Thickness-dependent optimization of \( \text{Er}^{3+} \) light emission from silicon-rich silicon oxide thin films

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Abstract

This study investigates the influence of the film thickness on the silicon-excess-mediated sensitization of Erbium ions in Si-rich silica. The \( \text{Er}^{3+} \) photoluminescence at 1.5 \( \mu \)m, normalized to the film thickness, was found five times larger for films 1 \( \mu \)m-thick than that from 50-nm-thick films intended for electrically driven devices. The origin of this difference is shared by changes in the local density of optical states and depth-dependent interferences, and by limited formation of Si-based sensitizers in “thin” films, probably because of the prevailing high stress. More Si excess has significantly increased the emission from “thin” films, up to ten times. This paves the way to the realization of highly efficient electrically excited devices.

Background

The realization of efficient Si-based optical emitters for photonics is one of the most challenging objectives for the semiconductor community [1]. Such a purpose is confronted to the indirect band gap of bulk silicon which makes difficult the light emission from Si, and then presents a major obstacle to full photonic-electronic integration. However, the indirect sensitization of emission from erbium ions, via Si nanoclusters (Si-nc), in the technologically important 1.5- \( \mu \)m spectral region is a promising approach that has received significant attention. Such a sensitizing effect of Si-ncs increases the effective excitation cross section of Er by \( 10^3-10^4 \) over a broad band in Si-rich silicon oxide (SRSO) systems [2]. This leads to the observation of enhanced Er photoluminescence (PL) and electroluminescence in the standard telecommunications wavelength band around 1.54 \( \mu \)m [2,3]. Depending on the targeted application, the thickness of the active layer can vary over a large range, from a micrometer-scale for planar waveguide amplifiers [4] to a few tens of nanometers for electrically driven LEDs [3] or slot waveguides [5]. According to recent studies, layer thickness was shown to influence the nucleation and growth of Si-ncs [6-8], as well as the effective intensity of the pump beam [9] and the local density of optical states (LDOS) [10,11]. This thickness dependence is crucial since each application requiring a given thickness may necessitate a specific optimization of the material.

In this paper, we investigate the impact of layer thickness on the optical properties of SRSO:Er thin films. The results demonstrate that the photoluminescence in very thin layers is hindered by some thinness-related limiting factors. To overcome this drawback of thin layer, more Si excess was gradually incorporated until a level of Er emission that was found surprisingly higher than that observed in optimized micrometer-thick layers.

Experimental details

The SRSO films doped with Er were grown onto a p-type, 250-\( \mu \)m thick, (100) silicon wafer, by magnetron co-sputtering of three confocal cathodes (Si\(_2\)O\(_3\), Si, and Er\(_2\)O\(_3\)) under a plasma of pure Argon at a pressure of 2 mTorr. The power densities applied on the three confocal targets were kept constant, while the deposition was performed at two temperatures \( T_d \), room temperature (RT) and 500°C, for various durations between 20 min and 10 h. To examine the influence of Si excess for a set of thin films of about 50 nm in thickness, the power density on the Si target was subsequently increased. The thickness and refractive index \( n \) were measured by spectroscopic ellipsometry for films thinner than 500 nm and by m-lines techniques for films exceeding 500 nm in thickness. The thickness shows a linear variation with the deposition duration. The PL spectra were recorded...
using the non-resonant 476-nm excitation wavelength in order to ensure that Er$^{3+}$ ions are only excited through the sensitizers. The samples were excited with 45° incident spot of approximately 3 mm$^2$ with a power of 180 mW, i.e., a power density of 0.06 W/mm$^2$. The Er content was obtained by time-of-flight secondary ion mass spectroscopy technique after calibration by a reference SRSO:Er sample containing a known Er concentration. The erbium concentration was found nearly constant for all samples at about $3 \times 10^{20}$ at. cm$^{-3}$. The Si excess was evaluated by two methods: X-ray photoelectron spectroscopy (XPS) exploring beyond 100-nm depth (or total thickness for thinner films) in different places, and Fourier transform infrared (FTIR) spectroscopy with a spot covering a large area of the sample. Transmission electron microscopy (TEM) observations were performed using a JEOL 2010F operated at 200 kV.

**Results**

Typical Si 2$p$ and O 1$s$ XPS spectra of the sample deposited at 500°C for 1 h are displayed in Figure 1. The values of Si excess were determined by measurement of the ratios of the atomic concentration of Si and O ($x = [O]/[Si]$), that were deduced from the area of the Si 2$p$ and O 1$s$ spectra and compared to a stoichiometric SiO$_2$ sample. The XPS measurements are performed while etching the sample with Ar in the same time, allowing the determination of the Si excess depth profile. The reported values correspond to the value read in the flat region (see inset Figure 1b). For the thinner layer, the thickness is still large enough to be able to obtain a good depth resolution. The flatness of the profiles along almost the whole thickness demonstrates that the thickness of the material has no influence on the stoichiometry of the deposited SiO$_x$. However, the $x$ parameter was found to increase from $x = 1.555 \pm 0.004$ for RT-deposited samples to $x = 1.616 \pm 0.009$ for $T_d = 500°C$. This reflects a lowering of Si excess due to the increasing desorption of SiO with $T_d$, as observed in our recent work [12]. For the FTIR approach, which is based on the shift of the TO$_3$ peak towards that of stoichiometric SiO$_2$ [13], the detection of Si excess is limited to the Si atoms bonded to O, and does not take into account the agglomerated Si atoms [13]. However, this limitation can be used to advantage by comparing values of Si excess measured by FTIR to those determined by XPS, enabling evaluation of the fraction of agglomerated Si. Since the phase separation between Si and SiO$_2$ is incomplete for the as-deposited samples, the following relation holds:

$$\text{SiO}_x \rightarrow \frac{x}{y} \text{SiO}_y + \left( \frac{y-x}{y} \right) \text{Si}$$  

(1)

with $y$ the stoichiometry parameter (SiO$_y$) detected by FTIR, implying $x < y < 2$. The atomic percentage of agglomerated Si, %Si$_\text{agglo}$ can be estimated from $(y - x)/y(1 + x)$ and its evolution with thickness is shown in Figure 2 for the two series deposited at RT and 500°C. A single isolated Si atom is highly likely not able to act as a sensitizer, therefore this parameter (%Si$_\text{agglo}$) includes the total population of Si-based sensitizers consisting in either Si-ncs, the so-called luminescent centers of Savchyn et al. [14], or the atomic scaled agglomerates suggested recently by our group [15]. To effectively play their sensitizing role, these entities should be located at less than about 1 nm of an optically active Er ion. Figure 2 shows that the agglomeration of Si is favored by increased $T_d$ and/or film thickness. While the raise of $T_d$ from RT to 500°C is expected to enhance the clustering of silicon during deposition, the most striking aspect is the pronounced increase of %Si$_\text{agglo}$ versus thickness. Note that the fraction of agglomerated Si in both RT-deposited and 500°C-deposited samples shows a similar
increasing trend, but less pronounced for the former one, suggesting that this phenomenon stems from the influence of the thickness. Such an influence has been demonstrated earlier and assigned to the existence of a nucleation barrier for the formation of Si-nc as a function of the separation distance from the substrate, i.e. the film thickness [6-8]. This barrier is likely induced by the stress that is inversely proportional to film thickness [6-8], and thus prevents a complete phase separation of Si-ncs around 750 nm, and from Er ions around 1.5 μm (see inset), as a function of the annealing temperature (T_a). The influence of T_a on the agglomeration of Si excess was previously studied [19] and it was shown that the value of %Si_{agglo} increases almost linearly versus T_a before reaching a complete agglomeration at 1,100°C, whatever the temperature of deposition and the %Si_{excess}. Three major observations can be made: (1) Er PL shows the same evolution for both “thin” and “thick” samples, with an optimum for T_a = 900°C. (2) The Si-nc-PL detected from the thick sample rises spectacularly for T_a = 1,100°C. This opposite behavior of the Si-nc and Er emissions for thick films has been already observed and explained [20,21]. By contrast, no Si-nc PL emission is detected from the thin films, even after a 1,100°C annealing. This phenomenon is due to the low fraction of agglomerated Si (see Figure 2), and is confirmed in Figure 4 by TEM images of both thin and thick samples annealed at 1,100°C that shows the presence of well-defined crystallized Si-ncs in thick samples but not in the thin one. Such inhibition of the nucleation of Si-nc in thin films was already assumed in several studies based on PL results [6,10] but these TEM images are direct evidence of this phenomenon. (3) The Er emission is almost four times lower for the thin sample for all T_a. Such a gap between the Er PL from the “thin” and “thick” samples deserves further attention. The above-mentioned limitations (stress) and depth-dependent optical effects (LDOS, interference) related to
the film thinness are to be circumvented and/or considered. To estimate the impact of both interference-induced variations of the pumping and LDOS effects, we made calculations based on the methods described in Refs. [9] and [10], respectively. Their specific contributions at a distance $z$ from the substrate were then estimated, and their product integrated over the thickness has allowed the calculation of their combined contributions, $I_{\text{cal}}$, on the measured Er PL intensity, $I_{\text{PL}}$. The calculated intensity $I_{\text{cal}}$ is compared in Figure 5a to $I_{\text{PL}}$. For the sake of comparison, both $I_{\text{cal}}$ and $I_{\text{PL}}$ are normalized to the highest values, at 1,400 nm where the stress effect on the Er PL intensity can be relatively neglected. While $I_{\text{PL}}$ shows an abrupt decrease at about 200 nm, indicated by the vertical dashed line of Figure 5b, $I_{\text{cal}}$ shows a smaller reduction down to a level significantly higher than the corresponding level for $I_{\text{PL}}$. An approximately five-time lowering of $I_{\text{PL}}$ and nearly 1.5 times decrease of $I_{\text{cal}}$ occur at the thickness threshold of approximately 200 nm, beyond which the above-mentioned limitations are less effective. The additional reduction of $I_{\text{PL}}$, compared to $I_{\text{cal}}$ can be attributed to a stress effect which affects the formation and homogeneity of the sensitzers.

To overcome these limitations, we have gradually raised the Si excess in approximately 50-nm-thick films, with the objective of increasing the number of Si-based sensitzers. We show in Figure 5b the evolutions of $I_{\text{PL}}$ containing approximately 7.5 at.% Si excess (circles) as a function of the film thickness and $I_{\text{PL}}$ of thin films (approximately 50 nm) with different Si excess (squares) for the samples processed using optimized conditions ($T_d = 500^\circ$C, $T_s = 900^\circ$C, see Figure 3).

We plot in the inset of Figure 5b the evolutions of $I_{\text{PL}}$ in function of the Si excess for the 50-nm-thick films. The $I_{\text{PL}}$ optimum is reached for about 14 at.%, before decreasing for higher Si contents. In parallel, we observe a gradual and systematic decrease of the lifetime of Er emission, from nearly 1.8 ms to about 1 ms (not shown). This reflects the creation of new non-radiative decay channels [22], which should attenuate the Er PL. For Si excess lower than 14 at.%, such an attenuation is somehow dominated by the increase of excitation of Er$^3^+$ ions through more sensitzers. Beyond 14 at.%, the new non-radiative decay channels start to dominate, leading to the observed decline of Er PL [22]. The Er PL peak intensity is ten times that of the similar thin film containing 7.5 at.% excess Si, and five times that observed for optimized thick samples containing 7.5 at. % excess Si (see corresponding symbols at the left part of Figure 5). Such an optimisation of the Si excess for 1-μm-thick samples was made earlier [15]. The optimum Si excess in these 50-nm-thick films is almost twice the excess incorporated in the best thin layers studied so far by our team [3]. This offers the double advantage of minimizing the limiting factors present in thin films, and favoring the transport of electrically injected carriers. In addition, the proportion of Er ions
coupled to sensitizers is likely to be significantly improved, allowing one to expect a fraction of inverted Er much higher than the reported 20% [3].

Conclusions

In summary, the influence of layer thickness on the photoluminescence of Er ions has been investigated for SRSO:Er layers. It was shown that thickness-related effects decrease the PL for thin films by a factor of 5. These effects are mainly due to three origins: (1) high stress prevailing in thin films that inhibits the formation of Si nanoclusters, (2) changes in LDOS, and (3) changes in the pumping rates. To minimize the thickness-related limitations in thin films, the amount of Si excess was gradually increased until reaching an Er PL intensity one order of magnitude higher than that recorded earlier for similar thin samples. Such a route appears very promising for the improvement of electrically driven high-performance Si-based light sources.

Figure 5 The calculated intensity I_{cal} is compared to I_{PL} and evolutions of I_{PL} (a) Evolution of the experimental Er PL intensity at 1.54 μm, I_{PL} (circles), and calculated I_{cal} (squares) due to LDOS and interference effects (see text), as a function of film thickness. For the sake of comparison, both intensities are normalized to the highest values at 1,400 nm. (b) Variation of I_{PL} for 7.5 at.% of Si excess (circles) and for 50-nm-thick films with a varying Si excess (gray-scale squares). Inset: I_{PL} in function of Si excess for thin samples of about 50 nm.

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References

1. N Daldosso, L Pavesi, Nanosilicon photonics. Laser & Photonics Reviews. 3, 508–534 (2010)
2. AJ Kenyon, PF Twyoga, M Federighi, C Gitt, Optical properties of PECVD erbium-doped silicon-rich silica: evidence for energy transfer between silicon microclusters and erbium ions. J Phys: Condens Matter. 6, L319 (1994). doi:10.1088/0953-8984/6/21/007
3. O Jambois, F Gourbilleau, AJ Kenyon, J Montserrat, RR Rizk, B Garido, Towards population inversion of electrically pumped Er ions sensitized by Si nanoclusters. Opt Exp. 18, 2230 (2010). doi:10.1364/OE.18.02230
4. N Daldosso, D Navarro-Imizos, M Melchioni, C Garcia, P Pellegreni, B Garido, C Sada, G Battaglin, F Gourbilleau, R Rizk, L Pavesi, Er-coupled Si nanocluster waveguide. IEEE J Sel Top Quant Electron. 12, 1607 (2006)
5. CA Barrios, M Lippon, Electrically driven silicon resonant light emitting device based on slot-waveguide. Opt Exp. 13, 10092 (2005). doi:10.1364/OE.13.010092
6. YC Fang, WQ Li, LJ Qi, LY Li, YY Zhao, ZJ Zhang, ML Lu, Photoluminescence from SiO2 thin films: effects of film thickness and annealing temperature. Nanotechnology. 15, 494 (2004). doi:10.1088/0957-4484/15/5/016
7. J Ahmad, MP Temple, A Kallis, M Wojdak, CJ Oton, D Barber, H Saleh, AJ Kenyon, WH Loh, Silicon nanocluster-sensitized emission from erbium: The
role of stress in the formation of silicon nanoclusters. J Appl Phys. 104, 123108 (2008). doi:10.1063/1.3050324
8. M Zacharias, P Streitenberger, Crystallization of amorphous superlattices in the limit of ultrathin films with oxide interfaces. Phys Rev B. 62, 8391 (2000). doi:10.1103/PhysRevB.62.8391
9. R Ferre, B Garrido, P Pellegrino, M Perálvarez, C García, JA Moreno, J Carreras, JR Morante, Optical-geometrical effects on the photoluminescence spectra of Si nanocrystals embedded in SiO₂. J Appl Phys. 98, 084319 (2005). doi:10.1063/1.2115100
10. J Kalkman, H Genien, L Kupers, A Polman, Excitation of surface plasmons at a SiO₂/Ag interface by silicon quantum dots: Experiment and theory. Phys Rev B. 73, 075317 (2006)
11. P Horak, WH Loh, AJ Kenyon, Modification of the Er³⁺ radiative lifetime from proximity to silicon nanoclusters in silicon-rich silicon oxide. Opt Exp. 17, 1906 (2009)
12. S Cueff, C Labbé, J Cardin, JL Doualan, L Khomenkova, K Hijazi, O Jambois, B Garrido, R Rizk, Efficient energy transfer from Si-nanoclusters to Er ions in silica induced by substrate heating during deposition. J Appl Phys. 108, 064302 (2010). doi:10.1063/1.3481375
13. PG Pai, SS Chao, Y Takagi, G Lucovoy, Infrared spectroscopic study of SiO₂ films produced by plasma enhanced chemical vapor deposition. J Vac Sci Technol. A4, 689 (1986)
14. O Savchyn, FR Ruhege, PG Kik, RM Todi, KR Coffey, H Nukala, H Heinrich, Luminescence-center-mediated excitation as the dominant Er sensitization mechanism in Er-doped silicon-rich SO₂ films. Phys Rev B. 76, 195419 (2007)
15. K Hijazi, R Rizk, J Cardin, L Khomenkova, F Goutbilleau, Towards an optimum coupling between Er ions and Si-based sensitizers for integrated active photonics. J Appl Phys. 106, 024311 (2009). doi:10.1063/1.3177243
16. GG Stoney, The tension of metallic films deposited by electrolysis. Proc R Soc London Ser A. 82, 172 (1909). doi:10.1098/rspa.1909.0021
17. A La Magna, G Nicotra, C Bongiomo, C Spinella, MG Grimaldi, E Rimini, L Carista, S Coffa, Role of the internal strain on the incomplete Si/SiO₂ phase separation in substoichiometric silicon oxide films. Appl Phys Lett. 90, 183101 (2007). doi:10.1063/1.2734398
18. HZ Massoud, HM Przewlocki, Effects of stress annealing in nitrogen on the index of refraction of silicon dioxide layers in metal-oxide-semiconductor devices. J Appl Phys. 92, 2202 (2002). doi:10.1063/1.1489500
19. S Cueff, C Labbé, B Dierre, J Cardin, L Khomenkova, F Fabbri, T Sekiguchi, R Rizk, Cathodoluminescence and photoluminescence comparative study of Er-doped Si-rich silicon oxide. J Nanophoton. 5, 051504 (2011). doi:10.1117/1.3540071
20. S Cueff, Labbé, R Rizk, Impact of the annealing temperature on the optical performances of Er-doped Si-rich silica systems. IOP Conf Ser: Mater Sci Eng. 6, 012021 (2009)
21. S Cueff, C Labbé, B Dierre, F Fabbri, T Sekiguchi, X Portier, R Rizk, Investigation of emitting centers in SiO₂ co-doped with silicon nanoclusters and Er³⁺ ions by cathodoluminescence technique. J Appl Phys. 108, 113504 (2010). doi:10.1063/1.3517091
22. G Franzè, E Pecora, F Priolo, F Lacina, Role of the Si excess on the excitation of Er doped SiO₂. Appl Phys Lett. 90, 183102 (2007). doi:10.1063/1.2734050

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