ELSEVIER

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Applied Surface Science 218 (2003) 310–316

applied surface science

www.elsevier.com/locate/apsusc

The effects of ambient He pressure on the oxygen density of Er-doped SiO_x thin films grown by laser ablation of a $Si:Er_2O_3$ target

Seung Min Park[a], Chang Hyun Bae[a], Sang Hwan Nam[a], Young Rae Jang[b], Keon Ho Yoo[b], Jeong Sook Ha[c,*]

[a]*Department of Chemistry, Kyunghee University, Seoul 130-701, South Korea*
[b]*Department of Physics, Kyunghee University, Seoul 130-701, South Korea*
[c]*Department of Chemical and Biological Engineering, Korea University, Seoul 136-701, South Korea*

Received 12 February 2003; accepted 23 April 2003

Abstract

Er-doped SiO_x thin films were fabricated by laser ablation of a $Si:Er_2O_3$ target in He atmosphere. We have measured the photoluminescence (PL) at 1.54 μm for the films grown at different He pressures and found that the oxygen density of the grown film that strongly influences the PL intensity is highly correlated with the ambient He pressure. This manifests that oxygen density of the film can be controlled in an inert atmosphere to maximize PL intensity when we adopt pulsed laser deposition (PLD) technique to deposit Er-doped SiO_x thin films. Also, we have examined the temperature dependence of PL and observed that the thermal quenching is greatly reduced for the PLD-grown films.

PACS: 81.15.Fg; 81.07.-b

Keywords: Laser ablation; Er-doped SiO_x thin film; 1.54 μm photoluminescence

1. Introduction

Er-doped Si has been widely studied due to its possible applications in opto-electronic technology. In particular, Er-doped Si has attracted great attention since it produced light emission from the intra-4*f* transition ($^4I_{13/2}$–$^4I_{15/2}$) at around 1.54 μm, which corresponds to the absorption minimum in silica-based glass fibers [1–3]. A variety of techniques such as ion implantation, molecular beam epitaxy, and chemical vapor deposition have been employed to fabricate Er-doped Si films. Recently, pulsed laser deposition (PLD) method has been intensively investigated since PLD was turned out to be a very useful technique for achievement of controlled high density of Er in Si thin films [4].

The photoluminescence (PL) intensity of the Er-doped Si thin films is highly affected not only by the concentration of Er but also by the chemical environment of Er in Si; oxygen codoping has been proved to enhance the PL intensity at room temperature via increasing the density of optically active Er ions

* Corresponding author. Tel.: +82-2-3290-3303; fax: +82-2-3290-3303.
E-mail address: jeongsha@korea.ac.kr (J.S. Ha).

0169-4332/$ – see front matter
doi:10.1016/S0169-4332(03)00674-3

and reducing the thermal quenching effect [5]. In PLD, oxygen codoping has been achieved by using a hot-pressed target that is a mixture of Si and prescribed amount of Er_2O_3. Although the density of Er in the film grown by PLD was successfully controlled just by varying the amount of Er_2O_3 in the target, the concentration of oxygen in the film as well as the experimental methods of controlling it has seldom been seriously investigated in spite of the crucial importance of oxygen in the luminescence characteristics of the Er-doped Si films.

Here, we present experimental results on the fabrication of Er-doped SiO_x thin films by laser ablation of a Si:Er_2O_3 target in He atmosphere. Surprisingly, the oxygen density of the grown film turned out to be significantly affected by the ambient He pressure in the deposition chamber and in turn the PL intensity was highly dependent on the oxygen density of the films. Also, we have analyzed the characteristics of the films by SEM, RBS, and XPS as well as PL.

2. Experimental

A chemically cleaned Si(1 0 0) substrate was attached to a sample holder in a pulsed laser deposition chamber. The base pressure of the ablation chamber was 1×10^{-7} Torr. A hot-pressed Si:Er_2O_3 bulk target with 10 wt.% Er_2O_3 was mounted on a target holder, 22 mm apart from the Si substrate. A pulsed Nd:YAG laser (355 nm) beam was directed onto the target at room temperature. The spot size of the focused laser beam was 0.78 mm^2 and the fluence was 1.3 J/cm^2. The ejected particles were deposited onto the Si substrate under either high vacuum or ambient He (99.9999%) pressures ranging from 10 mTorr to 4 Torr. The PL measurements were performed at temperatures ranging from 13 to 325 K. The excitation wavelength was 488 nm.

3. Results and discussion

Fig. 1 shows the SEM images taken from the Er-doped SiO_x films fabricated by PLD at room temperature. The films grown under the ambient He pressure of 50 mTorr showed a very smooth surface morphology composed of nanoparticles with sizes in the order of approximately 10 nm. With increase in the He pressure above 1 Torr, however, the size of the particles increased noticeably and the surface morphology became very rough. The typical growth rate of the film as measured by the cross-section SEM image was 0.05 nm/s.

After deposition, the film was annealed at 500 °C for 20 min in He atmosphere. The PL spectra measured at temperatures ranging from 13 to 325 K are shown in Fig. 2. In order to confirm that the PL we have observed originates not from the direct excitation of Er^{3+} [6] but from the energy transfer from Si to Er^{3+} and the subsequent intra-4*f* shell transition from the excited ($^4I_{13/2}$) to the ground ($^4I_{15/2}$) state in Er^{3+} ions, we have measured the PL intensity at six different wavelengths between 458 and 514 nm as shown in Fig. 3 and found that there was no particular wavelength dependence. The 488.0 and 514.5 nm correspond to the $^4I_{15/2}$–$^4F_{7/2}$ and $^4I_{15/2}$–$^2H_{11/2}$ transitions of Er^{3+}, respectively.

The spectral width of the main peak and the long tails of the spectra result from the Stark splitting of the excited and ground state in the host electric field, plus additional homogeneous and inhomogeneous broadening. The peak position of the Er^{3+} emission hardly changed for the temperature variation whereas its peak intensity decreased with increase in temperature. The peak intensity at room temperature is about 25% of that at 13 K as illustrated in the inset of Fig. 2. Such thermal quenching is very small compared to that of the Er-doped crystalline Si [7] but comparable to that of the Er-doped nanocrystalline Si grown by laser ablation [8] and Er-doped porous Si [9].

The chemical composition of the films was measured by RBS. Fig. 4 shows the RBS intensity ratio of O-to-Si (left) and the PL intensity (right) taken from the films grown at different He pressures. At the beginning, the PL intensity increased with increase in He pressure up to 50 mTorr, then decreased with further increase in the gas pressure, and finally almost disappeared at the He pressures above 500 mTorr as depicted in Fig. 4. It has been previously reported that co-doping of oxygen is effective for obtaining strong Er-related PL [10]. It is of note that the He pressure that gives the highest PL intensity coincides with the pressure where the oxygen concentration in the film is maximized: the concentration of oxygen is maximized at the He

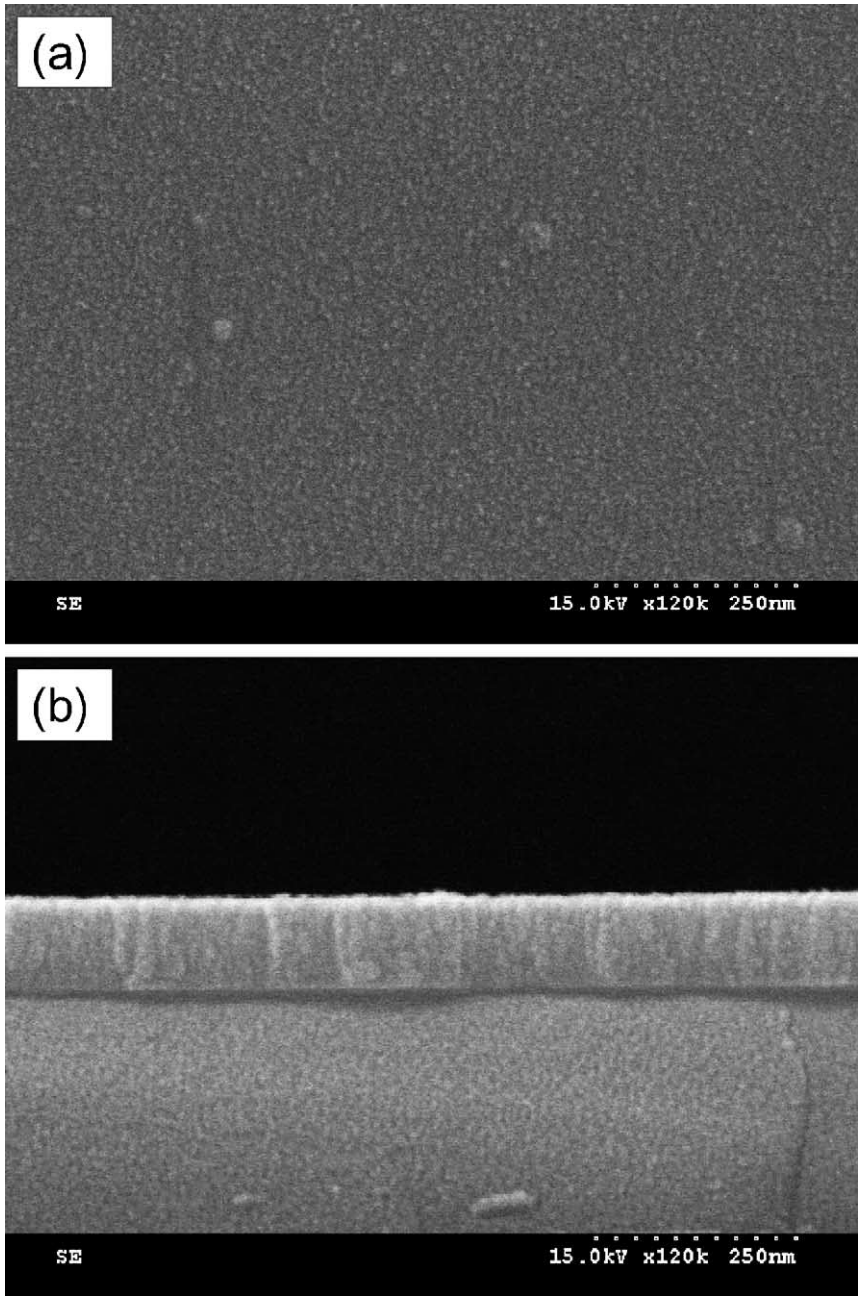

Fig. 1. The SEM images of an Er-doped SiO_x thin film deposited at room temperature by pulsed laser deposition. The ambient He pressure was 50 mTorr: (a) top view; (b) cross-sectional view.

pressure of 50 mTorr at which that of O-to-Si intensity ratio is its peak value. For the film grown under high vacuum without He, the concentration ratio of O-to-Si was estimated to be 0.4 and it increased with He pressure up to 50 mTorr, where it became 0.9. With further increase in He pressure above 50 mTorr, O-to-Si ratio became 0.2 at 4 Torr. The variation of the film thickness as the ambient He pressure was

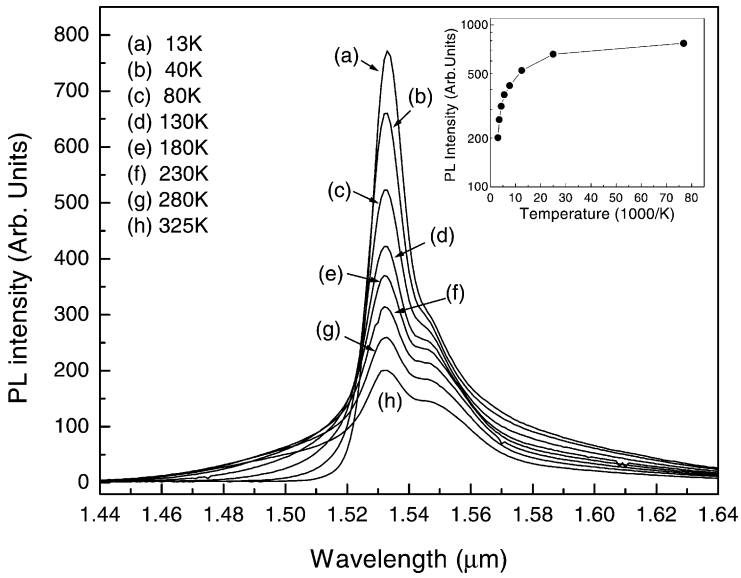

Fig. 2. The PL spectra at various temperatures taken from an Er-doped SiO_x thin film grown at room temperature and post-annealed at 500 °C for 20 min. The inset depicts the PL intensity as a function of temperature, showing the thermal quenching effect.

changed was not significant enough to influence the PL intensity.

The concentration of Er, however, decreased monotonously from 1.6 to 0.5 at.% as the He pressure was increased from 1×10^{-6} to 4 Torr. Although such pressure dependences are not clearly explained, it may be possible to speculate that slow Er atoms in the laser-produced plasma plume are scattered more severely by the ambient He atoms at higher pressures [11]. Also, the optimum pressure for the maximum

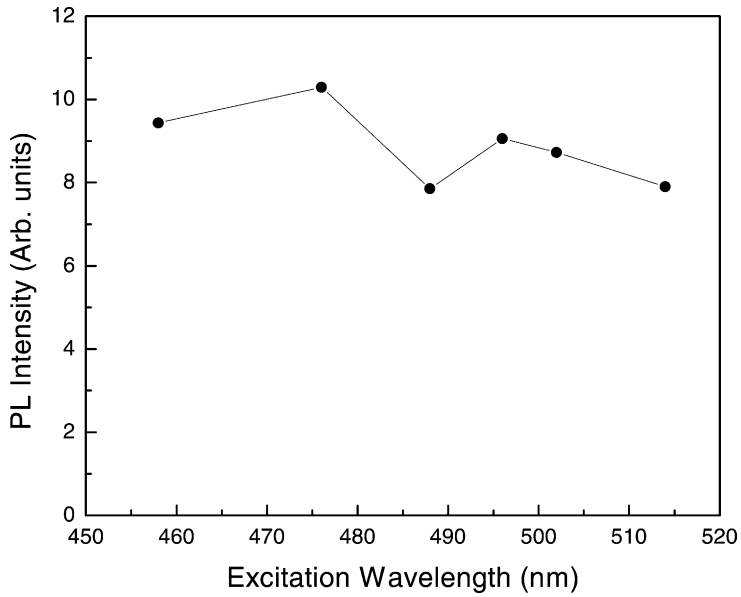

Fig. 3. The PL intensity at 1.54 μm as a function of the excitation wavelength.

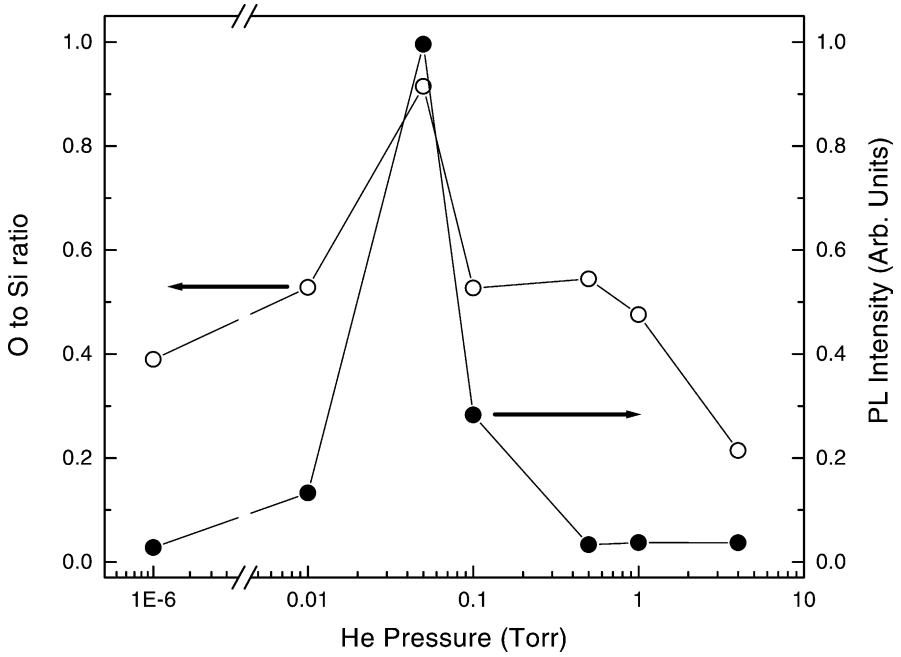

Fig. 4. The RBS intensity ratio of O-to-Si and PL intensity measured from Er-doped SiO_x thin films as a function of the ambient He pressure in the PLD chamber.

inclusion of oxygen into the film is thought to have to do with the plume temperature whose temporal and spatial variations are strongly affected by the ambient gas pressure [12].

Fig. 5 shows the XPS spectrum of Si $2p_{3/2}$ taken from the Er-doped films. The Si $2p_{3/2}$ peak showed double peaks at 99.1 and 101.7 eV. The peaks at 99.1 and 101.7 eV are considered to originate from the element Si and SiO_2, respectively. The XPS and RBS data imply that the film consists of Si nanoparticles embedded in amorphous SiO_x matrix. It is not clear whether Er^{3+} ions responsible for the strong PL are located inside the Si or SiO_2 phases or they exist at the interfacial regions. Considering the low solubility of Er in Si, Fujii et al. [13] reported that Er^{3+} ions around the interface are the origin of the strong PL at 1.54 μm. They also reported that the 1.54 μm PL intensity was more than 50 times stronger in the SiO_2 film containing nc-Si than those of SiO_2 films not containing nc-Si under the same concentration of Er. According to Zhao et al. [8], the average Si crystallite size of the nc-Si thin film was determined by X-ray diffraction to be ∼30 nm. They suggested that the 30 nm Si crystallites should play a role in enhancing the Er-related PL by depressing the thermal quenching and thereby gaining an intense room temperature PL.

The bandgap of amorphous SiO_x is as high as approximately 2 eV that is substantially larger than that of crystalline Si, which reduces the rate of back-transfer significantly. In silicon oxide matrices, the PL intensity may increase significantly by the energy transfer from the Si nanoclusters embedded in the silicon oxide matrix to Er^{3+} ions. In particular, amorphous Si with a high (2–50 at.%) oxygen content was reported to increase the concentration of optically active Er without serious segregation or precipitation problems [5]. As oxygen atoms are incorporated into the film, the segregation of Er is suppressed by reducing Er mobility or forming Er–O complexes [14].

When the Er-doped SiO_x thin films grown by PLD was post-annealed at high temperatures, the PL intensity increased dramatically: it increased as much as about 100 times by post-annealing at 500 °C for 20 min. After the post-annealing of the sample grown under 50 mTorr He at 500 °C, the composition and chemical structure of Si did not change noticeably. The increase in the PL intensity with post-annealing is

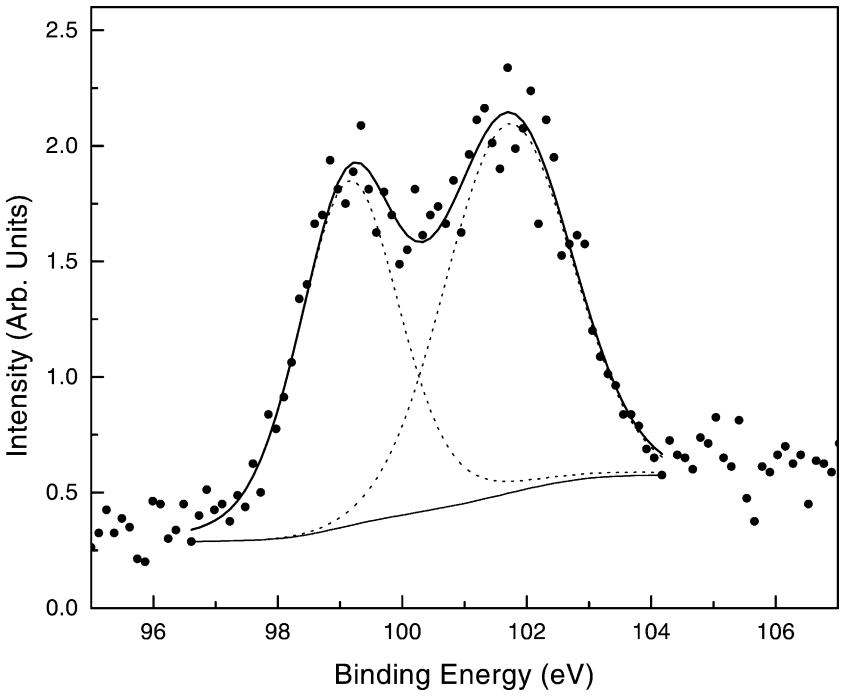

Fig. 5. The XPS spectrum of the Er-doped SiO_x thin film: Si $2p_{3/2}$ spectral region. The dual peaks at 99.1 and 101.7 eV stem from the element Si and SiO_2, respectively.

due to the positioning of Er at an optically active configuration in the host lattice [15,16]. The PL intensity decreased, however, as the film was annealed at temperatures above 500 °C, which can be attributed to oxygen outdiffusion or phase separation and Er precipitation. The recrystallization of the film may result in decreased absorption of the pump light and hence a lower Er excitation efficiency [5,17,18].

4. Conclusions

By adopting the laser ablation technique, Er-doped SiO_x thin films emitting a strong PL at 1.54 μm were successfully grown. The films turned out to be composed of Si and SiO_x phase as analyzed by XPS and RBS. The reduced thermal quenching is considered to stem from the enlarged bandgap of the amorphous SiO_x matrix. Also, the effects of the ambient He pressure on the oxygen density of the Er-doped SiO_x films that strongly affects the PL intensity at 1.54 μm were examined. We have successfully demonstrated that the oxygen density can be widely controlled by varying the ambient He pressure, which manifests that the oxygen density can be changed even in an inert atmosphere without using oxygen as an ambient gas in PLD.

Acknowledgements

This work has been financially supported by the Korean Ministry of Information and Communications and the special fund from Korea University.

References

[1] S. Coffa, F. Priolo, G. Franzo, V. Bellani, A. Carnera, C. Spinella, Phys. Rev. B 48 (1993) 11782.
[2] H. Przybylinska, W. Jantsch, Yu. Suprun-Belevitch, M. Stepikhova, L. Palmetshofer, G. Hendrofer, A. Kozanecki, Phys. Rev. B 54 (1996) 2532.
[3] J. Stimmer, A. Reittinger, J.F. Nutzel, G. Abstreiter, Appl. Phys. Lett. 68 (1996) 3290.
[4] S. Komuro, S. Maruyama, T. Morikawa, X. Zhao, H. Isshiki, Y. Aoyagi, Appl. Phys. Lett. 69 (1996) 3896.

[5] G.N. van der Hoven, J.H. Shin, A. Polman, S. Lombardo, S.U. Campisano, J. Appl. Phys. 78 (1995) 2642.
[6] S. Komuro, T. Katsumata, T. Mrikawa, X. Zhao, H. Isshiki, Y. Aoyagi, Appl. Phys. Lett. 74 (1999) 377.
[7] A. Polman, J. Appl. Phys. 82 (1997) 1.
[8] X. Zhao, S. Komuro, H. Isshiki, Y. Aoyagi, T. Sugano, Appl. Phys. Lett. 74 (1996) 120.
[9] X. Zhao, S. Komuro, H. Isshiki, S. Maruyama, Y. Aoyagi, T. Sugano, Appl. Surf. Sci. 113–114 (1997) 121.
[10] X. Zhao, S. Komuro, H. Isshiki, Y. Aoyagi, T. Sugano, Appl. Phys. Lett. 74 (1999) 120.
[11] S.M. Park, J.Y. Moon, J. Chem. Phys. 109 (1998) 8124.
[12] S. Wee, S.M. Park, Opt. Commun. 165 (1999) 199.
[13] M. Fujii, M. Yoshida, Y. Kanzawa, S. Hayashi, K. Yamamoto, Appl. Phys. Lett. 71 (1997) 1198.
[14] D.J. Lockwood (Ed.), Light Emission in Silicon: From Physics to Devices, Academic Press, New York, 1998 (Chapter 4).
[15] W.L. Ng, M.P. Temple, P.A. Childs, F. Wellhofer, K.P. Homewood, Appl. Phys. Lett. 75 (1999) 97.
[16] Y.S. Tang, Z. Jingping, K.C. Heasman, B.J. Sealy, Solid State Commun. 72 (1989) 991.
[17] A.R. Zanatta, L.A.O. Nunes, L.R. Tessler, Appl. Phys. Lett. 70 (1997) 511.
[18] S. Lombardo, S.U. Campisano, G.N. van den Hoven, A. Cacciato, A. Polman, Appl. Phys. Lett. 63 (1993) 1942.