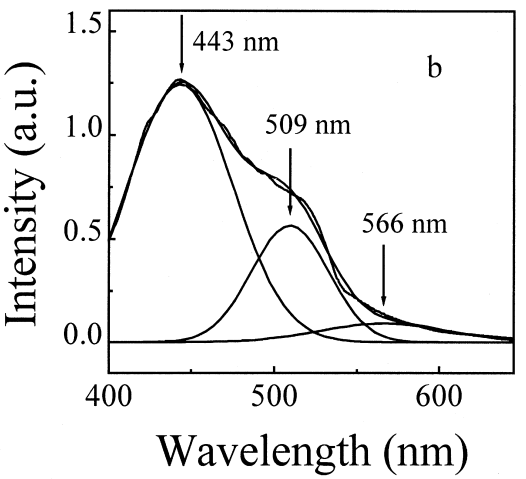


Fig. 3. (a) The deconvolution of the 604 nm PL band. Three PL bands centered at around 585, 604 and 620 nm with the FWHM of 24.1, 20.3 and 9.5 nm, respectively, were defined. (b) The deconvolution of the 443 nm PL band. Three PL bands centered at around 443 nm, 509 nm and 566 nm with the FWHM of 64, 46, 78 nm, respectively, were defined.

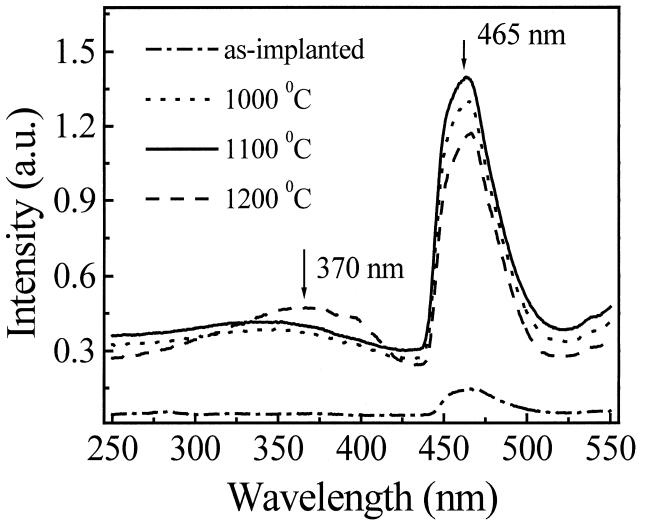


Fig. 4. The PL excitation spectra of SiO_2:Eu^{3+} films with implantation dose of $1\times10^{15}/cm^2$, annealed at different temperature and monitored at 604 nm.

of the PL spectrum with T_a at 1100°C is shown in Fig. 3 (a). Three PL bands centered at around 585, 604 and 620 nm with the full width at half maximum (FWHM) of 24.1, 20.3 and 9.5 nm, respectively, were defined. Compared with the standard spectra of Eu^{3+}, these peak positions show a red shift of 5 nm, which is likely caused by the amorphous SiO_2 host network.

Fig. 4 shows the PL excitation spectra of SiO_2:Eu^{3+} films with implantation dose of $1\times10^{15}/cm^2$ for as-implanted film and films annealed at different temperatures. The excitation spectra were monitored at 604 nm. The 465 nm PL excitation band and a small hill at around 370 nm were observed. It is known that the excitation peak of

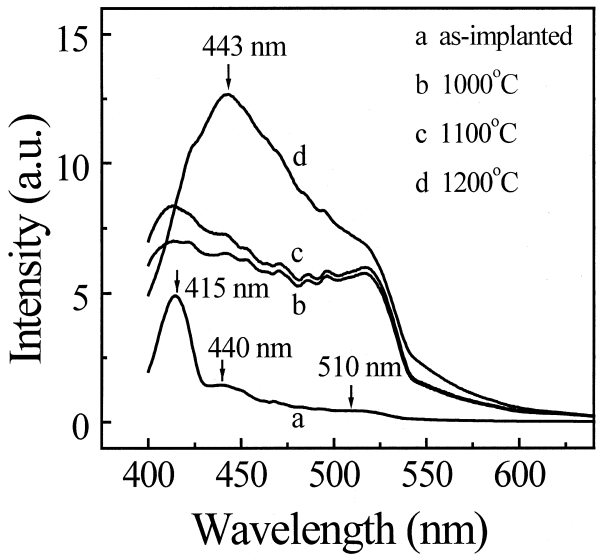


Fig. 5. The PL spectra of SiO_2:Eu^{3+} films with implantation dose of $1\times10^{15}/cm^2$. The excitation wavelength is at 377 nm.

Eu^{3+} at around 465 nm is identified to the $^7F_0-^5D_2$ transition. Our results are fully agreed with the typical $^7F_0-^5D_2$ transition. The 465 nm PL excitation band exhibits the same annealing behavior as the red light emission band, as shown in Fig. 6(a). From above analysis, we conclude that the 604 nm light emission is attributed to the Eu^{3+}.

In order to define the small hill at around 370 nm emerged in the PL excitation spectra, the PL spectra of SiO_2:Eu^{3+} films excited at 377 nm were measured as shown in Fig. 5. The PL band centered at around 415 nm accompanied with two shoulders at around 440 nm and 510 nm were observed from as-implanted sample. With increasing T_a, the rapid increase in the intensity of blue/green band makes the curve to be a plateau. As T_a= 1200°C, the PL band exhibits a dominant peak at around 443 nm. The intensity of the blue PL band is about one order of magnitude higher than that of the 604 nm PL band. This PL band can be deconvoluted into three bands centered at 443 nm, 509 nm and 566 nm with the FWHM of 64, 46 and 78 nm, respectively, as shown in Fig. 3(b), which are coincident with that of the PL band from the as-implanted sample.

Now, we discuss the origin of the PL bands in Fig. 5. The 415 nm PL band appears in the PL spectrum from as-implanted film. It is seen that the intensity of the 415 nm PL band decreases with increasing T_a and almost disappears as T_a rises up to 1200°C. The 415 nm light emission shows the similar annealing behavior as the 410–430 nm PL from amorphous SiO_x:H films reported by Zhu et al. and S. Tong et al. [8,9]. We suggest that the 415 nm PL band is attributed to the Si–O related defects.

The $4f^65d^1-4f^7(^8S_{7/2})$ transition of Eu^{2+} is related with the 450 nm light emission and correspondingly the PL excitation peak is at around 375 nm. The 443 nm PL band and the 370 nm PL excitation band are correlated in our experiment. Both of them are observed in Figs. 4 and 5. The temperature dependence of intensity of the 450 and 370 nm PL bands exhibits the similar annealing behavior as shown in Fig. 6(b).

Combining Fig. 6(a) with Fig. 6(b), we find that the intensities of the 604 nm PL and the 465 nm PL excitation from SiO_2:Eu^{3+} firstly increase then decrease as T_a rises to 1200°C, as we have mentioned above. It is noticed that the intensity of the 443 nm light emission and the 377 nm PL excitation are much enhanced as $T_a\geq$1200°C. We consider that the conversion from Eu^{3+} to Eu^{2+} probably happens. Nogami et al. observed the conversion of Eu^{3+} to Eu^{2+} as Al_2O_3:SiO_2/Eu^{3+} annealed in the forming gas [4]. Annealing in the deoxidize atmosphere, the formation of the covalent Eu–O bond causes the conversion of Eu^{3+} to Eu^{2+}. Although N_2 is not a strong reducer. It can act as the deoxidant at the high temperature and leads to the conversion of Eu^{3+} to Eu^{2+}. Our observation confirms above argument.

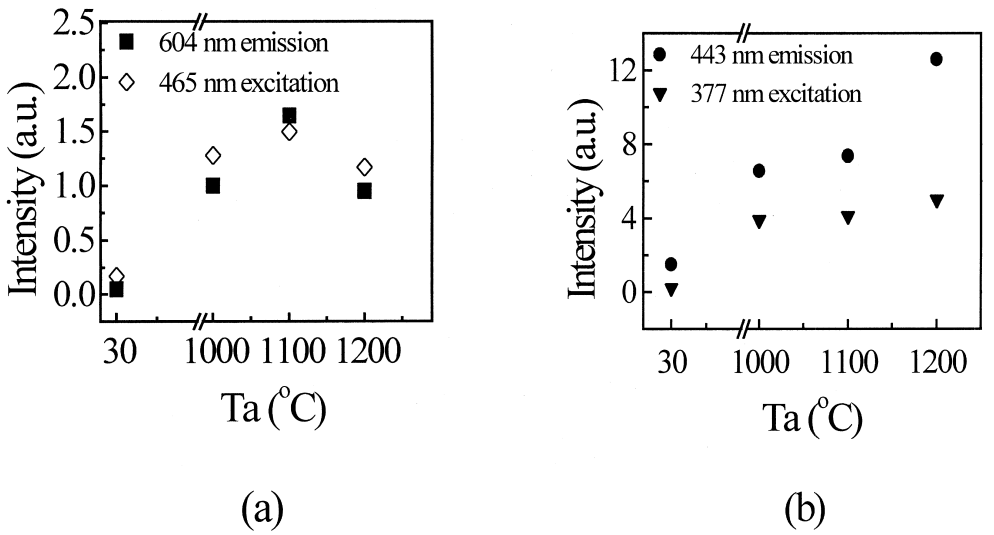


Fig. 6. The T_a dependence of intensities of (a) 604 nm light emission band [■] and 465 nm PL excitation band [◊], (b) 443 nm light emission band [●] and 377 nm PL excitation band [▼].

4. Conclusion

The red and blue light emissions from Eu ions doped SiO_2 films prepared by ion-implantation were successfully observed. The strong 450 nm blue light emission was observed after samples annealed in N_2 at 1200°C, which is related to the $4f^6 5d^1 – 4f^7(S_{7/2})$ transition of Eu^{2+} and indicates the conversion of Eu^{3+} to Eu^{2+}.

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