Silicon nanocrystals into silicon dioxide: comparison between obtaining techniques

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Abstract

A comparative analysis (compositional and optical) was carried out on silicon rich oxide (SRO) films deposited by low pressure chemical vapor deposition (LPCVD) and plasma enhanced chemical vapor deposition (PECVD). The SRO films have been obtained at different flow ratio between precursor gasses (N_2O/SiH_4), to varying the silicon excess and then analyze its effect on the luminescent characteristics. X ray photoelectron spectroscopy and Fourier transform infrared spectroscopy spectra exhibit significant differences as in composition as in structure between both kind of films. In spite of differences, the SRO films show a strong room temperature photoluminescence. However, the strongest photoluminescence is emitted by SRO – LPCVD films. Results indicate that the mechanism of emission in SRO–PECVD films is associated to quantum confinement, whereas in SRO–LPCVD films, it can be related to defects surrounding silicon nanocrystals.

Keywords: Silicon Rich Oxide, XPS, FTIR, PL.

Introduction

The use of integrated optical sensors based in silicon technology requires the ensemble achievement of emitter/detector and optical transducer, avoiding the need of further alignment after fabrication. Although the detector and optical component integration has been demonstrated, the silicon based emitters has just begun.

Currently one of the most ambitious scientific and technologic goals is the development and realization of light emitters compatible to the CMOS technology. Materials containing silicon nanocrystals (Si-nc's) into a transparent dielectric matrix, such as silicon oxide and nitrate, have shown to be robust and efficient light emitters. The Si-nc's are obtained when the corresponding dielectric layers super enriched with silicon are subjected to thermal annealing.

Different techniques are used to obtain silicon rich oxide (SRO) films, being the most used: silicon implantation into thermal silicon oxide [1] and the chemical vapor deposition (CVD) [2-4]. Techniques based in CVD method allow obtaining thick SRO layers more stable as well as containing uniform silicon excess.

In this work, we present a comparative analysis carried out on SRO samples deposited by CVD techniques at low pressure (LPCVD) and plasma enhanced (PECVD). The SRO layers have been obtained at different flow ratios between N_2O and SiH_4 precursor gasses, to vary the silicon excess and analyze its effect on the luminescent characteristics. X ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) spectra exhibit significant differences as in composition as in structure of the SRO films obtained by both methods. So, the SRO–PECVD films contain a bigger nitrogen concentration than SRO–LPCVD ones; furthermore, SRO films deposited by PECVD present Si–H bonds, which do not appear in SRO films obtained by LPCVD. The FTIR spectra of the last material only exhibit absorption bands related to the silicon dioxide indicating a complete phase separation. In spite of differences, the SRO films obtained by both methods show a strong room temperature photoluminescence (PL). However, the strongest PL intensity is emitted by SRO – LPCVD films, although the silicon excess and the annealing temperature which were subjected are lower.

Results seem to indicate that the mechanism of emission in SRO–PECVD films is associated to Quantum Confinement (QC), whereas in SRO–LPCVD films the emission can be related to defects surrounding silicon nanocrystals (Si-nc).

Experiment

SRO films were deposited by LPCVD and PECVD techniques on n and p type Si (100) wafers, respectively, using SiH_4 and N_2O as precursor gas. Si excess in the films was obtained varying the $Ro=N_2O/SiH_4$ flow ratio. The SRO–LPCVD films were deposited at 720ºC with Ro values from 10 to 30, whereas SRO–PECVD films were deposited at substrate temperature of 300ºC with Ro values

from 5.5 to 22. The Ro value was selected according to the refraction index of the deposited SRO films to be in agreement between both techniques. The thickness of the films was around 100 nm. Table I summarizes the parameters of SRO deposited films.

A Gaertner L117 ellipsometer was used to obtain the thickness and the refractive index of the films. After deposition, the SRO–LPCVD films were annealed at 1100ºC and the SRO–PECVD films annealed at 1250 ºC, both for 60 minutes in N_2 atmosphere.

The Si excess in SRO films was obtained by PHI ESCA–5500 X–ray photoelectron spectrometer (XPS) using a monochromatic Al radiation source with energy 1486eV. Composition profiles into the films were obtained by etching the SRO films and then measuring. 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 radiation at 250 nm.

Table I. Thickness and refraction index of SRO films deposited by PECVD and LPCVD

Technique	Ro	Thickness (nm)	Refraction index: As deposited	Refraction index: After annealing
PECVD	5.50	84	1.75	1.90
	9.17	105	1.63	1.75
	22.00	99	1.51	1.52
LPCVD	10.00	110	1.99	1.99
	20.00	104	1.64	1.77
	30.00	102	1.48	1.48

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Results

A. Compositional characterization.

Fourier transform infrared spectroscopy (FTIR)

Figure 1 shows the IR absorbance spectra of SRO-PECVD films before and after thermal annealing. The vibration modes observed are enlisted in Table II. Before thermal annealing, all the SRO-PECVD films show a dominant absorption band related to Si–O stretching (TO_3) around 1012 cm^{-1}. The vibration band Si–O rocking (TO_1) at 430 cm^{-1} was also observed. For low flow ratio, a vibration band at 870 cm^{-1}, assigned to Si-H, appeared with a shoulder at 810 cm^{-1} related to the TO_2 vibration band (Si–O bending). When the flow ratio was higher, the intensity of the TO_3 vibration band increased at the same time that the peak at 870 cm^{-1} disappeared, and the TO_2 (Si–O bending) vibration band became more apparent. Another vibration bands at 1600 and 3662 cm^{-1}, related to H–O–H and Si–OH stretching, respectively, were also present in all the films.

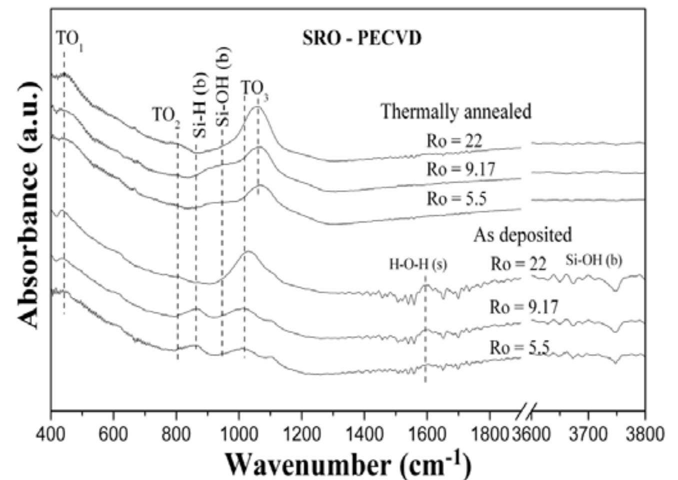

Fig. 1. Infrared absorption spectra of SRO–PECVD films before and after thermal annealing.

Table II. IR vibration bands [3] of SRO PECVD films before and after thermal annealing.

Vibration mode	SRO PECVD Ro = $[N_2O / SiH_4]$: As deposited 5.50	As deposited 9.17	As deposited 22	Annealed 5.50	Annealed 9.17	Annealed 22
Si-O rocking	438	436	438	442	442	446
Si-O bending	813	812	810	802	802	802
Si-O stretching	1012	1012	1030	1066	1066	1062
Si-H bending	864	866	874	–	–	–
Si-OH bending	942	947	–	–	–	–
H-O-H stretching	1604	1604	1600	–	–	–
Si-OH stretching	3662	3660	3662	–	–	–

After the SRO–PECVD films were thermally annealed, the bands at 1600 and 3662 cm^{-1} disappeared. For all films, the intensity of the band at 870 cm^{-1} related to Si-H decreases becoming a shoulder of the main band TO_3, and the TO_2 band around 817 cm^{-1} was more noticeable. The TO_3 band shifted to higher frequencies after thermal annealing indicating a phase separation. Its intensity slightly increased when the flow ratio was higher.

In the IR absorbance spectra obtained for SRO–LPCVD films before and after thermal annealing only three bands related to Si–O vibration appear, as shown in figure 2. In the IR spectra, the TO_3 band slightly shifts toward higher frequencies and

ISBN: 9974-0-0337-7

its width reduces as Ro 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. Due to the silicon excess in these films, we can assign these changes to the phase separation induced by the thermal annealing. Table III summarizes the vibration bands exhibited by the SRO–LPCVD films.

A possible cause on the hydrogen and nitrogen incorporation in SRO films obtained by PECVD could be the reaction mechanism pathway, which is under study.

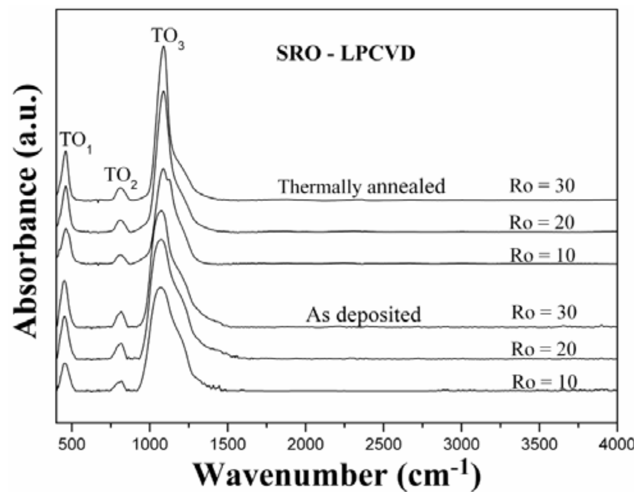

Fig. 2. Infrared absorption spectra of SRO–LPCVD films before and after thermal annealing.

Table III. IR vibration bands [3] of SRO LPCVD films before and after thermal annealing.

Vibration mode	SRO LPCVD; Ro = [N_2O / SiH_4]					
	As deposited			Annealed		
	10	20	30	10	20	30
Si–O rocking	458	452	451	461	461	459
Si–O bending	818	817	817	811	811	811
Si–O stretching	1069	1072	1073	1088	1088	1088

X-ray photoelectron spectroscopy (XPS)

The composition was also studied by XPS technique. Table IV display the composition of the SRO LPCVD and PECVD films. XPS profile of SRO PECVD with Ro = 5.5 is shown in figure 3. The nitrogen incorporation in these films is corroborated in the spectra. SRO-PECVD films have nitrogen content around 10%, as reported in other works [4]. The spectra show a uniform silicon excess in depth of the SRO films. Due to the high content of silicon in the films, a SiO_2 layer is formed at the surface of the film.

On the other hand, the nitrogen concentration in SRO films obtained by LPCVD is relatively low, as reported in Table IV. Figure 4 indicates the composition of the SRO film with flow ratio, Ro=20. The nitrogen profile is relatively low. It stabilizes around 0.8 at.% being this value on the lower detection limit of the equipment. Thus, we could deduce that the SRO–LPCVD films do not contain nitrogen.

Table IV. Composition (at. %) of SRO films deposited by PECVD and LPCVD

Technique	Ro	Composition (at. %)		
		Si	O	N
PECVD	5.50	45.0	43.0	12.0
	9.17	40.5	49.5	10.0
	22.00	37.0	60.5	2.5
LPCVD	10.00	44.5	55.5	0.0
	20.00	38.4	60.8	0.8
	30.00	37.3	62.0	0.7

Si → Silicon, O → Oxygen, N → Nitrogen

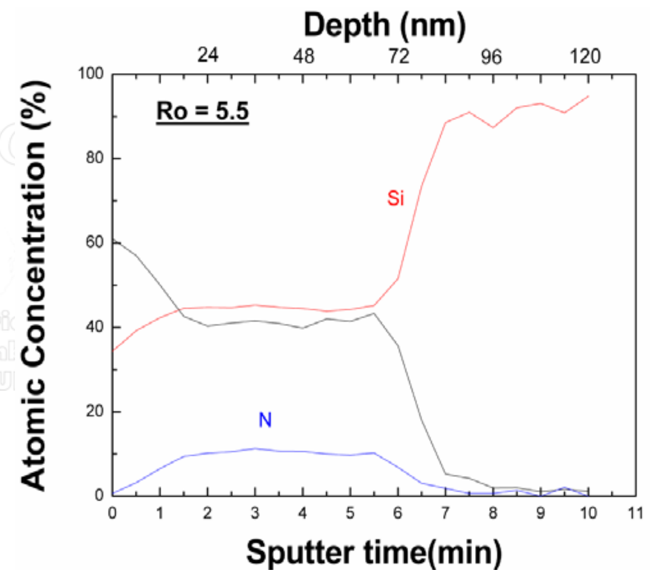

Fig. 3. XPS spectra for SRO–PECVD film with Ro = 5.5.

It can be appreciated that the silicon concentration into the SRO-LPCVD films is very uniform. As well as in the case of the presence of a SiO_2 layer in the surface of the SRO PECVD film, the XPS spectra of SRO LPCVD film with flow rate Ro=20 showed a SiO_2 layer in the surface, that could be due to the oxidation of silicon at the surface.

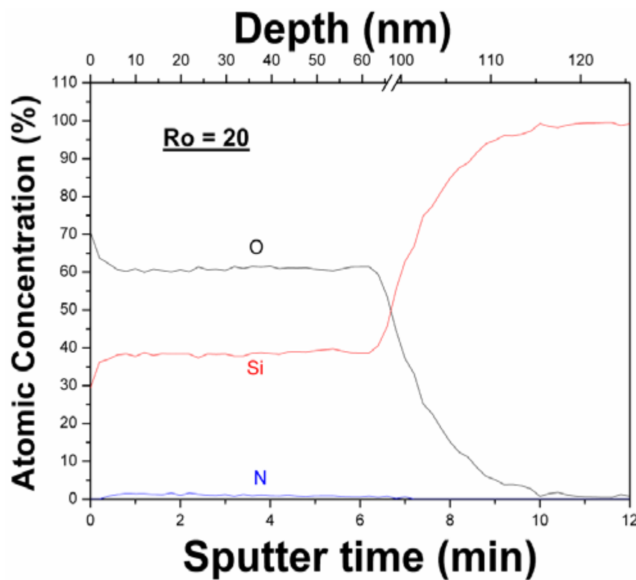

Fig. 4. XPS spectra for SRO–LPCVD film with Ro = 20.

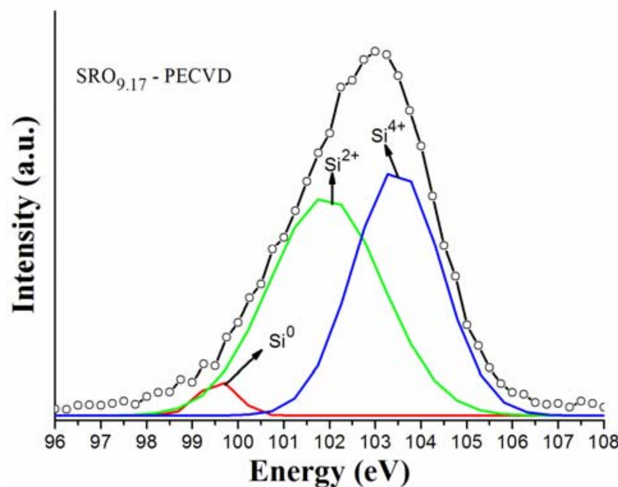

Fig. 5. XPS Si 2p spectra for SRO – PECVD films. The Si 2p peaks have been deconvoluted in the different silicon environments.

The Si2p peaks obtained from XPS-spectra of the SRO films were analyzed. Figure 5 shows the spectra of $SRO_{9.17}$–PECVD, in which a non symmetrical peak can be observed, it presents evidence of different Si environments. Si oxidation states related to Si^0, Si^{2+} and Si^{4+} were present, being the strongest contribution due to SiO_2 (Si^{4+}). 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 103.5eV; the suboxide contribution was only given by Si^{2+} as shown in figure 6. In SRO–LPCVD, only the SRO_{10} film showed a composition of Si^0, Si^{2+} and Si^{4+}.

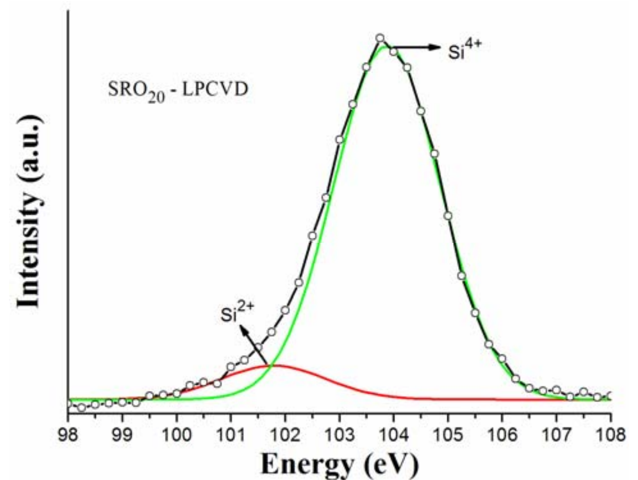

Fig. 6. XPS Si 2p spectra for SRO – LPCVD films. The Si 2p peaks have been deconvoluted in the different silicon environments.

B. Optical characterization.

Figure 7 shows the dependence of the PL peak energy 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. 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 behaviour 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 figure 8. Data demonstrates that a critical value exists for the Si excess where the maximum PL intensity is obtained.

Both SRO–LPCVD 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.

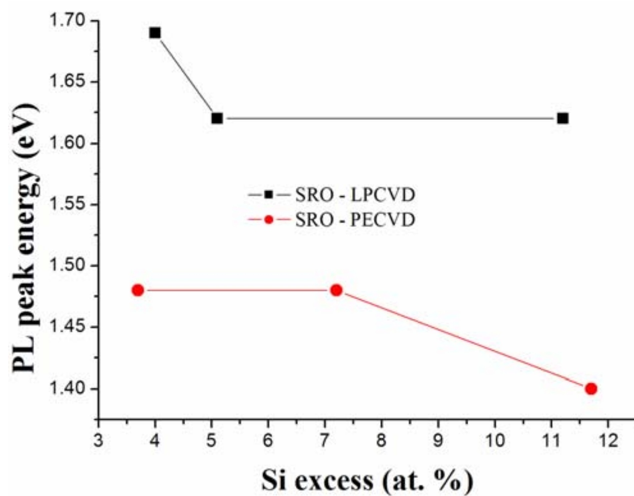

Fig. 7. Dependence of PL peaks energy on the Si excess in SRO–PECVD and SRO–LPCVD films.

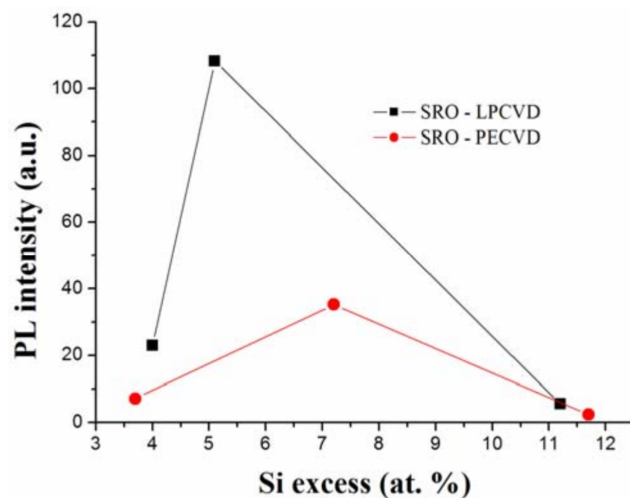

Fig. 8. Dependence of PL intensity on the Si excess in SRO–PECVD and SRO–LPCVD films.

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 reaction mechanism pathway (under study).

The origin of the PL emission is still object of debate; two models have been proposed. The first model relates the PL to Quantum Confinement Effects (QCE) [4, 5] in Si-nc's. The second model attributes the PL to defects in the matrix or the interface SiO_2/Si-nc [6, 7].

Based in the analysis of the Si2p spectra, we studied the microstructure [1-2] of SRO films. Si2p spectra indicated a combination of different coordination 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 Si-O_4 phases, respectively. Then, Si-nc's are 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 SRO-PECVD films, the SRO_{10} film is composed by 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 and it slightly shifted 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 lower than the emitted by SRO–PECVD films. Besides, in films with low Si content, Si^0 contribution was no observed indicating that Si-nc can not be present in these films. When the Si^0 contribution was present in the SRO film with highest Si concentration, the PL intensity strongly decreased, even lower than the PL intensity of SRO_{30} film, and its PL peak stayed at the same energy 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.

Both kind of SRO films exhibit excellent optical properties, besides, they have shown be stable and robust materials, as well as being efficient light emitters, and compatible to the CMOS technology, therefore, they can be used for integrated optical sensors based in silicon technology.

Conclusion

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 then 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 reaction mechanism pathway.

Si2p spectra showed that SRO–PECVD films are composed by Si^0, indicating the presence of Si-nc's, Si^{2+} y Si^{4+} (SiO_2), just as the SRO_{10}–LPCVD film. In addition, PL emitted by these films was observed in the typical region in systems Si-nc/SiO_2. Nevertheless, Si2p spectra form SRO–LPCVD films did not show the presence of Si^0, but Si- clusters 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 1100ºC for 60 minutes.

Acknowledgment

Mr. A. Morales and Mr. J. Barreto acknowledge the grants received from CONACYT and CSIC. This work has been partially supported by the project NANOMAGO: MAT2002-04484, financed by the Spanish Ministry of Education and Science.

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