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Effects of the thickness on the properties of erbium-doped silicon-rich silicon oxide thin films

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The present study examines the influence of the layer thickness on the emission of Er ions coupled to Si nanoclusters within a silica matrix obtained by magnetron co-sputtering at two typical temperatures (ambient and 500 °C). Such an investigation is essential to optimise the material for specific applications, inasmuch as thin layers of tens of nm are requested for electrically-excited devices, while much thicker films ($\geq 1 \mu\text{m}$) are necessary for optically-excited waveguides, lasers, etc. The Er PL was detected from as-deposited samples with significant intensity for that grown at 500 °C. This PL improves with annealing and also with the layer thickness, up to a factor 4 when the thickness is increased from few tens to more than 1.3 μm .

The origin of this behaviour seems to lie in some limiting factors related to the film thinness, such as barriers for nucleation and growth of sensitizers (Si-ncs), stresses affecting the onset of phase separation and then the formation of Si-ncs. To favour the growth of Si-ncs in films as thin as tens of nm, the increase of the amount of Si excess was found to be necessary to enhance the Er PL through an increase of the density of Si-ncs and, therefore, the coupling with Er ions. Such an enrichment with Si offers an additional advantage of favouring the injection and transport of carriers by electrical excitation.

1 Introduction A great interest is paid since fifteen years to Er-doped silicon-rich silicon oxide (SRSO:Er) as a promising material for integrated photonics devices, such as planar waveguide amplifier, laser or light sources [1]. An intense effort is, indeed, devoted to two categories: (i) active devices to be used as low cost, compact and broad band planar waveguide amplifier in the standard wavelength of 1.5 μm for high rate optical communication [2], and (ii) Si-based sources for optical interconnections assumed to overcome the drawbacks and limits of the multi-level metallization schemes [3]. The basic and main advantage of SRSO:Er material is to benefit from the high and broad-band absorption of Si nanoclusters (Si-nc) to excite indirectly the Er ions [4-8]. The Er-Si-nc interaction was found to be highly distance-dependent with a critical spac-

ing as low as 0.5 nm [9,10] that is assumed to be responsible of the small fraction of Er^{3+} ions coupled to Si-nc sensitizers [11,12]. Recently, this fraction has been significantly improved by our group to about 22% [13], implying the necessity of further efforts to reach and exceed the 50% of inversion required for transparency. However, the nano-engineering of the composition needed to optimise the material was found to depend on the layer thickness. This thickness-dependence must be, therefore, taken into account when we consider one application or another: layers thicker than 1 μm for planar amplifier [14] or thinner than 100 nm for an electrically-driven Si light emitting devices (LED) [15,16]. Such thin layers are also considered for slot waveguide configuration [17]. In this connection, one should also mention that earlier studies reported the thick-

ness dependence in terms of nucleation barrier for Si nanoclusters [18] or stress-induced promotion of Si-nc formation [19].

This study aims at examining the influence of the layer thickness on the composition, microstructure and optical properties of SRSO:Er thin films deposited by magnetron co-sputtering. The thickness effects were investigated by photoluminescence for two typical temperatures of deposition (ambient and the optimum value of 500 °C) and post-deposition annealing (600 and 900 °C) temperatures. The results demonstrate a clear thickness-dependence of the formation of Si-nc sensitizers, which is favoured when the thickness exceeds a threshold value. For thin films requested for electrically excited devices, the amount of Si excess should be substantially increased to favour the formation of Si-nc.

2 Experimental details The SRSO:Er layers used in this study were deposited onto a p-type, 250- μm thick silicon wafer, by the magnetron co-sputtering of three confocal cathodes (SiO_2 , Si and Er_2O_3) under a plasma of pure Argon at a pressure of 2 mTorr. Two series were deposited at Room Temperature (RT) and 500 °C. The duration of the depositions was varied between 20 mn and 10h, while the power densities applied on the three confocals targets $P_{\text{SiO}_2} \approx 8.88 \text{ W/cm}^2$, $P_{\text{Si}} \approx 1.63 \text{ W/cm}^2$, $P_{\text{Er}_2\text{O}_3} \approx 0.44 \text{ W/cm}^2$ were kept constant. The Er content was measured by Time-of-Flight Secondary Ion Mass Spectroscopy (TOF-SIMS) and was found constant at about $3 \times 10^{20} \text{ at.cm}^{-3}$ for all deposition durations. The Si excess was measured by X-ray Photoelectron Spectroscopy (XPS) that allows the measurements of the ratio $x = [\text{O}]/[\text{Si}]$, representing the stoichiometry parameter for SiO_x . It was found that $x = 1.555 \pm 0.004$ for RT-deposited samples and $x = 1.616 \pm 0.009$ for 500 °C-deposited samples. The deposition duration was found to not influence significantly neither the stoichiometry of the deposited films nor the Er content. Fourier Transform Infrared (FTIR) spectroscopy was used to investigate structural parameters following an approach detailed elsewhere [14]. The thickness was measured using spectroscopic ellipsometry (SE) for thin films and by m-lines techniques for films exceeding 1 μm in thickness. The photoluminescence spectra were recorded in the visible (550-850 nm) and infrared (around 1.5 μm) regions using the non-resonant 476 nm excitation wavelength from an Ar^+ laser, in order to ensure that Er ions are only excited through the Si-nc. The spot diameter of the laser beam was determined by a “moving knife-edge” method and was found to be around 2 mm. A 1-m single grating monochromator and a liquid-nitrogen-cooled Germanium detector were used to collect the Er PL, while the visible emission was collected with a photomultiplier tube. The spectra were recorded by using the standard lock-in technique referenced with a chopping frequency of 9 Hz. Time-resolved measurements were obtained by the 435 nm excitation wavelength of a pulsed OPO. The pulse duration was $\sim 5 \text{ ns}$ and the spot size was estimated to be about 0.8 mm. The

PL signal of the time-resolved measurements was collected by an InGaAs detector.

3 Results

3.1 Structural and compositional properties

The structural changes have been deduced from the evolution of FTIR spectra. Figure 1 shows typical evolution of the spectra with the thickness for the as-deposited at 500°C recorded under Brewster incidence, after normalisation with respect to the TO_3 peak. Two main information are provided by these spectra: (i) the decrease of LO_3 peak ($\sim 1250 \text{ cm}^{-1}$) with the thickness reflecting a gradual reduction of the number of Si-O links as well as a decrease of the atomic disorder, (ii) the shift of the TO_3 peak towards that of stoichiometric SiO_2 , indicating a progressive phase separation between SiO_2 and Si nanoclusters.

Indeed, the shift of the TO_3 peak position with respect to that of stoichiometric SiO_2 , enables a rough estimate of the excess of Si atoms bonded to oxygen within the SiO_x matrix, following an approach detailed elsewhere [20-22]. The SiO_2 layer considered in this study is that obtained by the sputtering of pure and stoichiometric silica target. This allows including as a background the sputtering-induced disorder which may shift the TO_3 peak with respect to the stoichiometric silica and then leads to an ‘artificial’ Si excess. We have, therefore, adopted for each deposition conditions (Td, duration) a reference SiO_2 sample doped with Er and grown in the same conditions.

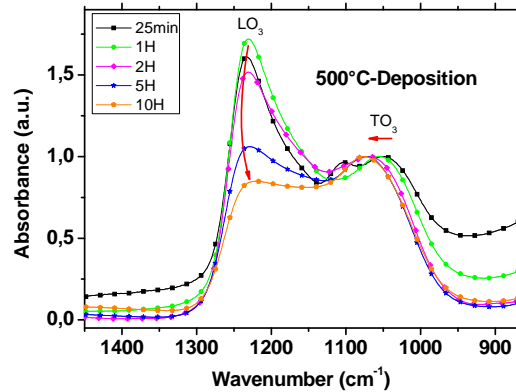


Figure 1 FTIR spectra recorded at Brewster angle.

Such a reference sample is, therefore, *considered as free from silicon excess* and its TO_3 peak is then compared to its counterpart SRSO:Er sample. The evolution of the non agglomerated Si excess obtained by FTIR in function of the thickness is compared to that of the Si excess determined by XPS. As can be seen in Table 1, the values of stoichiometry obtained by XPS values are higher than those obtained by FTIR all along the thickness range. This is well explained by the fact that XPS detect all the Si excess, whereas FTIR is only sensitive to Si atoms bonded to oxygen, i.e. Si being non agglomerated.

Table 1 Samples characteristics and composition.

RT-deposition			
Deposition duration	Thickness (nm)	SiO _x (XPS)	SiO _y (FTIR)
25 min	69	1.559	1.670
1h	165	-	1.641
2h	365	-	1.689
5h	918	-	1.757
10h	1763	1.551	1.797
500 °C deposition			
Deposition duration	Thickness (nm)	SiO _x (XPS)	SiO _y (FTIR)
25 min	54	1.613	1.760
1h	149	1.613	1.737
2h	338	-	1.811
5h	826	1.622	1.902
10h	1391	-	1.949

Therefore, those two methods are complementary and their comparison allows the estimation of the fraction of clustered Si. As for the as-deposited samples the phase separation between Si and SiO₂ is incomplete, the following relation prevails:

$$SiO_x \rightarrow \frac{x}{y} SiO_y + \left(\frac{y-x}{y}\right) Si \quad (1)$$

with x = stoichiometry detected by XPS, and y = stoichiometry detected by FTIR $1 < x, y < 2$ and $x > y$.

This relation allows the estimation of the fraction of clustered Si. $\%Si_{agglomerated} = ((y-x)/y)/(1+x)$. Figure 2 displays the evolution of this $\%Si_{agglomerated}$ with the thickness for the two samples deposited at RT and 500 °C. It appears clearly that, the fraction of clustered Si is favoured by either or both thickness and growth temperature.

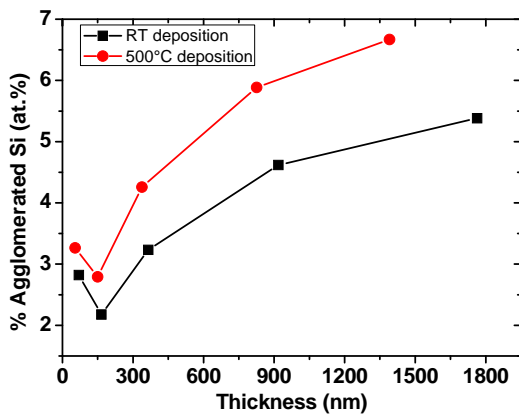


Figure 2 % Agglomerated Si according to the thickness.

3.2 Photoluminescence properties

3.2.1 Effects of annealing

Figure 3 shows a typical evolution of the PL spectra in both visible and IR regions for SRSO:Er samples deposited at RT during 10 h and then annealed at 600 and 900 °C.

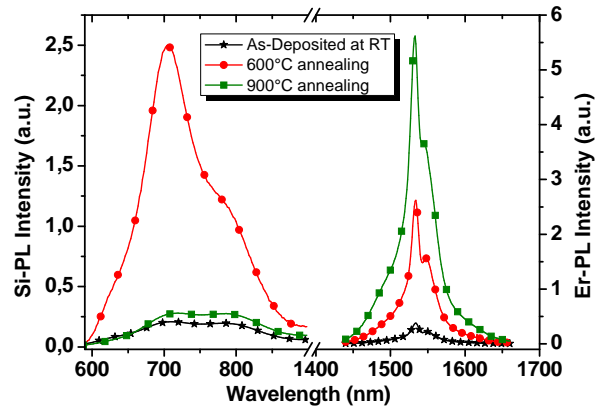


Figure 3 PL Spectra of the visible and IR range.

The post-deposition treatment provides an improvement of the Er PL which scales with the annealing temperature. On the contrary, the visible emission decreases when the annealing temperature is raised to 900 °C, hence indicating an increasing sensitizing role of Si-nc. A similar behavior was observed for all samples. Annealing at higher temperature is detrimental for those compositions of SRSO:Er [23].

3.2.2 Comparison RT/500 °C for thin and thick layers

Figure 4 compares the Er PL spectra recorded on typical thin and thick layers annealed at 900 °C after being deposited at RT and 500 °C. For the sake of comparison, all spectra are normalized to the thickness.

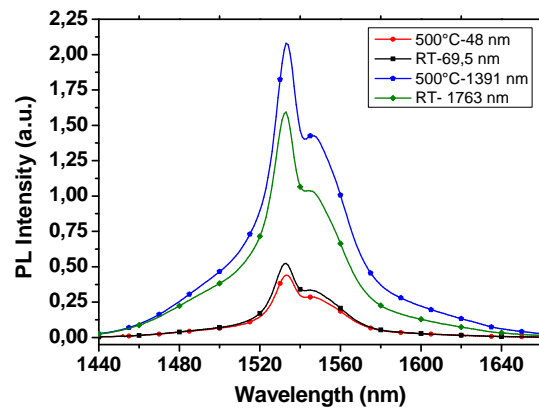


Figure 4 PL spectra of the first excited state of erbium ion, normalized to the thickness.

It appears that, whatever is the deposition temperature, the thick samples are approximately 4 times more emitting than the thin samples, after annealing at 900 °C. We remind the reader that this annealing is usually used for applications relating to optically excited thick layers or electrically excited thin layers [14, 16, 24]. To shed some light on the origin of this difference between thin and thick layers, we performed a more careful study of the effects of the thickness for samples processed with optimized conditions for maximum Er PL (500 °C-deposition, 900 °C annealing). Figure 5 displays the normalized PL intensities of samples with thickness ranging from 48 nm to ~1.4 μm according to the photon flux.

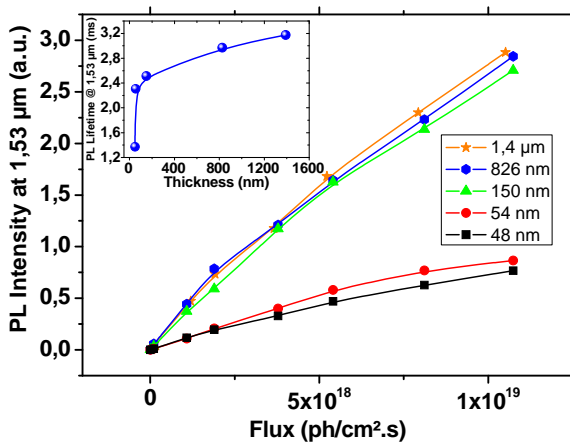


Figure 5 Normalised PL Intensity at 1.53 μm wavelength versus photon flux for 500 °C deposition annealed 900°C. Inset: Corresponding lifetime values.

We can see that, all along the photon flux, the PL intensity for the thin films is significantly lower than that for the thicker ones. A gap even exists when the thickness is increased from about 50 nm to 150 nm, increasing the PL intensity by a factor of 4. The PL remains unchanged when the thickness is further increased from 150 nm to about 1.4 μm. An abrupt change was also observed for the evolution of the lifetime, displayed in the inset, showing a steep increase from 1.3 ms to more than 2.6 ms when the thickness reaches 150 nm. Such a behaviour of the lifetime towards the thickness, for an unchanged amount of Si excess and Er content can be explained by the evolution of the Local Density of Optical States (LDOS) which increases with the proximity of the substrate, giving rise to a concomitant reduction of the lifetime [25]. The lifetime improves more smoothly for thicker samples, reaching a value of 3.2 ms at 1.4 μm.

4 Discussion The data reported in Table 1 deserve some comments. First, the quasi linear evolution of the thickness with the deposition duration is largely expected, as being merely due to the constancy of the growth rate. This growth rate appears however slightly lower for the deposition at 500 °C, due to some increasing interac-

tions/reactions between the deposited species, resulting in the formation of volatile elements such as SiO for $T_d \geq 300$ °C [26-28]. Such processes could be, therefore, responsible of the small inflexion of both growth rate and amount of Si excess (Table 1), for the sample grown at 500 °C when compared to that deposited at RT. Apart from this small difference of about 1 at %, the total Si excess determined by XPS appears unchanged with the duration for either RT or 500 °C deposition. By comparison, the amount of Si excess determined by FTIR is significantly lower for each temperature deposition and it shows, additionally, a systematic decrease with the deposition duration. We have already mentioned that the FTIR approach is unable to detect the Si atoms agglomerating in the form of Si-ncs. The increasing discrepancy between the XPS and FTIR values can be easily explained by the increasing formation of Si-nc when the duration of the deposition is prolonged. This effect is more pronounced for the deposition at 500 °C, with the same evolution than a RT deposition, as illustrated by the variation of the fraction of pure Si within Si-ncs, in function of the thickness (Fig. 2). It is clear that the increase of the deposition temperature from RT to 500 °C is expected to favor the formation of Si-nc, through the increasing surface mobility of the sticking elements. For a given thermal budget, the formation of Si-nc is also favored by the thickness increase. In this regards, two corroborating origins have been demonstrated earlier for the thickness dependence of Si-nc formation: (i) the existence of a nucleation barrier for Si-nc in function of the separation distance from the substrate, i.e. the thickness [18,29], (ii) the stress-induced effect which affects the phase separation and then the formation of Si-nc. [19]

Concerning the PL properties, consistent results were obtained, as shown by the typical spectra of Fig. 3 for the thicker sample deposited at RT. These results allow one to infer that:

- the detection of PL from the as-deposited is indicative of the formation of Si-nc, even at RT, compatible with the ~5% of pure Si estimated for this sample (Fig. 2). To note that higher emission was detected from the counterpart layer grown at 500 °C (not shown)

- the Er PL is improved with annealing up to the optimum temperature of 900 °C, whereas the visible emission at about 750 nm, usually assigned to Si-nc, collapses after increasing the annealing temperature from 600 to 900 °C. This indicates that, in this range of annealing, we are dealing with an increasing sensitizing role of Si-nc which are more coupled to Er ions and then less emitters in the visible. The effects of the thickness is also evidenced by the comparison of the spectra (normalized to the thickness) displayed in Fig. 4 for typical thin and thick sample annealed at the optimum 900 °C. It appears that, for both deposition temperatures, the Er emission from the thicker samples is nearly 4 times higher than the thinner ones. This supports the earlier mentioned suggestions concerning the favoring character of the thickness increase for the formation of Si-nc. The benefit of thickness increase is slightly accentuated when the deposition is performed at higher temperature (500 °C). From the evolution of the Er PL in-

tensity vs the photon flux, displayed in Fig. 5 for various thicknesses, one can also notice the existence of kind of threshold for the thickness to favorably allow the formation of Si-nc. For the case of Fig. 5 that concerns the samples deposited at 500 °C and then annealed at 900 °C, this thickness threshold is somewhere between 50 and 150 nm. Note also that the observed lifetime for thinnest film (inset Fig. 5) is twice lower than for thicker films, hence contributing to the half decrease for the Er-PL emission of the thin film. The remaining half part of the four-fold reduction of Er PL should be due to lower Si-nc's sensitization, as the result of lower formation of sensitizers. For the amount of Si excess present in our sample, the layer should be thicker than the threshold value to allow the formation of a substantial density of Si-nc sensitizers. However, since the thickness of the layer should not exceed some tens of nm for electrically-driven Si light emitting devices [16-17,24], the alternative solution is apparently lying in the variation of the Si excess. We have consequently varied the Si excess in thin films (~50nm) deposited at 500 °C and annealed at 900 °C, by increasing the power applied on Si cathode. The evolutions of their Er PL intensities vs the flux are shown in Fig. 6.

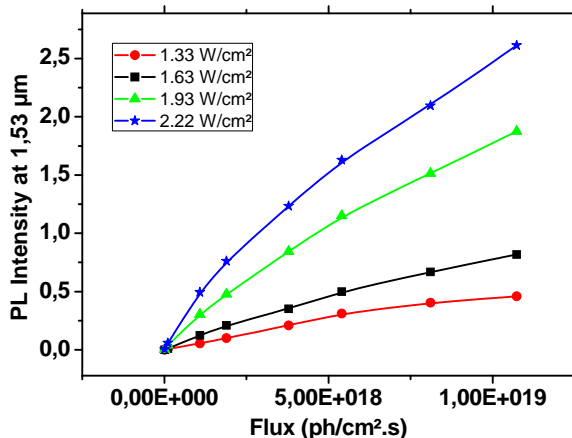


Figure 6 PL Intensity versus photon flux for different power applied on the Si cathode, deposited at 500 °C. The reference sample is the '1,63 W/cm²'.

It can be seen that the increase of the Si excess leads to a significant improvement of the Er PL to a level compared to that observed for thick samples. Besides, the Er lifetime is continuously decreasing from ~1.8 ms to ~1 ms. This indicates that more and more sensitizers are formed in the thin films. The key solution consists, therefore, in more enrichment with Si, which offers the double advantage of minimising the limiting factors related to the film thinness, and favouring the transport of the electrically injected carriers.

5 Conclusions In summary, the influence of the layer thickness on the formation of Si nanocluster sensitizers have been investigated for two typical deposition tempera-

tures, ambient and 500 °C. It was found that the formation of such Si-ncs is highly thickness dependent, requiring either layers thicker than a threshold value or more Si excess. The thinness-induced limitations may consist in some barrier for the nucleation and growth of Si-ncs, as well as stress-induced effects affecting the phase separation. For the films as thin as tens of nm required for the electrical excitation approach and applications, the alternative was found in more incorporation of Si excess which seems to minimize the thinness-related limiting factors.

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