Effect of annealing on structural properties of SiO$_x$ films obtained by HWCVD technique

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Abstract: SiO$_x$ films were deposited in the temperature range of 800-1000 °C by hot wire chemical vapor deposition (HWCVD) technique. Annealing treatment for as-deposited samples was performed in nitrogen (N$_2$) atmosphere at 1100 °C. The effect of annealing atmosphere on the structural properties of the deposited films was investigated by means of micro Raman, X-ray diffraction (XRD), Photoluminescence (PL) and high resolution electron microscopy (HRTEM) measurements. Micro-Raman studies revealed an increase in the crystalline volume fraction ($X_c$) in the deposited films after annealing. XRD patterns of the annealed films showed the formation of silicon crystals. HRTEM images confirmed the presence of silicon nanocrystals (Si-ncs) in both as-deposited and annealed films. Furthermore, the annealing treatment on the as-deposited samples at 900 and 1000 °C resulted in the observation a large number of Si-ncs with sizes between 3-15 nm. PL measurement shows a broad emission from 400 to 1100 nm. This emission was related with both Si-ncs and interfacial defects present in SiO$_x$ films.

1. Introduction
Since the discovery of the luminescent properties of Si/SiO$_2$ multilayers [1, 2], Si-ncs embedded in SiO$_x$ films have been extensively studied, mainly because they exhibit more stable optical properties than porous silicon. Recent publications [3, 4, 5], have suggested that SiO$_x$ films with embedded Si-ncs can be an alternative in the development of silicon-based photovoltaic devices. Nanocrystalline material is more stable and has broader absorption range in the visible part of the solar radiation [5, 6]. In this direction, one of the most promising routes is exploiting the quantum confinement effect (QCE) in silicon nanocrystals. Some interesting effects based on the QCE are the multiple exciton generation in Si quantum dots (QDs) [4] or the optical band gap modulation with the QDs size [7].

Several techniques have been used in the production of Si-ncs embedded in SiO$_x$ matrix such as: sputtering [8], ion implantation [2], plasma enhanced chemical vapor deposition (PECVD) [9], and HWCVD [10, 11].

In this work evolution of the structural properties of SiO$_x$ films obtained by HWCVD were investigated. To achieve this goal, samples of SiO$_x$ were annealed in N$_2$ atmosphere at 1100 °C. It was found that both the mean size and the number of Si-ncs is increased by effect of annealing process. These features should be considered to improve the quantum confinement effects and to absorb sunlight in a more efficient way in a solar cell.
2. Experimental Details
The HWCVD process has been already described elsewhere [11]. The filament-source distance was kept constant at 3 mm, while the filament-substrate distances were 1.32, 1.16 and 1.0 cm, to obtain deposition temperatures of 800, 900, and 1000 °C respectively. The growth time was 10 minutes on each experiment. The quartz substrates were carefully cleaned with a MOS standard cleaning process before being introduced into the reactor. After deposition the samples were annealed in N₂ atmosphere for two hours at a temperature of 1100 °C.

The XRD diffractograms were measured with a Bruker D8 Discover diffractometer using Cu Kα radiation (λ=0.15418 nm). Micro-Raman measurements were performed at room temperature using a He-Ne laser (632.8 nm). A laser with a wavelength of 405 nm and 40 mW of power was used to excite the sample in PL measurements; the range detected by monochromator was from 400 to 1100 nm. Finally, a high-resolution transmission electron microscopy (HRTEM) FEI Tecnai F30 STWIN G2 was used to observe the presence and evolution of the Si-ncs.

3. Results and Discussion
In our previous work structural and optical properties of Si-ncs in SiOₓ films were reported [11], micro-Raman studies suggest that during the HWCVD process some formed silicon clusters can be crystallized to form Si-ncs due to an apparent in-situ annealing at growth temperatures of 900 and 1000 °C. In order to have a better understanding of this phenomenon, some samples were annealed at 1100 °C in N₂ atmosphere for two hours. Figure 1 shows micro-Raman spectra of samples grown at 800, 900, and 1000 °C with subsequent annealing at 1100 °C. The peak at 521 cm⁻¹ related to the nanocrystalline phase is detected in the samples. It is noteworthy that before annealing, the samples growth at 900 and 1000 °C causes crystallization in silicon clusters [11]. When the samples are annealed both crystallization in silicon clusters and the number of Si-ncs increases. One factor that may give information about the previous discussion is the crystalline volume fraction (X_c) parameter.

The crystalline volume fraction X_c can be estimated from micro-Raman spectra. X_c is given by, $X_c = I_{TO2} / (I_{TO2} + I_{TO1} * m)$, where $I_{TO2}$ is the integrated micro-Raman intensities of the crystalline peak, $I_{TO1}$ the integrated micro-Raman intensities of the amorphous peak, m is a factor, which can be obtained from; $m = 0.1 + \exp(-d/25)$, where d (nm) is the diameter of the grain obtained from the XRD spectrum, and m=1 [6]. Table 1, shows the crystalline fraction for different conditions. For as-deposited samples the X_c factor increases from 4 to 10%. For samples annealed at 1100 °C, the X_c

![Figure 1](image1.png) **Figure 1.** Micro-Raman spectrum of films growth at 800, 900 and 1000 °C with subsequent annealing at 1100 °C.

![Figure 2](image2.png) **Figure 2.** XRD patterns for samples deposited at 800, 900 and 1000 °C with subsequent annealing at 1100 °C.
factor increases from 27 to 50% by changing the growth temperature. The increase in the $X_c$ factor can be understood as a modification in the number of the Si-ncs as well as their mean size.

The mean size of the Si-ncs was investigated by XRD and HRTEM analyses. XRD characterization revealed the presence of crystalline planes in SiO$_x$ films. Figure 2 shows XRD patterns for samples deposited at 800, 900 and 1000 °C with subsequent annealing at 1100 °C. Three main peaks are localized at 28.4, 47.4, and 56.1° corresponding to the silicon (111), (220), and (311) planes, respectively. Table 1, shows the data of the mean size of the Si-ncs obtained by Scherrer approximation for samples deposited at 800, 900, and 1000 °C with subsequent annealing at 1100 °C. As can be seen, the size of Si-ncs increase with the growth temperature. This is expected because in as-deposited films, the Si-ncs diameter is larger at 1000 °C than those growth at 900 °C [11]. Therefore, when the films are annealed, Si-ncs continues growing.

| Temp. °C | As Deposited $X_c$ (%) | Annealed at 1100 °C $X_c$ (%) | Annealed (1100 °C) and Average Size of Si-ncs by XRD (nm) |
|----------|------------------------|-----------------------------|--------------------------------------------------|
| 800      | ----                   | 27                          | 3.24                                             |
| 900      | 4                      | 30                          | 4.39                                             |
| 1000     | 10                     | 50                          | 19.8                                             |

Figure 3 and 4 show the HRTEM images from samples deposited at 900 and 1000 °C with subsequent annealing at 1100 °C. It is confirmed the existence of Si-ncs with a mean square value around 5 nm. The mean size of the Si-ncs for the sample deposited at 900 °C varies between 3 and 5.5 nm as shown in the histogram (inset from Figure 3), while for the sample deposited at 1000 °C, Si-ncs between 5 and 15 nm were measured (see inset in Figure 4). The results are consistent with the average particle size calculated by the Scherrer formula (Table 1).

Figure 3. HRTEM image and histogram for the sample deposited at 900 °C with subsequent annealing at 1100 °C.

Regarding the number of nanocrystals, HRTEM images of as-deposited samples were analyzed [11]. The average size particle found on the sample deposited at 900 °C was 3 nm and for sample at 1000 °C varied between 3 and 6 nm as shown the histograms. The HRTEM images showed greater number of Si-ncs compared to the as-deposited samples. We proposed that formation of Si-ncs is carried out entirely by diffusion mechanism of silicon in SiO$_2$ [12]. This diffusion is dependent on growth temperature. When the samples are annealed the diffusion coefficient of silicon in SiO$_2$ is higher and Si-ncs should therefore be larger. Furthermore, amorphous silicon remains present and
crystallizes resulting in new Si-ncs. Thus, it can be confirmed that both the mean size and the number of Si-ncs is increased by effect of annealing process.

PL measurements were performed on SiO$_x$ films at room temperature in the range of 400-1100 nm. In Figure 5, we compare the PL spectra of SiO$_x$ films before and after annealing. It can be observed an increase in the PL intensity when the samples are annealed. The peak around 930 nm increases in intensity and undergoes a slight shift toward higher wavelengths. We propose that this peak is associated with radiative defects [11]. The increase in the number of Si-ncs with annealing is related to defects: an increase in the number of nanocrystals causes more radiative defects in this wavelength.

On the other hand after annealing, the band around 600-847 nm increases in intensity due to the large amount of nanocrystals formed, this band corresponds to nanocrystal sizes between 3 and 7 nm observed by HRTEM. In this case the model of quantum confinement might explain the radiative emission in this range of energy. We propose that both effects must be responsible for the PL phenomenon in our samples. However, a thorough study is needed to support these assumptions.

Figure 5. PL spectra of SiO$_x$ films before and after annealing.

4. Conclusion
The effect of annealing on structural properties of SiO$_x$ films obtained by HWCVD technique was studied. The different analysis showed an increase in the crystallization of silicon clusters when the samples were annealed. In both by HRTEM and XRD the size and the number of Si-ncs increases compared with the as-deposited samples. PL measurements in SiO$_x$ films revealed an intense photoluminescence in the samples after annealing due to an increase in both the number of nanocrystals and increased of radiative defects.

References
[1] Lu Z H, Lockwood D J, and Baribeau J M 1995 Nature 378 258.
[2] Shimizu I T, Nakao S and Saitoh K 1994 Appl. Phys. Lett 65 1814.
[3] Mirabella S, Di Martino G, Crupi I, et al. 2010 J. Appl. Phys. 108 093507.
[4] Nozik J 2008 Chem. Phys. Lett. 457 3.
[5] Yuan Z, Pucker G, Marconi A, et al. 2011 Sol. Energy Mater. Sol. Cells. 95 1224.
[6] Anbarasan P M, Senthilkumar P, Manimegalai S et al. 2010 Silicon 2 7.
[7] Conibeer G, Green M, Corkish R, et al. 2006 Thin Solid Films 511–512 654.
[8] Mota E, Meléndez M A, et al. 2010 J. Appl. Phys 108 094323.
[9] Zhang X W 2005 Phys. Status Solidi A 202 1773.
[10] Matsumoto Y, Godavarthi S, Ortega M, et.al. 2011 Thin Solid Films 519 4498.
[11] Coyopol A, et al. 2012 Journal of Nanomaterials, ID 368268, 7 pag. doi:10.1155/2012/368268.
[12] Nesbit L A. 1985 Appl. Phys. Lett. 46 38.