

Compositional study of Silicon Rich Oxide films.

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Abstract – A compositional study of silicon rich oxide (SRO) films obtained by low pressure chemical vapor deposition (LPCVD) and plasma enhanced chemical vapor deposition (PECVD) is presented. As deposited and annealed SRO films were characterized by mean Infrared (IR) and x-ray photoelectron spectroscopy (XPS) techniques.

IR spectra from SRO obtained by PECVD showed absorption bands related to silicon-hydrogen bonds. However, for SRO–LPCVD, only vibration bands due to Si–O motion were observed. Moreover, XPS analysis demonstrated that SRO–PECVD films contain a higher nitrogen concentration than the LPCVD ones. All the SRO films were subjected to thermal annealing in order to investigate the changes in the composition of the films. The hydrogen and nitrogen have shown being an important parameter to influence the optical properties of these films.

Keywords – Infrared, Silicon Rich Oxide, Vibration bands, X-ray photoelectron spectroscopy.

I. INTRODUCTION

A great interest on substoichiometric silicon oxide (SiO_x, x<2) films have been attracted since the discovered of light emission in porous silicon [1]. This fact has been stimulated the potential use of these films in the integration of electrical and optical properties in the same ship. However, it is known that SRO films obtained from mixtures of SiH₄ and N₂O generally contain large concentration of chemical contaminants such as hydrogen and nitrogen. The optical properties of the SRO films are strongly influenced when they are present into the films [2].

In this work, we show that LPCVD technique produce SRO films without H and N contamination (below the detection limit of IR) whereas SRO films obtained by PECVD does. Photoluminescence studies reported on SRO–PECVD[3] films show that the energy of the peak emission is different that the SRO–LPCVD films [4]. These differences about optical properties are related to the incorporation of H and N into the films.

II. EXPERIMENT

SRO films were deposited by low pressure chemical vapor deposition and plasma enhanced chemical vapor deposition techniques on Si (100) substrates using SiH₄ and N₂O as precursor gas. The flow ratio $Ro = N_2O/SiH_4$ was varied to obtain different silicon contents in the SRO films.

The SRO–LPCVD films were deposited at 720°C with $Ro = 10, 20$ and 30 . SRO–PECVD films were deposited at substrate temperature of 300°C with $Ro = 5.5, 9.17$ and 22 . The Ro values were selected to obtain the same material composition of both types of SRO films. The thickness of the films was around 100nm. Table I summarizes the parameter of SRO films deposited.

An ellipsometer Gaertner L117 was used to obtain the thickness and the refractive index of the films. After deposition, the SRO–LPCVD and PECVD films were annealed at 1100 and 1250 °C, respectively, in N₂ atmosphere during 60 minutes. Infrared spectroscopy (BRUCKER Vector 22) and a PHI ESCA–5500 X–ray photoelectron spectrometer (XPS) with monochromatic Al radiation and energy 1486eV were employed to study the composition of the SRO films.

III. RESULTS

A. IR characterization.

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 (TO₃) around 1012cm⁻¹. The vibration band Si–O rocking (TO₁) at 430cm⁻¹ was also observed. For low flow ratio, a vibration band at 870cm⁻¹, assigned to Si–H, appeared with a shoulder at 810 cm⁻¹ related to the TO₂ vibration band (Si–O bending). When the flow ratio was higher, the intensity of the TO₃ vibration band increased at the same time that the peak at 870 cm⁻¹ disappeared, and the TO₂ (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.

TABLE I
THICKNESS AND REFRACTION INDEX OF SRO FILMS DEPOSITED BY PECVD AND LPCVD

Technique	Ro	Thickness (nm)	Refraction index	
			As deposited	After annealing
PECVD	5.5	84	1.75	1.9
	9.17	105	1.63	1.75
	22	99	1.51	1.52
LPCVD	10	110	1.99	1.99
	20	104	1.64	1.77
	30	102	1.48	1.48

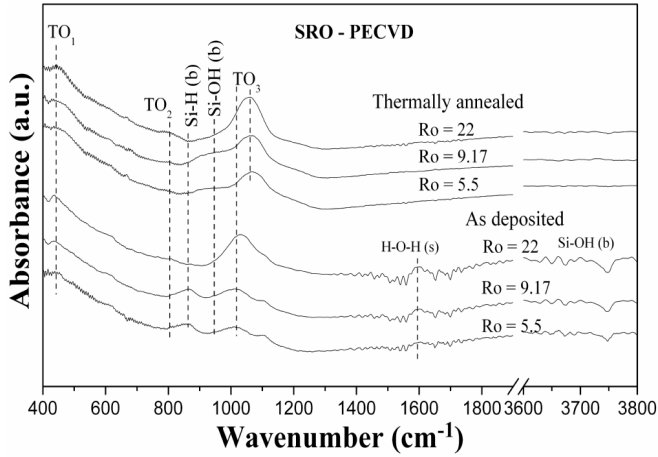


Fig. 1. Infrared absorption spectra of SRO-PECVD films before and after thermal annealing.

TABLE II
IR VIBRATION BANDS OF SRO PECVD FILMS BEFORE AND AFTER THERMAL ANNEALING

Vibration mode	SRO PECVD Ro = [N ₂ O / SiH ₄]					
	As deposited			Annealed		
	5.5	9.17	22	5.5	9.17	22
Si-O Rocking [2]	438	436	438	442	442	446
Si-O Bending [2]	813	812	810	802	802	802
Si-O Stretching [2]	1012	1012	1030	1066	1066	1062
Si-H Bending [2]	864	866	874	-	-	-
Si-OH Bending [2]	942	947	-	-	-	-
H-O-H Stretching [2]	1604	1604	1600	-	-	-
Si-OH Stretching [2]	3662	3660	3662	-	-	-

After the SRO-PECVD films were thermally annealed, the bands at 1600 and 3662cm⁻¹ disappeared. For all the films, the intensity of the band at 870cm⁻¹ related to Si-H decreased becoming a shoulder of the main band TO₃, and the TO₂ band around 817cm⁻¹ was more noticeable. The TO₃ 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 appeared three bands related to Si-O vibration, as shown in figure 2. In the IR spectra, the TO₃ band slightly shifts toward higher frequencies and the width reduces as Ro is increased due to an increment in the oxygen concentration. Another shift in the TO₃ 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.

TABLE III
IR VIBRATION BANDS OF SRO LPCVD FILMS BEFORE AND AFTER THERMAL ANNEALING

Vibration mode	SRO LPCVD; Ro = [N ₂ O / SiH ₄]					
	As deposited			Annealed		
	10	20	30	10	20	30
Si-O Rocking [2]	458	452	451	461	461	459
Si-O Bending [2]	818	817	817	811	811	811
Si-O Stretching [2]	1069	1072	1073	1088	1088	1088

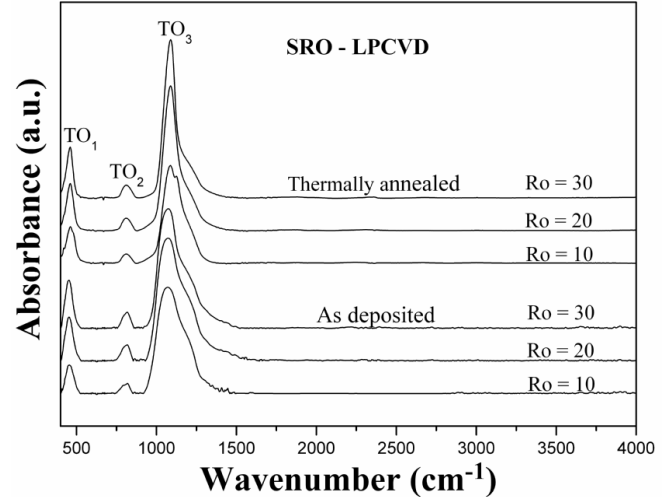


Fig. 2. Infrared absorption spectra of SRO-LPCVD films before and after thermal annealing.

B. X-ray photoelectron spectroscopy.

The composition was also studied by XPS technique. Table IV displays 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 previously reported in other works [5] by using Rutherford backscattering spectroscopy (RBS). The spectra show a uniform silicon excess in depth of the SRO films. Due to the high content of silicon in the films, a SiO₂ 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.

TABLE IV
COMPOSITION (AT. %) OF SRO FILMS DEPOSITED BY PECVD AND LPCVD

Technique	Ro	Composition (at. %)		
		Si	O	N
PECVD	5.5	44.8	40.8	10.7
	9.17	40.5	49.5	10
	22	37	60.5	2.5
LPCVD	10	44.5	55.5	0
	20	38.4	60.8	0.8
	30	37.3	62	0.7

Figure 4 indicates the composition in the SRO film with flow ratio, $R = 20$. The nitrogen profile is relatively low. It stabilizes around 0.8 at.% being this value on the lower detection limit of the equipment. Thus, the SRO-LPCVD films do not contain nitrogen.

We can appreciate 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 $R_o = 22$ showed a SiO_2 layer in the surface, that could be due to the oxidation of silicon at the surface.

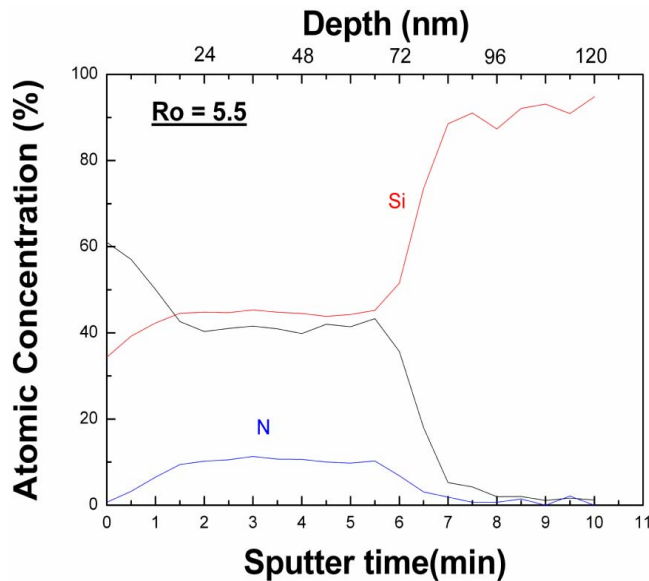


Fig. 3. XPS spectra for SRO-PECVD film with $R_o = 5.5$.

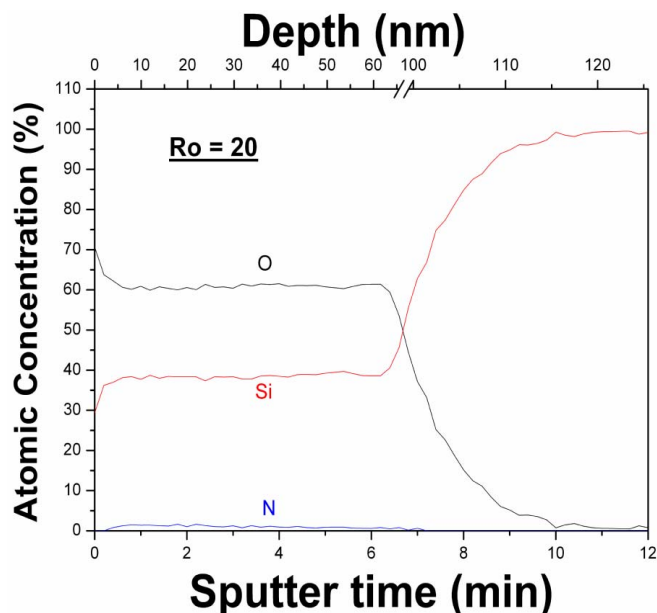


Fig. 4. XPS spectra for SRO-LPCVD film with $R_o = 20$.

IV. DISCUSSION

SRO films deposited by PECVD showed N and H concentration. As we could observe from IR spectra, a thermal annealing carried out on these films effectively released the hydrogen atoms incorporated in the films.

As a consequence of the H released, silicon dangling bonds are produced. The nitrogen present in these films could be saturating the dangling bonds during the lattice arrangement.

It is known that the N acts as a diffusion barrier [6] and it has been also reported to affect the Si grain formation reaction [7, 8]. Due to the IR and XPS results showed that SRO films deposited by LPCVD do not contain N and H, we can conclude that the phase separation into Si and SiO_2 in the SRO PECVD films is slower than the SRO LPCVD films. As a result, different optical properties can be expected in both types of SRO films.

Figure 5 shows the PL spectra of both types of SRO films. Before thermal annealing (not shown), evidence of photoluminescence in SRO PECVD films with flow ratio higher than 5.5 was not observed. However, the SRO film with $R_o = 5.5$, the PL spectra exhibited a PL peak at 2.45 eV with a shoulder around 2.2 eV.

When these films were thermally annealing, we observed two different PL peaks depending on the flow ratio. For SRO PECVD films with flow ratio higher than 5.5, a PL peak at the blue region of the spectra was detected, as shown in figure 5(a). Its intensity increased when the flow ratio was higher. This emission can be attributed to defects produced due to the hydrogen evolution as a result of high temperature of annealing and as we could see in the IR absorbance spectra. The PL peak of the SRO film with the lower flow ratio ($R_o = 5.5$) shifted toward 1.6 eV as a result of the elimination of impurities present in the films after thermal annealing.

In SRO LPCVD films, the PL appears only in the near infrared region as shown in figure 5(b). All the SRO LPCVD films showed PL peaks between 1.6 and 1.7 eV. We can observe a redshift when the flow ratio is decreased from 30 to 20. The intensity of the PL peak was higher for flow ratio of 20. PL peaks at high energies were not detected in this type of films. The differences between both the SRO films obtained by PECVD and LPCVD can be attributed to the H and N content as we can have deduced.

Furthermore, a study of the nitrogen effect on the PL properties of SRO films deposited by LPCVD, where ammonia has been introduced in the deposition process was also reported. Nitrogen incorporation has been detected in these films by IR spectroscopy studies. A PL peak at blue

region was observed in the as deposited films and its intensity increased with the N incorporation.

When the SRO films were thermally annealed, the PL peak of low intensity appeared at the near infrared region as a result of the release of the Nitrogen incorporation. The biggest intensity was observed in SRO films where the ammonia was no incorporated and thus N is not present.

Other PL studies on SRO films obtained PECVD [4] at different temperatures have shown different photoluminescence peaks emission. The peaks energy as well as silicon content depend on the temperature deposition and, hence, on the H content. SRO films deposited at temperature of 30°C with different flow ratio, showed peaks in the blue region of the visible spectra. When these films are annealed, the H is released and a peak PL emission now is placed at a lower energy (around near infrared). According to this, different PL peak can be obtained in the SRO films deposited by PECVD.

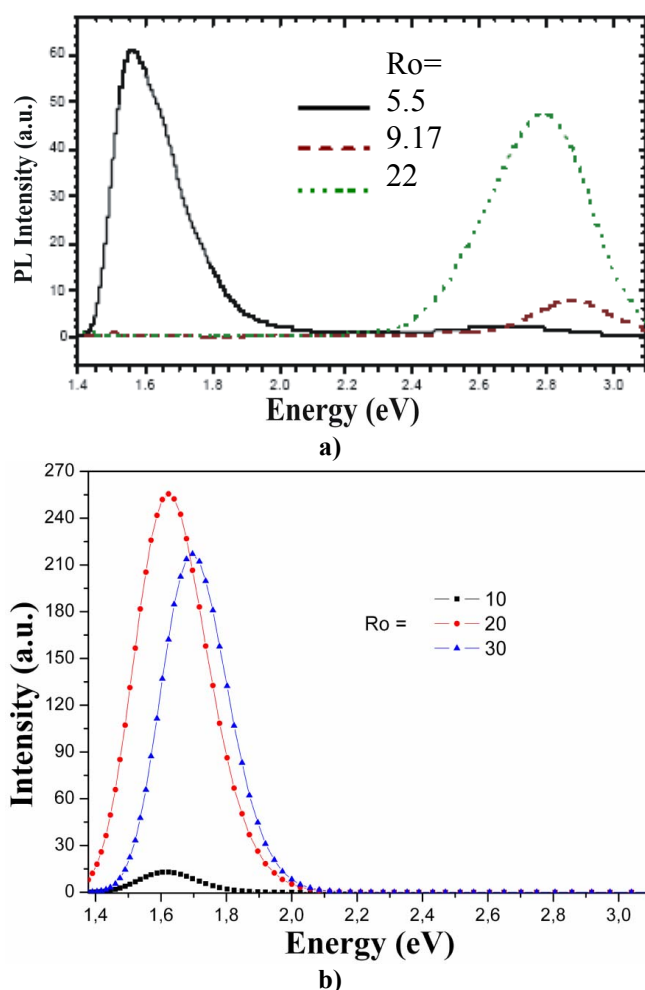


Fig. 5. Photoluminescence spectra of SRO a) PECVD and b) LPCVD films after thermal annealing.

V. CONCLUSIONS

The composition of silicon rich oxide films obtained by LPCVD and PECVD has been studied. FTIR and XPS techniques were used as the characterization tools. IR absorbance spectra for SRO films were obtained before and after thermal annealing. Hydrogen incorporation into SRO films obtained by PECVD was observed forming H–O–H, Si–H and Si–OH bindings. When these films were subjected to thermal annealing, the H bonds disappear. Nitrogen concentration was also present in SRO PECVD films as measured by XPS.

IR absorbance spectra for SRO films deposited by LPCVD did not show any vibration band related to H or N. XPS studies revealed that these films are compound only of Si and O atoms. A possible explanation on the hydrogen and nitrogen incorporation in SRO films obtained by PECVD could be the reaction mechanism pathway.

From results about photoluminescence in SRO films, it can be seen that the N incorporation strongly affects their optical properties. Because of these, both kind of SRO films present differences in photoluminescence emission.

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