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Photoluminescence enhancement through silicon implantation on SRO-LPCVD films

A. Morales-Sánchez[a,*], K.M. Leyva[a], M. Aceves[a], J. Barreto[b], C. Domínguez[b], J.A. Luna-López[c], J. Carrillo[c], J. Pedraza[a]

[a] INAOE, Electronics Department, Apartado 51, Puebla 72000, Mexico
[b] Instituto de Microelectrónica de Barcelona, IMB-CNM (CSIC), Barcelona, Spain
[c] CIDS-BUAP, Apdo. 1651, Puebla 72000, Mexico

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ABSTRACT

Photoluminescence (PL) properties of thin and thick silicon-rich oxide (SRO) and silicon implanted SRO (SI-SRO) films with different silicon excess fabricated by low pressure chemical vapor deposition (LPCVD) were studied. The effects of the annealing temperature and silicon implantation on the PL were also studied. Maximum luminescence intensity was observed with an annealing temperature of 1150 and 1100 °C for thin and thick SRO films, respectively. The PL intensity is strongly enhanced when SRO films are implanted with silicon, especially for thin SRO films. Thin SI-SRO films emit up to six times more than non-implanted films, meanwhile the PL in thick SI-SRO films is only improved less than two times. Therefore, thin SI-SRO films are an interesting alternative for applications such as the fabrication of efficient Si-nps based LEDs.

1. Introduction

Observation of luminescence in porous silicon [1] seemed to solve the physical inability of the silicon (Si) to act as light emitter. However its poor chemical stability, robustness and luminescence degradation made it unsuitable for such applications [2]. Also nanometric-sized silicon crystallites embedded in a dielectric matrix show a strong and stable luminescence. Therefore they are considered as the best alternative for light emitting devices (LEDs) fabrication based on silicon [3–7]. A great variety of techniques to produce Si-nanoparticles (Si-nps) have been reported, such as Si-implantation into thermally grown SiO_2 films [4–7,8], plasma enhanced chemical vapor deposition (PECVD) [3,6,8–10] and low pressure chemical vapor deposition (LPCVD) [8,10–12].

In addition to the Si-nps, it is well known that exist other several luminescent centers (LCs) in silicon-rich oxide films due to the presence of weak oxygen bonds (WOB), neutral oxygen vacancy (NOV) and non-bridging oxygen hole center (NBOHC) defects. Such LCs emit at about 415, 455, and 600 nm, respectively and they are obtained depending on the used technique [5–8,10]. Some of these LCs are eliminated after a thermal annealing in an inert ambient.

Although the LCs are known and their photoluminescent (PL) intensity can be improved, in the luminescent devices these materials exhibit poorer electroluminescence (EL) than photoluminescence (PL). Therefore, many efforts have been done to improve the PL intensity in SRO films by changing the technological parameters such as silicon excess, temperature and time of anneal [6,8–11]. However, there are a few reports on silicon implantation into SRO films, which already have silicon excess [8,12,13]. Silicon-rich oxide films with controlled and uniform silicon excess are easily deposited by LPCVD. Silicon excess is easily controlled by changing the partial pressure ratio (Ro) between nitrous oxide (N_2O) and silane (SiH_4). Silicon excess as high as 17 at.% is obtained with Ro = 3, and stoichiometric oxide can be obtained with Ro = 100 [10–12,14]. Comparative studies about the luminescence properties of SRO films obtained by different techniques have been done [8,10]. Results have shown that SRO films deposited by LPCVD emit a stronger PL than those obtained by PECVD and Si implanted SiO_2 films. Moreover, recent comparative studies made by other researchers on the PL properties of SRO films obtained by LPCVD and PECVD have corroborated this asseveration [15]. A spectroscopic analysis has revealed the presence of amorphous Si-nps embedded in SRO films with low silicon excess [11]. An increase of PL intensity has been already reported for thick SRO-LPCVD and SRO-PECVD films when implanted with silicon (SI-SRO) [12,13].

In this work, PL properties of thin and thick SRO films with different silicon excess implanted with silicon (SI-SRO) fabricated by LPCVD and annealed at different temperatures were studied. The

* Corresponding author. Tel.: +52 222 2663100, fax: +52 222 2470517.
E-mail addresses: amorales@inaoep.mx, amorales@cnyn.unam.mx, amorales7901@yahoo.com.mx (A. Morales-Sánchez).

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Table 1
Characteristics of the SRO and SI-SRO films studied. Silicon excess was taken from references [10–12,17].

SRO	Thickness (nm) @ 1150 °C	Ro = $[N_2O]/[SiH_4]$	Silicon excess (at.%)	Anneal (°C) 2 h, N_2			Implantation $2 \times 10^{16}/cm^2$		Anneal 1150 °C 2 h, N_2
				1050	1100	1150	20 keV	110 keV	
Thin	61.4 ± 2.5	22	~5.0	×	×	×	×		×
	83.3 ± 3.0	30	~4.0	×	×	×	×		×
	97.8 ± 1.9	37	~2.8	×	×	×	×		×
	76.2 ± 2.6	45	~2.0	×	×	×	×		×
Thick	403.0 ± 23.0	22	~5.0		×	×		×	×
	402.0 ± 10.0	30	~4.0		×	×		×	×
	441.3 ± 10.5	37	~2.8		×	×		×	×
	593.0 ± 44.0	45	~2.0		×	×		×	×

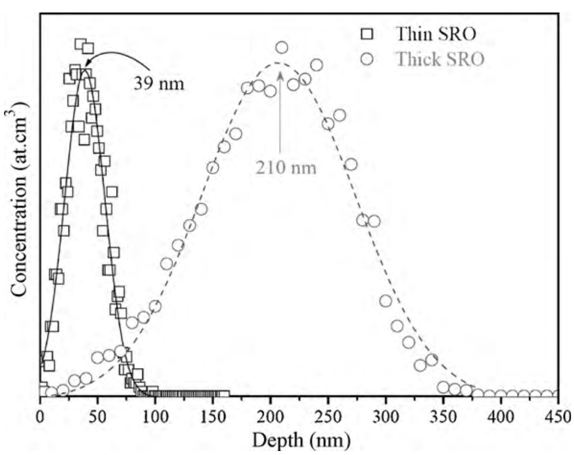

Fig. 1. Depth profile of Si ions implanted in thin and thick SRO films.

PL intensity is strongly enhanced when SRO films are implanted with silicon, especially in thin SI-SRO films which emit up to six times more than non-implanted films. Therefore, SRO films combined with the Si ion implantation are an interesting alternative for the fabrication of efficient Si-nps based LEDs.

2. Experimental

SRO films were deposited on n type (1 0 0) Si wafers in a LPCVD hot wall reactor using N_2O and SiH_4 as the reactant gasses at 720 °C. The flow ratio (Ro) between N_2O and SiH_4 was used to control the amount of silicon excess into the SRO films. SRO films were classified as thin (~70 nm) and thick (~400 nm).

After deposition, a set of thin SRO films were thermally annealed at 1050, 1100, and 1150 °C for 2 h; meanwhile thick SRO films were annealed at 1100 and 1150 °C for 2 h.

Another set of thin and thick SRO films as-deposited and annealed at 1150 °C were implanted with Si at energy of 20 and 110 keV for thin and thick samples, respectively. The implanted dose for both thin and thick samples was of $2 \times 10^{16}/cm^2$. Finally, after implantation, thin and thick SI-SRO films were thermally annealed at 1150 °C for 2 h. All annealings were done in N_2 atmosphere. Table 1 summarizes the main characteristics of the SRO films studied. The expected profiles of the implanted Si atoms in the SRO layers were estimated using SRIM [16] and they are shown in Fig. 1.

A Gaertner L117 ellipsometer was used to obtain the thickness of the films. PL at room temperature was carried out with a Fluoromax 3 spectrofluorometer from Horiba Jobin Yvon, which is controlled with a computer. The samples were excited using a 290 nm (4.27 eV) radiation. PL measurements were scanned between 400 and 900 nm (3.1–1.37 eV) with a resolution of 1 nm.

3. Results and discussion

Table 1 reports the thickness of SRO films annealed at 1150 °C and their silicon excess. The photoluminescence spectra of SRO films annealed at 1150 °C are shown in Fig. 2. It is clear that the PL intensity is affected by the silicon excess (Ro), especially for thin SRO films, as observed in Fig. 2(a). Both thin and thick SRO films emit a visible-red-luminescence. Nevertheless, thick SRO film with

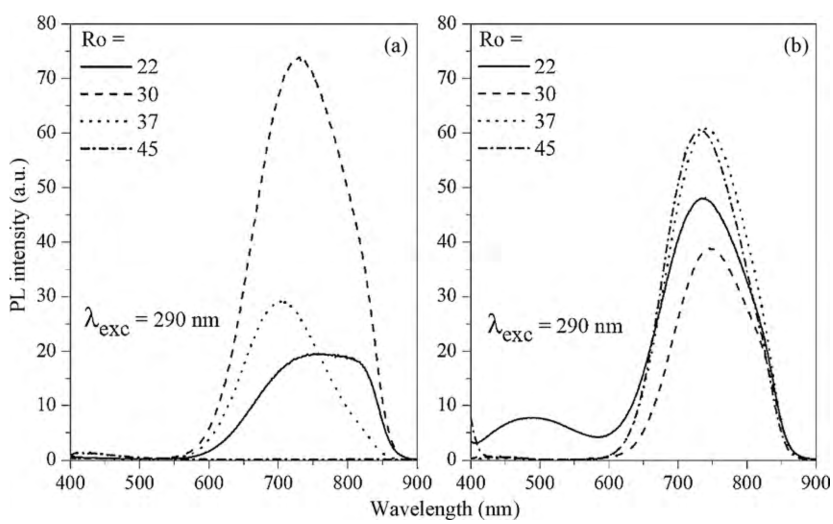

Fig. 2. PL spectra from (a) thin and (b) thick SRO films thermally annealed at 1150 °C.

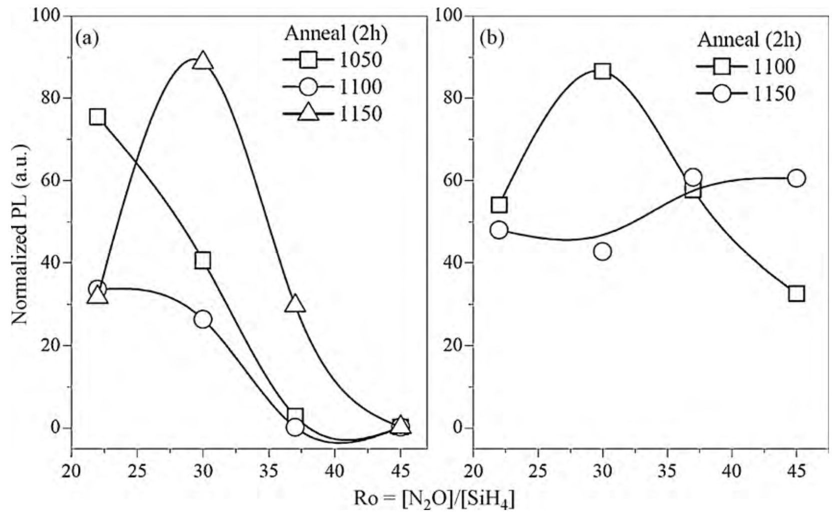

Fig. 3. PL intensity normalized to thickness for (a) thin and (b) thick SRO films as a function of the flow ratio (Ro) and annealing at different temperatures (lines are plotted as an eye-guide).

the highest silicon excess (Ro = 22) emits an additional band placed at ~485 nm, as shown in Fig. 2(b). The blue emission (485 nm) has been related to defects such as neutral oxygen vacancies (NOV) [4–8]. In spite of that the optical and microstructural properties of silicon-rich oxide layers have been extensively studied, there is no a clear consensus on the origin of the red-luminescence due mainly to differences in experimental results [8,11,12].

Defects, Si-nps, as well as interaction between defects at the SiO_2/Si-nps interface and Si-nps have been proposed as the origin of luminescence on SRO films depending on the emission wavelength. The red emission has been explained according to two main models: the first one describes that the luminescence takes place in silicon nanoparticles by quantum confinement effects (QCE) [6,9] meanwhile the second model relates the PL with the presence of defects in the SiO_2/Si-np interface [5,7,8,11,17]. It is widely accepted that when SRO films are annealed at high temperature the silicon excess agglomerates creating Si-nps or silicon compounds [3–14]. In SRO-LPCVD films with low silicon excess, a spectroscopical analysis has revealed the presence of amorphous Si-nps [11]. Si-nps are not present in as-deposited SRO-LPCVD films but a PL emission of low intensity at the blue region has been observed and related with oxygen vacancies [18]. After the thermal annealing, the red emission is enhanced and the blue emission decreased. Therefore, the red-luminescence from SRO films after thermal annealing results of the presence from Si-nps [18].

The effect of the anneling temperature on the PL properties in SRO-LPCVD films was also studied. As shown in Fig. 3, the maximum PL emission depends on the annealing temperature. For thin SRO films with Ro ≥ 30 the PL becomes intense as the temperature increases. Maximum emission is obtained with 1150 °C and Ro = 30, as observed in Fig. 3(a). For Ro = 22 the optimum temperature is 1050 °C, meanwhile a higher temperature reduce the emission. On the other hand, thick SRO films exhibit the strongest PL when they are annealed at 1100 °C and the maximum emission is also obtained with Ro = 30, see Fig. 3(b).

Once the optimum annealing temperature is found to be 1150 °C, some as-deposited and annealed (at 1150 °C) samples were implanted wih silicon in order to observe their PL response. Fig. 4 exhibits the PL spectra of thin SI-SRO films with Ro = 37. As shown, all SRO films exibit the visible-red-luminescence but with different intensity. The PL intensity increases up to 6 times after the SRO is implanted with silicon (implanted and annealed) compared to the non-implanted SRO film. This strong luminescence enhancement represents an excelent alternative in order to get efficient electroluminescent devices. The annealing before the implantation (annealed and implanted and annealed) also increases the PL intensity compared with non-implanted SRO film.

Fig. 5 shows the PL intensity normalized to the thickness of the SI-SRO films. For thin SRO films with Ro = 22, the PL intensity remains almost at the same value in spite of the silicon implantation, as shown in Fig. 5(a). Two maximum PL emission can be observed for thin SRO films. For samples annealed before implantation, the maximum emission is obtained with Ro = 30 and then it shows a slight saturation. Meanwhile for implanted and annealed samples, the maximum emission is found with Ro = 37. Nevertheless, the highest PL is obtained when SRO films are only implanted and then annealed and with Ro = 37. On the other hand, the Si-implantation into thick SRO films only increases the PL intensity less than 2 times for the best case (Ro = 37), as shown in Fig. 5(b).

Analysis of energy filtered transmission electron microscopy (EFTEM) and PL on thick SRO-LPCVD films before and after implantation have been done [11,12]. EFTEM demonstrated the presence of Si-nps within the SRO films with different sizes depending on the silicon excess. An increase of the PL intensity on these thick SRO films was obtained after implantation, similar to this work. That stronger luminescence was directly related with an increase of the number of Si-nps of similar size, as measured by EFTEM and reported in [12]. Therefore, the increase of the PL intensity at both

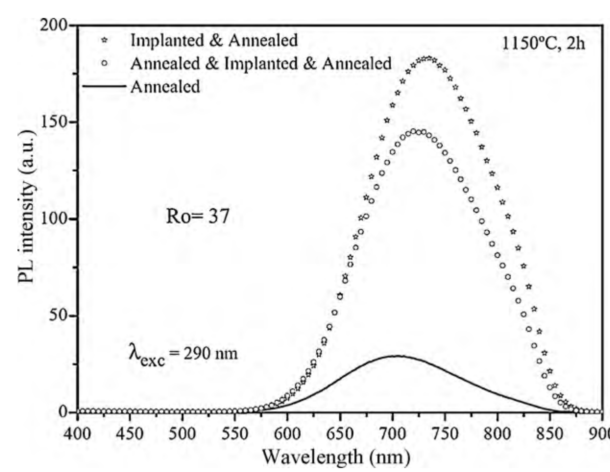

Fig. 4. PL spectra from thin SRO films with Ro = 37 implanted with silicon and thermally annealed at 1150 °C.

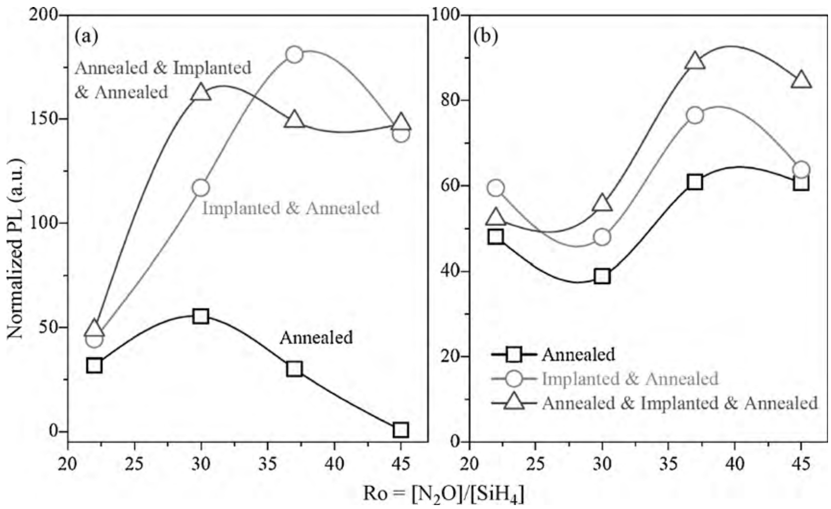

Fig. 5. PL intensity normalized to thickness for (a) thin and (b) thick SI-SRO films as a function of the flow ratio (Ro) and annealing at 1150 °C (lines are plotted as an eye-guide).

thin and thick SRO films studied from this work could be also related with the increase in the number of Si-nps. Nevertheless, EFTEM analysis from implanted SRO films from this work needs to be done. Particularly, the thin SRO films are strongly affected by the silicon implantation. Both thin and thick SRO films were implanted with the same dose and the main difference is the thickness. So, there could exist a larger density of Si-nps per volume in thin SI-SRO than in thick SI-SRO films. Therefore, in thin SI-SRO films, a larger quantity of Si-nps can be excited leading to a strongly improved PL.

4. Conclusion

The luminescent properties of thin and thick SRO films deposited by LPCVD and implanted with silicon were studied. An analysis of the annealing temperature showed that the optimum value, to obtain maximum PL, is 1150 and 1100 °C for thin and thick SRO films, respectively. SRO films with Ro = 30 and 37 showed maximum PL emission.

The silicon implantation into SRO films (SI-SRO) enhanced the PL intensity, especially for thin SRO films. Thin SI-SRO films emit up to six times more than non-implanted films, meanwhile the PL in thick SI-SRO films is only improved less than 2 times. This behaviour was related with the increase in the number of Si-nps within the SRO films after implantation.

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