

Photoluminescence and cathodoluminescence characteristics of SiO₂ and SRO films implanted with Si

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Silicon rich oxide films (SRO) were obtained by silicon implantation in silicon dioxide and PE – LPCVD techniques. Also, PECVD and LPCVD SRO films were implanted with silicon to get super-enriched SRO. Photo- and Cathodo-Luminescence (PL and CL) studies of these materials are presented. All the samples show similar bands related with an excess of silicon, but with different behavior in the intensity of the signal. PL results from silicon implanted LPCVD films show an emission stronger than the emission from the other films under study. The strongest PL intensity is related with an optimum annealing time and an optimum silicon excess, and consequently with an optimum size of the nanocrystals.

Keywords: Silicon rich oxide; Photoluminescence; Nanocrystals

Se obtienen películas de óxido rico en silicio (SRO) por implantación de silicio en dióxido de silicio y por técnicas PE-LPCVD. También las películas PECVD y LPCVD se implantan con silicio para obtener SRO superenriquecido. Se presentan estudios de Foto y Cátodoluminiscencia (PL y CL) de estos materiales. Todas las muestras muestran bandas similares relacionadas con un exceso de silicio, pero con diferente comportamiento en la intensidad de la señal. Los resultados de PL de las películas LPCVD implantadas con silicio muestran una emisión más intensa que la emisión de las otras películas bajo estudio. La mayor intensidad de luminiscencia está relacionada con un tiempo de aleación óptimo y con un exceso de silicio óptimo, y consecuentemente con tamaño óptimo de los nanocristales.

Palabras clave: Óxido rico en silicio; Fotoluminiscencia; Nanocristales

1. Introduction

Some researches have studied the emission on silicon rich oxide (SRO) obtained by LPCVD and PECVD [1, 2, 3]. Different bands have been observed and attributed to different origins: quantum dots [4, 5, 3], interaction between quantum dots and the surrounding oxide [6], and several types of defects [7, 8, 9]. However, no one has studied the emission from SRO obtained by CVD and implanted with Si. In this work, new experimental evidence of PL and CL of SRO additionally enriched with silicon implantation is presented. The characteristic emissions of silicon rich oxide obtained by PECVD (SRO-PECVD), silicon implanted SRO-PECVD (SISRO-PECVD) and silicon implanted SRO obtained by LPCVD (SISRO-LPCVD) are compared with the emission

characteristics of the silicon implanted thermal oxide (SITO) films.

These experimental results can provide new information to better understand the process of light emission in these materials. The different emissions can be related to the Si excess in the films and the thermal treatments. In addition, important results were found: the implantation doses required to obtain emission could be reduced, and the PL emission from silicon implanted LPCVD films is the most intense.

2. Experimental

SRO-LPCVD films with various silicon excesses [10, 11, 12] were obtained by varying the relation (R₀) between N₂O and SiH₄ fluxes as shown in Table 1, according to:

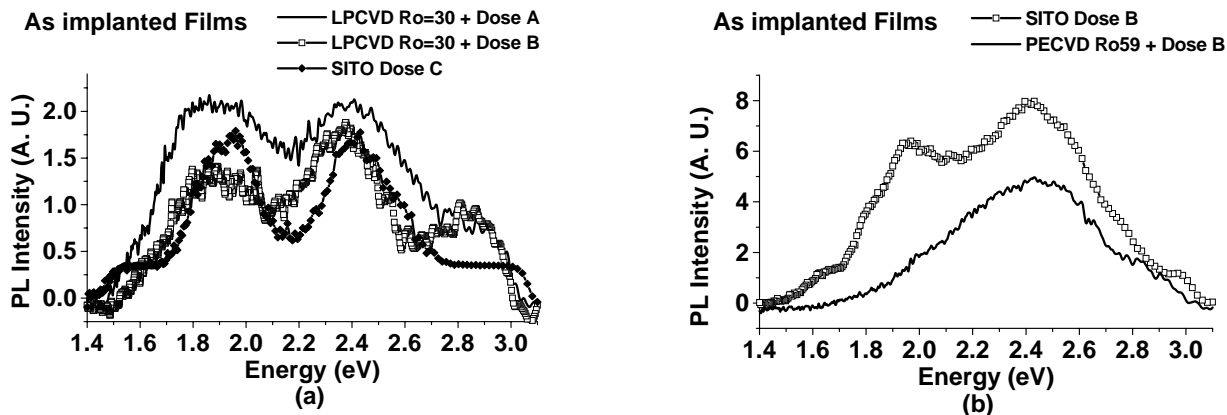


Figure 1. PL spectra of no annealed SRO films. a) Spectra from SITO with dose C and LPCVD films Ro = 30, b) Spectra from SITO dose B and SISRO-PECVD films.

$$R_0 = \frac{N_2 O}{SiH_4} \quad (1)$$

The Si-excess and its distribution were calculated from SRIM simulations [13, 14].

The thickness of the SRO films was 550 nm. The substrates are n-type silicon wafers (100), 2 inch diameter, and 3-5 Ω-cm of resistivity. Si ions were implanted into the SRO at 150 KeV with two doses: one dose (A) of $5 \times 10^{15}/\text{cm}^2$ and another (B) of $2 \times 10^{16}/\text{cm}^2$. After Si-implantation, the films were thermally treated at 1100 °C in N₂ atmosphere by 30, 60 and 180 min. PL and CL spectra were obtained after thermal treatments. PL spectra were obtained with a Perkin Elmer Luminescence spectrofluorometer model LS50B with excitation light of 250 nm (~5 eV). CL spectra were obtained with a Luminoscope equipment, Nuclide Corp. model ELM2-144 with 10 kV acceleration voltage and 0.5 mA current.

SRO-PECVD films with thickness of 550 nm were obtained in a PECVD system PlasmaLab 80, Oxford Instruments at 13.56 MHz frequency. Ro values of 5 and 59 were used. The deposition conditions were: temperature of 300 °C; total pressure of 0.2 Torr; total flux of 300 sccm and 30 W of power, equal to a power density of 0.07 W/cm². The substrates are p-type silicon wafers (100), 2 inch diameter, and resistivity of 1.0 Ω-cm. We studied two PECVD film groups: one without silicon implantation (SRO-PECVD films) and the other one, silicon implanted with the dose B (SISRO-PECVD films). All the films were thermally treated at 1100 °C in N₂ atmosphere by 30, 60 and 180 min. After each annealing PL and CL spectra were acquired.

SITO films were obtained from Si ionic implantation at 150 keV (projected range: 228.5 nm) into 550 nm thermal

oxide films grown by wet oxidation at 1100 °C on Si substrates. We used Si wafers 4 inches in diameter, n-type (100), 2 to 5 Ω-cm. We cut the wafers to form two groups: the first one was silicon implanted with dose B and the second group with a dose of 1×10^{17} ions/cm² (dose C). The implantation energy was chosen so that the maximum in the implanted ion distribution would be located approximately in the middle part of the oxide film. The Si-excess and its distribution were calculated from SRIM simulations [13, 14]. After implantation, the SITO samples were thermally treated at 1100 °C in N₂ atmosphere by 30, 60 and 180 min. Amorphous phase of Si (α-Si) and crystalline phase of Si (c-Si) were detected by spectroscopic ellipsometry (Table 2).

3. Results and comparison

3.1 PL in as implanted films

The Fig. 1 shows the PL spectra from as-implanted SISRO-LPCVD, SISRO-PECVD and SITO films. All bands decrease or disappear with annealing; then we can conclude that these bands are produced by defects created during the implantation process.

It is important to point out that the spectroscopic ellipsometry analysis detected a little quantity of α-Si. This α-Si disappear with the thermal annealing in the same way that the mentioned bands disappear.

It's known that E' centers are defects associated with the SiO_x matrix [15]. These are defects of type ≡Si•, where ≡ denotes bonding with three oxygen's atoms and • denotes an odd electron. The number of these defects decrease with thermal treatments above 600 °C in the same way that the PL at 1.9 eV decreases [2].

Some authors have found PL bands from 1.8 eV to 2.9 eV associated with diverse defects into the oxide matrix. In

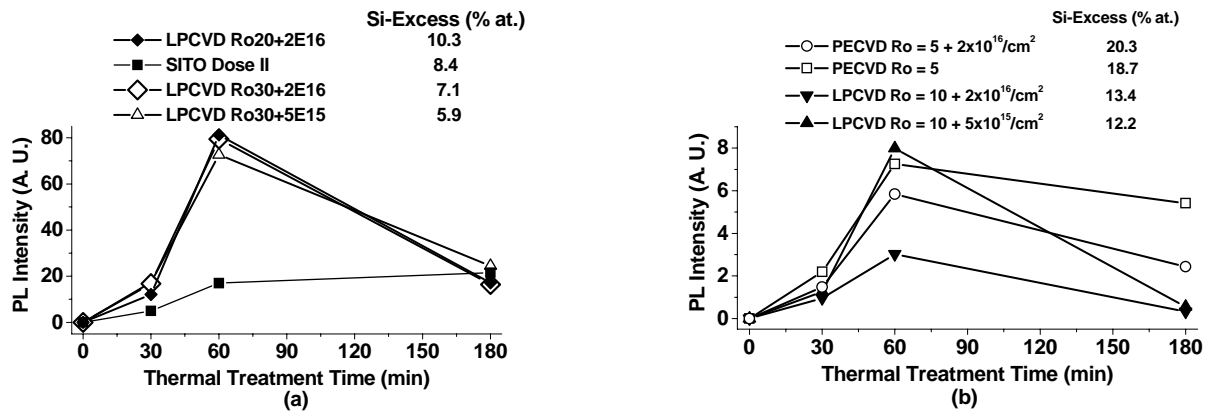


Figure 2. PL Intensity from the different films related to thermal treatment time. The PL intensity is greatest with 60 minutes of annealing.

addition to E' defects, the band at 2.4 eV can be related with the called NBOHC (Non Bonding Oxygen Hole Centers, ≡Si-O• [16], or B₂ centers: (≡Si-O)₃≡Si••(≡Si-O)₃≡Si [8, 9]. In the case of CVD films, this band could be related with defects in that oxygen and hydrogen take part.

3.2. PL in annealed films

After annealing, the PL spectra of PECVD films with Ro=59 with and without Si implantation, and SITO films with dose B show bands at 2.7 eV. Their amplitude decreases with the thermal treatments, and again we conclude that these bands are due to defects like B₂ centers, or neutral oxygen vacancies [17]. This defect is not only due to the damage made by the silicon implantation, but is related with the non stoichiometric composition of the film. This luminescent center is produced by the existence of Si-Si bonds in the oxide matrix and sometimes is described

like a ≡Si-Si≡ center.

The PL spectra of films with Si-excess greater than or equal to 5.9 % at., exhibit bands on around 1.7 eV (Tables 1).

The fig. 2 shows the curves of PL intensity vs. annealing time for the 1.7 eV PL band. PL band from CVD films have higher intensities with 60 minutes of thermal treatment. The highest intensities were obtained in films with Si-excess between 5.9 and 10.3 % at. (Fig. 2a). When the Si-excess exceeds this value, the PL intensity decreases (Fig. 2b). The LPCVD samples with Ro=20 and 30 showed the highest intensity.

Fig. 3 shows the PL intensity of the 1.7 eV PL band vs. Si-excess. With Si-excesses greater than 10.3 % at., the PL intensity decreases significantly. The PL bands from the annealed samples, shift to higher energies with the annealing treatment (Fig. 4), but the PL spectra from

Table 1. Si excess in SRO films

Type	Ro	Si Excess (% at)	+ Si dose implanted	Total Si Excess (% at)	Position of the Bands after annealing (eV)	
					PL	CL
LPCVD	30	5.5	A	5.9	1.7	1.7 & 2.7
			B	7.1	1.7	1.7 & 2.7
	20	8.7	A	9.1	1.7	1.7 & 2.7
			B	10.3	1.7	1.7 & 2.7
	10	11.8	A	12.2	1.7	1.7 & 2.7
			B	13.4	1.7	1.7 & 2.7
PECVD	59	0	-	0	2.7	2.7
			B	1.6	2.7	2.7
	5	18.7	-	18.7	1.7	1.7 & 2.7
			B	20.3	1.7	1.7 & 2.7
SITO			B	0.8	2.7	2.7
			B	8.4	1.7	1.7 & 2.7
			C			
Doses:	A: 5x10 ¹⁵ /cm ²		B: 2x10 ¹⁶ /cm ²		C: 1x10 ¹⁷ /cm ²	

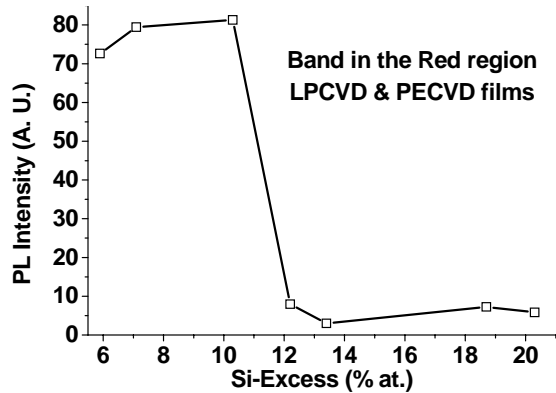


Figure 3. PL intensity vs. Si-excess.

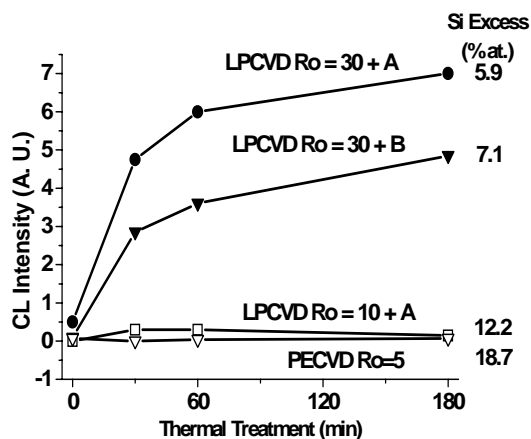


Figure 6. CL intensity.

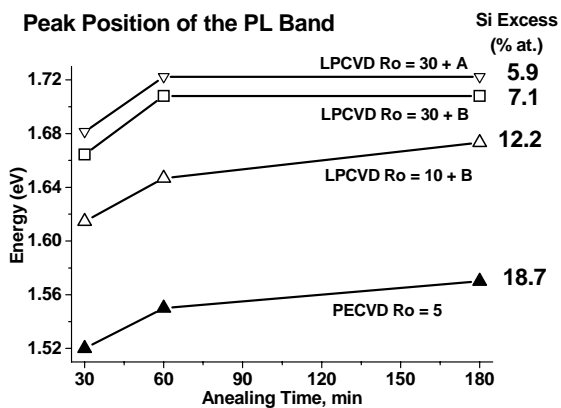


Figure 4. PL peak position of the red region band from annealed samples.

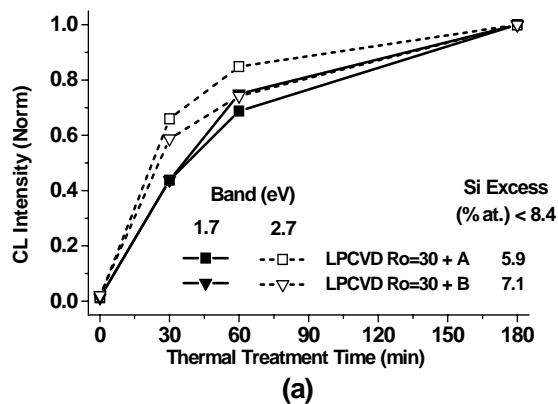


Figure 7. Normalized intensity of the bands A and C in the CL spectra.

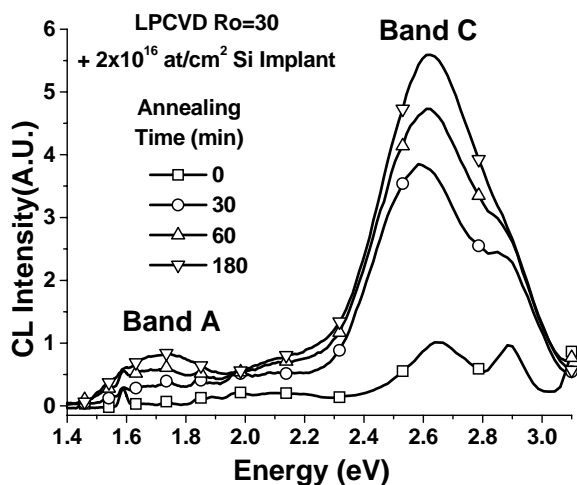


Figure 5. CL bands from SISRO-LPCVD films with Ro=30 + dose B.

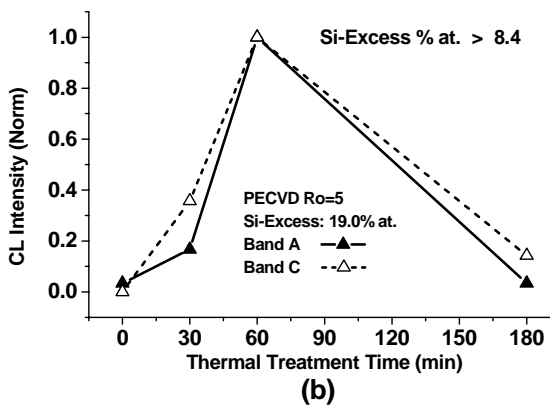


Table 2. α -Si and c-Si content in annealed Silicon Implanted Thermal Oxide (SITO) films

Si dose (at/cm ²)	Annealing Time (min)	α -Si (% vol.)	c-Si (% vol.)	PL Bands (eV)
B	0	0.03	-	1.9 & 2.7
	30	-	-	2.7
	60	-	-	2.7
	180	-	-	2.7
C	0	1.13	-	1.9 & 2.7
	30	-	2.63	1.7
	60	-	2.55	1.7
	180	-	2.23	1.7

samples with greater Si-excess show bands in lower energies.

3.2. CL Spectra

The CL spectra of all the films with Si excess greater than or equal to 5.9 % at. show bands at 1.7 eV and 2.7 eV (Table 1). Fig. 5 shows the CL bands from SISRO-LPCVD films with $R_o=30$ and dose B. The emission at 2.7 eV is visible with the naked eye. The CL intensity decrease when the Si-excess is greater than 5.9 % at. (Fig. 6).

Fig. 7a shows the behavior of the CL intensity peaks at 1.7 eV and 2.7 eV for samples with silicon excess ≤ 5.9 % at. The CL intensity is normalized for better comparison. The intensity grows in similar way for both bands. When the Si-excess is greater than 8.4 % at., the behavior of the CL bands is different (Fig. 7b); the intensity grows during the first 60 minutes of thermal treatment and then decreases. The energy position of the bands does not change with the thermal treatments.

4. Discussion

The bands at 1.9 and 2.4 eV in PL spectra from SITO and implanted LPCVD and PECVD films seem to be related with Si-implantation. They appear only in implanted films but they do not appear in non implanted PECVD films. Therefore, we can conclude that these bands are due to defects created during the silicon implantation. The behavior of SITO with dose B and PECVD films with $R_o=59$ (both with the lowest silicon excess), are similar.

In LPCVD films, the highest amplitude corresponds to films with high R_o although the intensity is higher when the Si dose implantation is higher. Maybe there is a critical Si-excess concentration or a critical nanocrystal size because, in general, these bands grow up with 60 minute of thermal treatment and then decrease with 180 minutes of annealing time. We found that it is not necessary a great Si dose implantation in LPCVD films to get a great intensity for the PL emission. The peak position of the band at around 1.7 eV from CVD films is also related with Si-excess. In high Si-excess films, the band tends to shift to smaller energies.

The PL bands in the films as implanted seem to be related with two types of defects: E' centers ($\equiv\text{Si}\cdot$) and oxygen vacancies ($\equiv\text{Si-Si}\equiv$). Both defects decrease in concentration with thermal annealing. It's possible that these defects become to silicon nanoclusters and even silicon nanocrystals with thermal annealing. The oxygen's vacancies are a kind of Si-Si bond and we can take it as a Si_2 cluster. When the suboxide silicon films have a great density of Si-Si bonds, it is possible the formation of Si_n agglomerates with $n>3$. The thermal treatments promote the silicon excess tend to agglomerate. The $\equiv\text{Si-Si}\equiv$ defects produce a band at 2.7 eV and the band at 1.7 eV are related with silicon nanocrystals. In this way, it is possible the coexistence of both kind of processes.

In general, all the PL spectra of annealed films are related with their Si-excess content. The PL spectra from films with Si-excess smaller than 5.9 % at., show PL bands at 2.7 eV. The PL spectra from films with higher Si-excess show bands at 1.7 eV. These bands rise only after thermal annealing, and can be related with Si precipitation. Several authors think that these bands, from 1.5 eV to 1.77 eV, are associated with quantum confinement [3, 5,], although some people think that the origin of the luminescence is in the interface of the nanocrystal and the oxide matrix [21, 22, 23, 24]

The PL excitation spectra of the films, shows a peak at 250 nm, corresponding to a silicon nanocrystals with average size of 0.85 nm [25, 26, 27] (at least with 0.5 nm in diameter). To radiate at 2.7 eV, the nanocrystal must have a diameter of around 1.5 nm, and to radiate at 1.7 eV, it must have

2.25 nm of diameter. The fig. 2 indicates that 60 minutes of annealing time is the very best time interval to have the greatest concentration of nanocrystals with enough size to radiate at 1.7 eV. When the annealing time is increased, the size of the

nanocrystal is greater that this necessary size and the PL intensity decreases.

Also, if the silicon excess is greater than 10.3 % at (Fig. 3), the PL intensity decreases significantly, because there is enough silicon and the thermal annealing makes them to grow up to a size such that they can not to radiate.

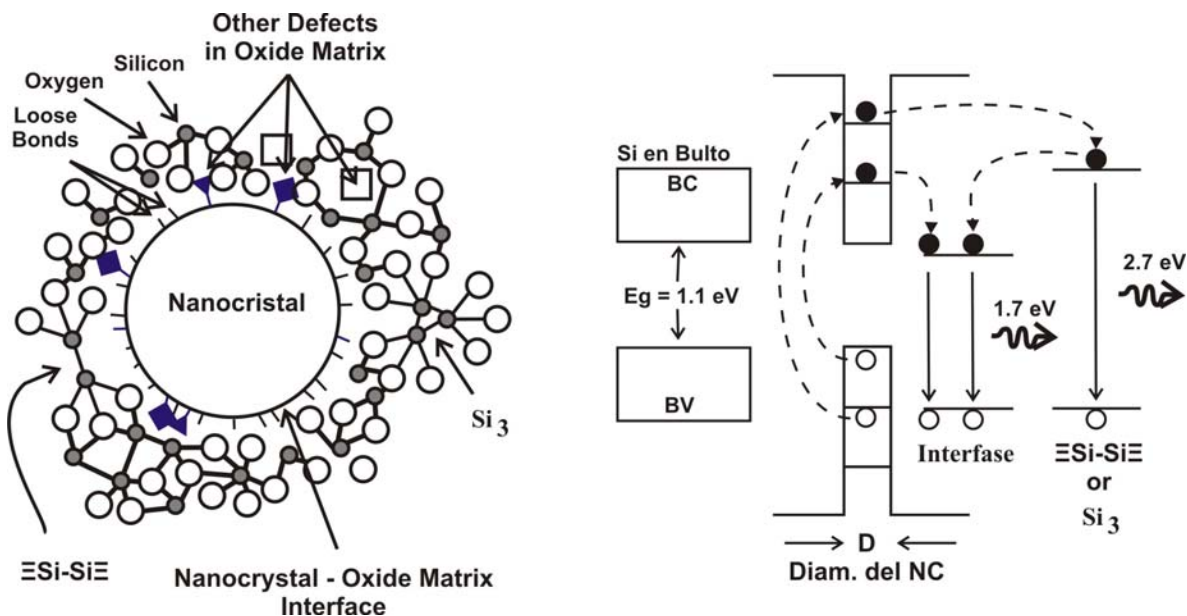


Figure 8. Model for the emission from Si-NC's. (a) The e-h generation is into the NC's. (b) The emission is due to recombination in at least two types of defects. The energy position of the luminescence depends of the energy levels into the NC's and the kind of interacting defect.

Finally, the fig. 4 indicates that greater silicon excesses lead to smaller energies for the emission, in agreement with quantum confinement theory.

On the other hand, CL emissions from PECVD and SITO with B dose (both with the lowest silicon excess content), shows bands at 2.7 eV. After the annealing the other films shows bands at 1.7 and 2.7 eV. The band at 1.7 eV is associated with nanocrystals [28] and the band at 2.7 eV with oxygen vacancies ($\equiv\text{Si-Si}\equiv$), Si_n clusters with $n \geq 3$ [29] and trivalent silicon. This last defect apparently produces an absorption band at 5.77 eV [30]. We found an absorption band at 5 eV and maybe our bands at 2.7 eV would be related with Si_3 defect.

With all the results we can propose a model to explain the PL and CL emissions (Fig. 8). The PL bands at 1.7 eV arise only in samples with silicon excess over 5.9 % at. and only after thermal treatments. Thus, we can conclude that the origin of these bands is related with silicon nanocrystals (Si-NC's). But if the bands at 1.7 eV are due only because of the silicon nanocrystals, they must change their energy position with the thermal treatments, because these treatments must change the size of the Si-NC's. Then we think the emissions are not due to pure quantum confinement effects.

We propose that the e-h pairs are generated into the Si-NC's, because we found an absorption band at 5 eV, and they recombine in different types of defects near the Si-NC's, maybe oxygen vacancies ($\equiv\text{Si-Si}\equiv$) and/or trivalent silicon for the 2.7 eV bands and recombination in the surface of the nanocrystals for 1.7 eV bands. Similar

excitation and deexcitation mechanisms have been found in Er implanted Si [31, 32]

When the nanocrystals have up to 1.5 nm, its size is enough to lead to the emission at 1.7 eV or 2.7 eV. If the nanocrystals continue growing, they could have a size such that the emissions at these energies are not possible.

When the size increases, it is stronger the effect in the luminescence process, but if they have enough size, the quantum confinement effects also disappear. The emission's amplitude is related with the density of nanocrystals with appropriate size to generate e-h pairs with energy larger than 1.7 or 2.7 eV.

We conclude that there are at least two different defects interacting with the Si-NC's. One of them produces the PL and CL bands at 1.7 eV and

another, produces the CL band at 2.7 eV. The band at 2.7 eV in the CL spectra arises because the electronic beam is more energetic than the light beam in PL experiments. The electrons can get higher levels into the Silicon nanocrystal. The PL band at 1.7 eV arises with lower energetic excitation.

For all these reasons, the CL bands at 1.7 and 2.7 eV have similar behavior, very probably with related origins.

5. Conclusions

There are bands related with defects created during silicon implantation. They disappear with the thermal treatments at high temperature.

There are another PL bands (at 1.7 eV) and their behavior is related with the silicon excess and the thermal treatments

applied to the samples. The PL intensity is greater for samples with silicon excess in the range between 5.9 and 10.3 % at. The amplitude is greater for SISRO-LPCVD samples with $R_o=30$. The PL amplitude was the highest when we applied thermal treatments for 60 minutes.

The peak position of PL bands at 1.7 eV does not change with silicon excess nor thermal treatments, only their amplitude changes.

CL spectra show bands at 1.7 and 2.7 eV. They grow in the same way, and then we conclude that they have similar origin.

A model is presented as consequence of the results. We postulate that the e-h pairs are generated into the Si-NC's, and the recombination (and thus the emission) is related with at least two different kinds of defects: the interface nanocrystal-oxide matrix and oxygen vacancies ($\equiv\text{Si-Si}\equiv$) or Si_n clusters with $n\geq 3$.

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