OPTICAL CHARACTERIZATION OF SILICON RICH OXIDE FILMS.

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Abstract: SRO films obtained by LPCVD have shown a strong visible photoluminescence (PL) after annealed at 1100°C. Since these materials are robust and efficient, they have shown having potential applications in optoelectronics. Structural and optical studies on these materials were carried out. The results suggest that the emission can be related to defects surrounding the Silicon clusters and nanocrystals.
Keywords: Silicon Rich Oxide, Si nanocrystal, Photoluminescence.

INTRODUCTION

Discovery of visible room temperature luminescence in Silicon porous [1] attracted a new effective way to obtain light emission in Silicon based materials. However, the porous silicon suffers from poor mechanical and chemical stability. Therefore, a great number of investigations have been carried out in order to find more stable materials from the last decade. The Silicon nanocrystals (Si-nc) embedded in SiO_2 matrix has attracted the main attention. The key which makes these materials excellent light emitter are the technological process which they are submitted in order to produce them. The most studied material has been the Silicon Rich Oxide (SRO). There are many techniques of producing SRO films (SiOx, x<2) such as ion implantation of Si inside thermal silicon oxide [2], Pulsed Laser Deposition (PLD) [3], Plasma Enhanced Chemical Vapor Deposition [4]–[7], Thermal evaporation [8], [9], as well as SiO/SiO_2 multilayers [10]. The mechanism of light emission is still controversial; some authors have related the PL to Quantum Confinement Effects (QCE) in Si-nc's [7], defects [2], and localized states on the surface of the Si-nc and Si-clusters [11]. In this work, we report a study about structure and optical properties of SRO films obtained by Low Pressure Chemical Vapor Deposition (LPVCD); as well as the effect of the technological parameters in order to obtain a maximum PL response.

EXPERIMENT

SRO films were deposited by LPCVD technique on Silicon (100) wafers n type, using SiH_4 y N_2O as precursor gasses. Silicon excess in the films was obtained varying the Ro = N_2O/SiH_4 flow ratio between 10 and 30. The thickness of the films was 700 nm. After deposition, SRO films were annealed at 1100°C for 60 minutes in N_2 atmosphere. Silicon excess in SRO films was obtained by PHI ESCA – 5500 X–ray photoelectron spectrometer (XPS). The results are listed in table 1. EFTEM images were obtained using an electronic microscopy JEOL JEM 2010F. The PL at room temperature was obtained by using a Perkin Elmer luminescence spectrometer model LS50B, which is controlled by computer. The samples were excited using radiation at 250 nm.

RESULTS

Fig. 1 shows the EFTEM image for the SRO_{20} film after annealing at 1100°C for 60 minutes. The observed image indicates the presence Si-nc's. The size distribution of Si-nc's extended up to 3.8nm, with an average size of 2.7 nm. The EFTEM images showed Si-nc's uniformly distributed in the film.

Table 1. Thickness, refraction index and silicon excess in SRO films.

Ro = N_2O/SiH_4	Thicknes s (nm)	Refraction index	Silicon excess (%at)
10	770	1.99	11.2
20	730	1.64	5.1
30	720	1.48	4

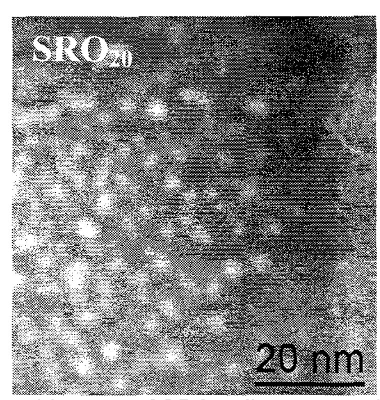

Fig. 1. EFTEM image of SRO_{20} film annealed at 1100°C for 60 minutes.

On the other hand, no Si-nc's were observed in the SRO_{30} film after annealing at 1100°C, in spite of having only 1% of silicon excess minus than SRO_{20} film.

Fig. 2 present the EFTEM image for SRO_{30} film, we can se clearly the inexistence of Si-nc. Although EFTEM equipment is able to detect Si crystallites of even 1nm in size, images on several places of the film did not show Si-nc. However, the SRO_{30} film analyzed was under the exposition of the electron beam for a few seconds, and Si-nc's were observed. Then, Silicon cluster can be presented inside of the SRO_{30} film such as in [12].

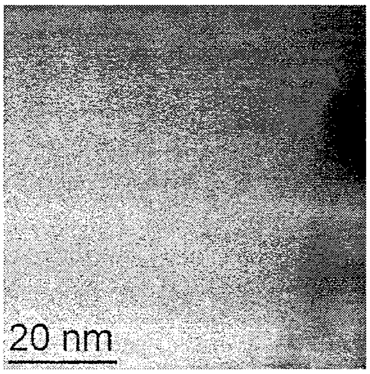

Fig. 2. EFTEM image of SRO_{30} film annealed at 1100°C for 60 minutes.

Fig. 3 shows the PL spectra normalized to thickness for the SRO films annealed at 1100 and 1250°C for 60 minutes. For the SRO_{30} film, which contains 4% silicon excess, a PL band with a peak in 1.69 eV was observed. A redshift was obtained when the silicon excess increased to 5% (SRO_{20}); the PL band appeared at 1.62 eV with a bigger intensity. The PL intensity of SRO_{10} film decreased by more than 20 times and no redshift was observed. In spite of the SRO_{30} does not contain Si-nc, it shows a strong PL close to the emitted by the SRO_{20}.

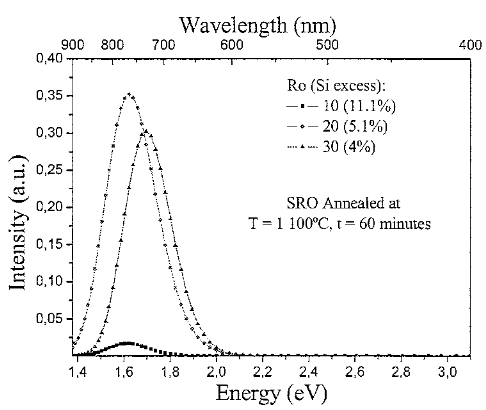

Fig. 3. PL spectra from SRO – LPCVD films annealed at 1 100°C for 60 minutes.

In [2], [8] have related the PL of SiOx films, which contain Si-nc with similar size to the obtained in the SRO_{20} film of our experiment, to quantum confinement effects (QCE); so, the emission of this film could be due to QCE; however, we have seen that SRO_{30} film have a strong PL intensity with a peak in 1.69eV. Since the appearing of Si-nc was no observed, silicon clusters can be formed inside of the film. We can consider that the Si-nc's and the Si clusters are surrounding by defects acting as localized states. Then, the PL peak is given for the transition between localized states and the ground state. When the size of the Si-nc or Si- Cluster is increased, the band gap and the energy between localized states (produced by defects surrounding the Si-nc's and Si-clusters) and the ground state are reduced producing a shift in the PL energy.

The increase in the PL intensity when the Si-nc are present in SRO_{20}, is given by a increasing the density of Si-nc's as a result of reduction of the Si-clusters.

CONCLUSIONS

We have studied the composition, structure and optical properties of SRO films annealed at 1100°C. EFTEM analysis showed Si-nc in the SRO_{20} film annealed at 1100°C. The images showed Si-nc's uniformly distributed in the film, with an average size of 2.7 nm. A strong PL was obtained with SRO_{20} and SRO_{30} films annealed at 1100°C. A redshift only took place when the Silicon excess was increased between SRO_{20} and SRO_{30}. However, Si-nc's were no found in the SRO_{30} film. The PL origin was related to defects surrounding to the Si-nc's and the Si-clusters. The increase in the PL intensity when the Si-nc are present in SRO_{20}, is given by a reduction of the Si clusters, increasing the density of Si-nc.

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