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# Comparative study between silicon-rich oxide films obtained by LPCVD and PECVD

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**Abstract**

A comparative study of compositional and optical properties of silicon-rich oxide (SRO) films deposited by low-pressure chemical vapor deposition (LPCVD) and plasma-enhanced chemical vapor deposition (PECVD) is presented. Infrared spectra revealed the presence of hydrogen bonded to silicon atoms in the SRO–PECVD films, whereas in SRO–LPCVD films the IR spectra looked like the stoichiometric thermal silicon oxide. Moreover, X-ray photoelectron spectroscopy (XPS) studies showed that the SRO–PECVD films contain a higher content of nitrogen than SRO–LPCVD films. In spite of differences, the SRO films obtained by both methods show a strong room-temperature photoluminescence (PL). However, the highest PL intensity was emitted by SRO films obtained by LPCVD.
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## 1. Introduction

It is an undeniable fact that silicon (Si) is the leading semiconductor in the microelectronic industry; however, due to the indirect band gap bulk silicon and the absence of linear electro-optic effects, which make it a poor light emitter, it has been considered unsuitable for optoelectronic applications. As a result of the progress in communication technology, the search for materials able to produce optoelectronic functions has increased in the last years. The discovery of light emission in porous silicon by Canham in 1990 [1] attracted a new effective way of obtaining light emission in Si-based materials. However, porous silicon suffers from poor mechanical and chemical stability. Therefore, more stable materials based on Si have been subjects of intense research in the last decade. Silicon nanocrystals (Si-ncs) embedded in $SiO_2$ matrix have attracted the main attention. Si-ncs are produced when silicon-rich oxide (SRO) films are subjected to thermal annealing. A great number of techniques are used in order to produce SRO films ($SiO_x$, $x<2$), such as ion implantation of Si in $SiO_2$ films [2], pulsed-laser deposition (PLD) [3], PECVD [4–6], LPCVD, thermal evaporation [7], and so on. SRO films produced by techniques based on CVD method have the advantage of being more stable as well as containing uniform Si excess. In this work, we show a comparative study of SRO films obtained by LPCVD and PECVD due to the SRO obtained by these methods, besides displaying the best optical properties, these techniques are simple and compatible with Si integration technology. We examined the differences of composition and optical properties obtained from SRO films as well as the effect of Si excess on the PL response.

## 2. Experiment

SRO films were deposited by LPCVD and PECVD techniques on n and p types, respectively, Si (1 0 0) wafers using $SiH_4$ and $N_2O$ as precursor gases. Si excess in the films was obtained by varying the $R_o = N_2O/SiH_4$ flow ratio. The SRO–LPCVD films were deposited at 720 °C

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with $R_o$ values from 10 to 30, whereas SRO–PECVD films were deposited at substrate temperature of 300 °C with $R_o$ values from 5.5 to 22. The $R_o$ value was selected according to the refraction index of the deposited SRO films to be in agreement with both techniques. The thickness of the films was around 100 nm. A Gaertner L117 ellipsometer was used to obtain the thickness and the refractive index of the films. After deposition, SRO–LPCVD films were annealed at 1100 °C and SRO–PECVD films annealed at 1250 °C, both for 60 min in $N_2$ atmosphere. Si excess in SRO films was obtained by PHI ESCA–5500 X-ray photoelectron spectrometer (XPS) using a monochromatic Al radiation source with energy 1486 eV. Depth composition profiles inside the SRO films were obtained measuring by XPS in the surface, then etching and measuring again. Infrared spectroscopy (BRUCKER Vector 22) was employed to study the composition of the SRO films. The PL at room temperature was obtained by using a Perkin-Elmer luminescence spectrometer model LS50B. The SRO films were excited using 250 nm UV radiation.

## 3. Results

### 3.1. Composition

SRO films were characterized by Si concentration ranging between 37 and 44 at%. Reported in Table 1 is the composition of each SRO film as well as a notation by using the $R_o$ value, like $SRO_{30}$. SRO films deposited by PECVD showed N concentration around 10 at%, whereas SRO films obtained by LPCVD had a smaller concentration, around 0.8 at%. Furthermore, direct information about compositional properties of SRO films was obtained by using FTIR measurements. Fig. 1a shows the absorbance spectra for SRO–PECVD films before and after annealing. All the films present a dominant absorption band related to Si–O–Si stretching vibration ($TO_3$) around 1062 $cm^{-1}$. The Si–O–Si rocking ($TO_1$) absorption band at 430 $cm^{-1}$ is also detected. The $TO_2$ vibration (Si–O–Si bending) was not observed in the SRO films as deposited, except for the $SRO_{22}$ film. Absorption bands around 870, 1600, and 3750 $cm^{-1}$ were present in the SRO films as deposited, related to Si–H bending, H–O–H and Si–OH stretching, respectively. After thermal annealing of the SRO–PECVD films, the bands at 1600 and 3750 $cm^{-1}$ disappeared. In $SRO_{5.5}$ and $SRO_{9.17}$, the intensity of the band at 870 $cm^{-1}$ related to Si–H vibration decreased, becoming a shoulder of the main $TO_3$ band, and the $TO_2$ band around 800 $cm^{-1}$ appeared. The $TO_3$ band shifted slightly to higher frequencies after thermal annealing, indicating a possible phase separation. In the absorbance spectra obtained for SRO–LPCVD films before and after thermal annealing only three bands related to Si–O–Si vibration appeared as shown in Fig. 1b. The differences between both spectra could be ascribed to the deposition temperature. In the IR spectra, the $TO_3$ band shifts slightly toward higher frequencies, and its width reduces as $R_o$ is increased due to an increment in the oxygen concentration. Another shift in the $TO_3$ band is obtained when SRO–LPCVD films are subjected to thermal annealing. We can attribute these changes to phase separation induced by thermal annealing.

Table 1
Composition (at%) of SRO films with different $R_o$ values, deposited by PECVD and LPCVD

| Technique | $R_o$ | Sample | Composition (at%) | | |
|---|---|---|---|---|---|
| | | | Si | O | N |
| PECVD | 5.50 | $SRO_{5.5}$ | 45.0 | 43.0 | 12.0 |
| | 9.17 | $SRO_{9.17}$ | 40.5 | 49.5 | 10.0 |
| | 22.00 | $SRO_{22}$ | 37.0 | 60.5 | 2.5 |
| LPCVD | 10.00 | $SRO_{10}$ | 44.5 | 55.5 | 0.0 |
| | 20.00 | $SRO_{20}$ | 38.4 | 60.8 | 0.8 |
| | 30.00 | $SRO_{30}$ | 37.3 | 62.0 | 0.7 |

The Si2p peaks obtained from XPS spectra of the SRO films were analyzed. Fig. 2a shows the spectra of $SRO_{9.17}$–PECVD, in which a nonsymmetrical peak can be observed. It presents evidence of different Si environments. Si oxidation states related to $Si^0$, $Si^{2+}$, and $Si^{4+}$, being the strongest contribution due to $SiO_2$ ($Si^{4+}$), were present. Similar Si2p peaks were obtained for the $SRO_{5.5}$–PECVD film. However, in SRO–LPCVD, the Si2p peak for $SRO_{20}$ and $SRO_{30}$ films is an almost symmetrical peak at 103.5 eV; the suboxide contribution was only given by $Si^{2+}$ as shown in Fig. 2b. In SRO–LPCVD, only the $SRO_{10}$ film showed a composition of $Si^0$, $Si^{2+}$, and $Si^{4+}$.

### 3.2. Photoluminescence (PL)

Fig. 3 shows the dependence of the PL peak energy and its intensity on the Si excess for SRO–LPCVD and PECVD films. SRO–PECVD films, with the lowest Si content, emitted a PL peak at 1.48 eV as shown in Fig. 3a. The energy of the PL peak was found to be the same when the Si excess was increased from 3.7 to 7.2 at%. However, a slight shift in the PL peak was detected when the Si content was higher. In spite of having SRO LPCVD and PECVD films with a similar Si concentration, different results were observed. The PL peak of the SRO–LPCVD films was found to be in a higher energy than the SRO–PECVD films. For SRO–LPCVD with the lowest Si content, the PL peak is observed at 1.69 eV. A redshift was obtained when the Si excess was increased from 4 to 5.1 at% opposite to the behavior of the SRO–PECVD films. Moreover, no redshift was detected when the Si content grew up to 11.2 at%. The dependence of the PL intensity on the Si excess is stronger in the SRO–LPCVD films than the SRO–PECVD films, as shown in Fig. 3b. Data demonstrate that a critical value exists for the Si excess where the maximum PL intensity is obtained. Both SRO–LPCVD

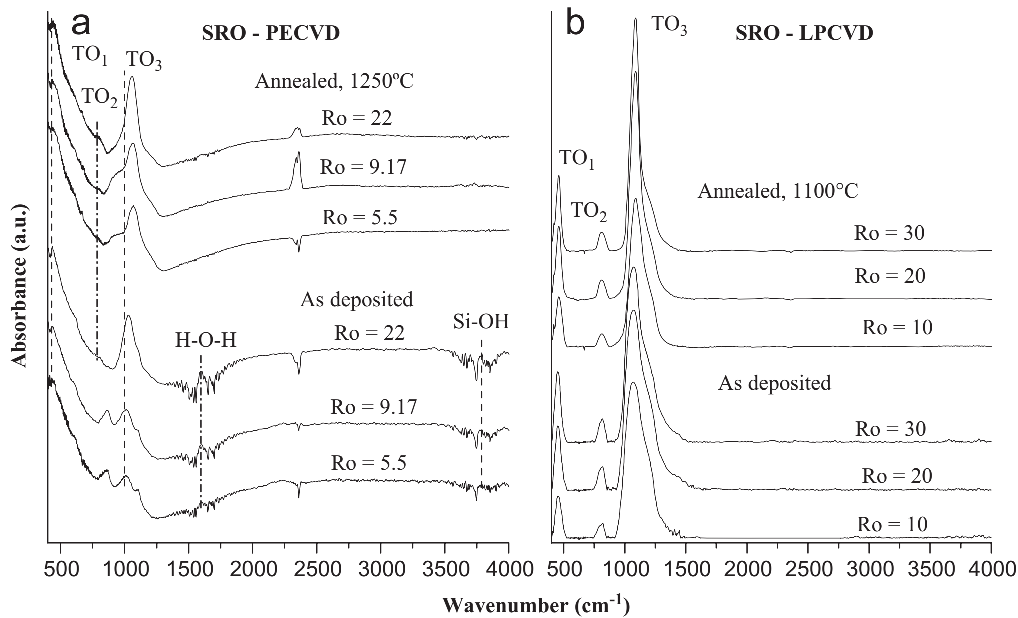


Fig. 1. FTIR absorbance spectra from (a) SRO–PECVD and (b) SRO–LPCVD films, before and after thermal annealing.

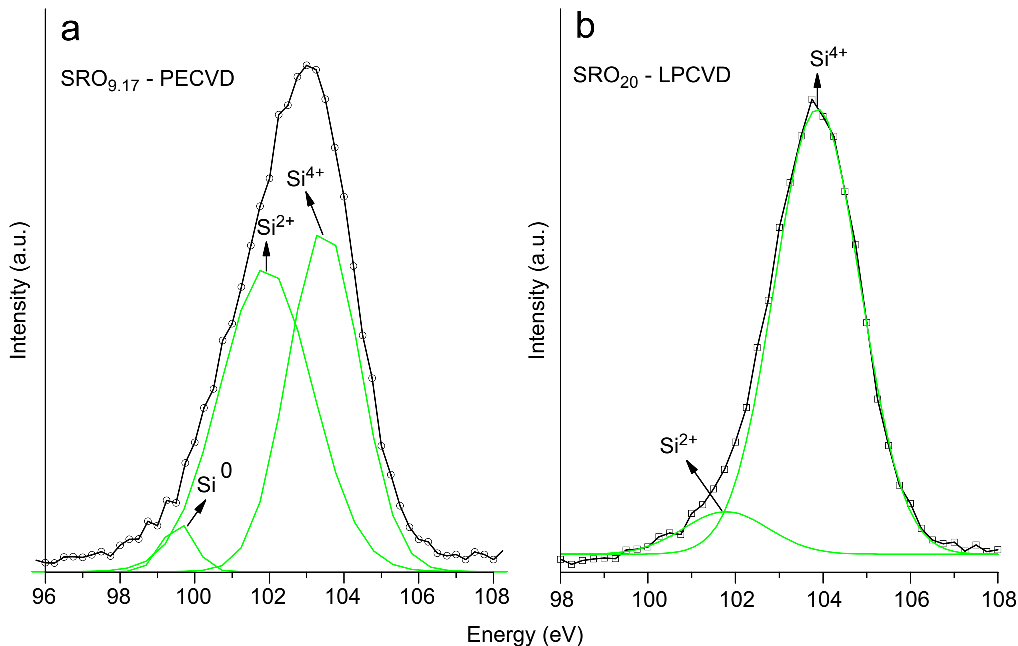


Fig. 2. XPS Si2p spectra for (a) SRO–PECVD and (b) SRO–LPCVD films. The Si2p peaks have been deconvoluted in the different silicon environments.

and SRO–PECVD films with extreme values in the Si excess showed relatively weak PL intensity. Maximum PL in SRO–PECVD films is obtained with 7.2 at% of Si excess, whereas SRO–LPCVD emits the strongest PL with 5.1 at% of Si excess. It is noticeable that the biggest emission is obtained with SRO–LPCVD. It has been reported [5,6] that the major problem in the optical properties of SRO films obtained by CVD is the incorporation of H. Then, H and N incorporation in SRO–PECVD films could be affecting the PL emission.

## 4. Discussion

SRO–PECVD films were characterized by the incorporation of H and N; in contrast, these impurities were not observed in the SRO–LPCVD films according to the IR and XPS studies. Then, the incorporation of H and N in SRO–PECVD films could be related to the low temperature of deposition.

The origin of the PL emission is still an object of debate; two models have been proposed. The first model relates the

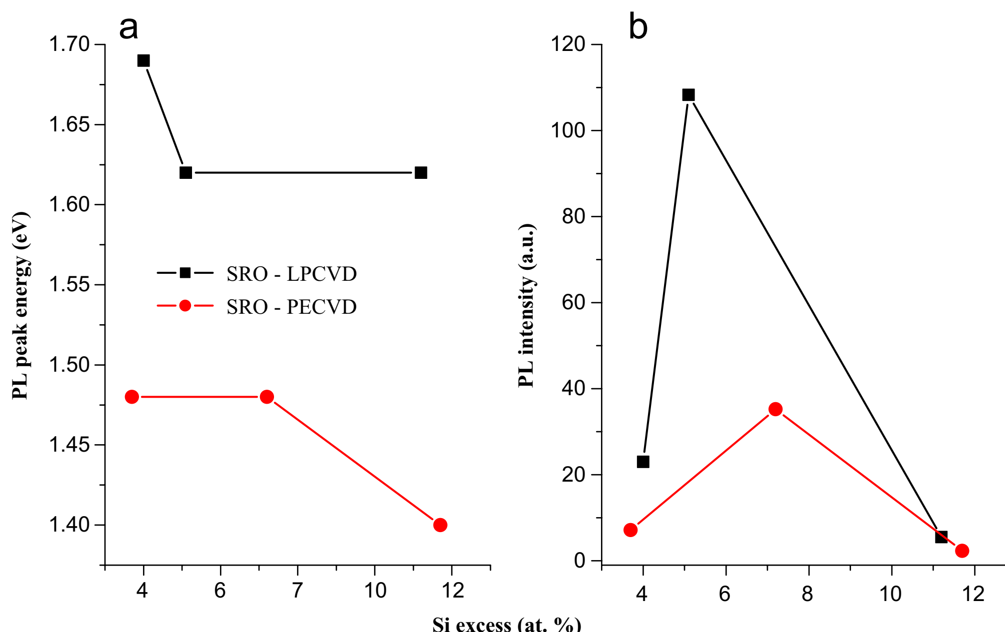


Fig. 3. Dependence of (a) energy and (b) intensity of PL peaks on the Si excess in SRO–PECVD and SRO–LPCVD films.

PL to quantum confinement effects (QCE) [3,6] in Si-ncs. The second model attributes the PL to defects in the matrix or the interface $SiO_2$/Si-nc [7,8]. Based on the analysis of the Si2p spectra, we studied the microstructure [2–4] of SRO films. Si2p spectra indicated a combination of different coordinations of Si in the SRO films. All the SRO–PECVD films are constituted by $Si^0$, $Si^{2+}$, and $Si^{4+}$, indicating the presence of Si–Si, Si–$Si_2O_2$ and $SiO_2$, phases, respectively. Si-ncs are then expected to appear in these films after thermal treatments. However, in SRO–LPCVD films with low Si content ($SRO_{20}$, $SRO_{30}$), only $Si^{2+}$ and $Si^{4+}$ were present. Just as in SRO–PECVD films, the $SRO_{10}$ film is composed of $Si^0$, $Si^{2+}$, and $Si^{4+}$. Because of this, we can assume that SRO–LPCVD films with the lowest Si content are composed by Si clusters.

SRO–PECVD films emitted a PL band in the region of 1.5 eV, which shifted slightly toward lower energies when the Si excess was increased. A stronger PL was observed in the SRO–LPCVD films; however, the energy of the PL peak was higher than that emitted by SRO–PECVD films. Besides, in films with low Si content, $Si^0$ contribution was not observed indicating that Si-ncs could not be present in these films. When the $Si^0$ contribution was present in the SRO film with highest Si concentration, the PL intensity decreased strongly, even lower than the PL intensity of $SRO_{30}$ film, and its PL peak stayed at the same energy rather than the SRO film containing 5.1 at% of Si content. The results obtained from SRO–PECVD films indicate that the PL could be due to a recombination of e–h pairs in Si-nc, whereas the PL in SRO–LPCVD films could be ascribed to defects surrounding Si clusters, where defects are acting as localized states. When the size of Si cluster is increased, the band gap and the energy between localized states and the ground state are reduced producing a shift in the PL energy.

## 5. Conclusions

The composition of SRO films deposited by PECVD and LPCVD methods were studied before and after thermal annealing by using FTIR and XPS techniques. Vibration bands related to Si–H, H–O–H, and Si–OH were observed in SRO–PECVD films before annealing, and they disappeared after thermal annealing. N was also present in these films. On the other hand, in SRO–LPCVD films, IR spectra absorption bands only appeared related to the vibration of Si–O–Si. Besides, the N content in these films was lower than SRO–PECVD films. We attribute this fact to the temperature of deposition. Si2p spectra showed that SRO–PECVD films are composed of $Si^0$, indicating the presence of Si-ncs, $Si^{2+}$ y $Si^{4+}$ ($SiO_2$), just as in the $SRO_{10}$–LPCVD films. In addition, PL emitted by these films was observed in the typical region in systems Si-nc/$SiO_2$. The PL was ascribed to QCE. Nevertheless, Si2p spectra form SRO–LPCVD films did not show the presence of $Si^0$, but Si cluster could be present in them. In spite of this, a stronger PL was observed. We ascribe the PL emission to defects, which are acting as localized states surrounding Si clusters. The greatest PL intensity was obtained with $SRO_{20}$–LPCVD film (5.1 at% Si excess) annealed at 1100 °C for 60 min.

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