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# Si nanocrystals deposited by HFCVD

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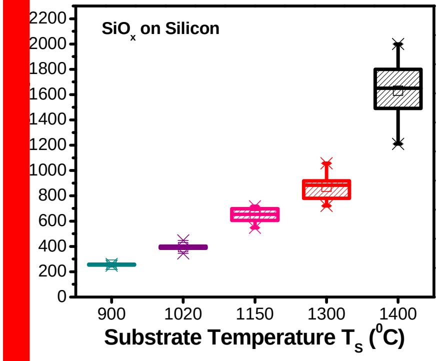
**Abstract.** The structural and optical properties of Si nanocrystal embedded in a matrix of off-stoichiometric silicon oxide ($SiO_x$, $x$<2) films prepared by hot filament chemical vapor deposition technique were studied. The films emit a wide photoluminescent spectrum from 400 nm to 800 nm and the maximum peak emission shows a blue-shift as the substrate temperature decreases. Also, a wavelength-shift of the absorption edge in transmittance spectra is observed, indicating an increase in the energy band gap. The Si nanocrystals size decreases from 6.5 to 2.5 nm as the substrate temperature is reduced from 1150 to 900 °C, as measured through High Resolution Transmission Electron Microscopy. A combination of mechanisms is proposed to explain the photoluminescence in the $SiO_x$ films, involving $SiO_x$ defects and quantum confinement effects.

## Introduction

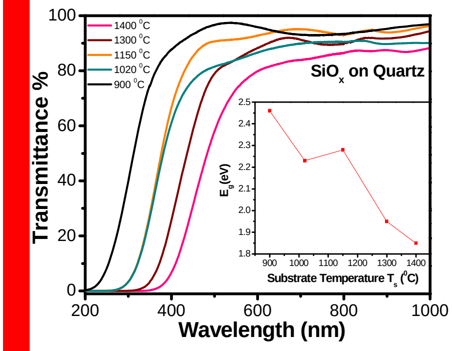
Silicon is the dominant semiconductor material in the microelectronics industry. However, due to its indirect band gap, it is a poor light emitter. Therefore, silicon has been considered for a long time not suitable for optoelectronic applications [1]. Nevertheless, several studies have reported room-temperature photoluminescence (PL) in Si-based materials [1, 2]; this opens the possibility of using Si as an efficient light source, which is attractive for potential applications in optoelectronics. In addition, Si-based materials are compatible with the existing manufacturing infrastructure of integrated circuits (IC´s) [3]. One of these materials is the off-stoichiometric silicon oxide ($SiO_x$, $x$<2), where the formation of Si nanocrystals embedded in this matrix has gained an increased interest, due to the low dimensionality effects, which determine an efficient visible light emission, even at room temperature [4, 5]. $SiO_x$ can be prepared by several techniques including silicon ion implantation into thermal dioxide films, reactive sputtering, co-evaporation, sol-gel, low pressure chemical vapour deposition (LPCVD), plasma enhanced chemical vapour deposition (PECVD) and hot filament chemical vapour deposition (HFCVD) [6-9]. In all of these techniques, the silicon excess is controlled by changing the process parameters. $SiO_x$ prepared by HFCVD (HFCVD-$SiO_x$) can be considered as a multi-phase material composed by a mixture of off-stoichiometric silicon oxide ($SiO_x$, $x$ < 2) and elemental silicon (as silicon nanoparticles (Si-nps)) [10-12]. In this work, the structural and optical properties of $SiO_x$ films obtained by HFCVD are reported. The effect of the substrate temperature (Ts) on the PL response has been also studied. Experimental results from High Resolution Transmission Electron Microscopy (HRTEM), PL and Transmittance measurements are discussed in order to understand the emission mechanism.

## Experiment

$SiO_x$ films were deposited on quartz substrates and $n$-type (100) high resistivity silicon wafers (2000-5000 Ω cm) by means of a horizontal hot filament CVD system. The substrates were carefully cleaned with the MOS standard cleaning process. Quartz and porous silicon were used as the solid sources. In the HFCVD system a hot filament at ~ 2000 °C dissociates the ultra-high purity molecular hydrogen that flows into the reactor at a rate of 50 sccm, producing atomic hydrogen. The filament-source distance was kept constant at 2 mm and the source-substrate distance was varied to change the Ts, and consequently to change the silicon excess in the $SiO_x$ films. The source-substrate distance was varied from 2 to 6 mm to change the substrate temperature from 1400 to 900 °C, respectively. The films´ thicknesses were measured using a Dektak 150 profilometer. PL was measured at room temperature using a Horiba Jobin Yvon spectrometer FluroMax 3 with a pulsed xenon source and its detector has a multiplier tube. The samples were excited using light of 250 nm and PL response was recorded between 400 and 900 nm with resolution of 1 nm. Room-temperature transmittance of the $SiO_x$ films was measured using an UV-Vis-NIR Cary 5000 system. The transmittance signal was collected from 190 to 1000 nm with a resolution of 0.5 nm. HRTEM measurements were done using a Titan 80-300 kV model with an energy spread of 0.8 eV.



igure 1. Variation of the thickness of iO$_x$ films as a function of Ts.



igure 2. Transmittance spectra and nergy band gap of $SiO_x$ films on uartz substrate as a function of Ts.

## Results

Figure 1 shows the thickness of the $SiO_x$ films as a function of the substrate temperature (Ts). It is observed that Ts clearly affects the thickness: thinner and more uniform $SiO_x$ films are obtained at lower temperatures. Such behaviour can be due to the temperature gradient in the HFCVD system; i. e., increasing the distance between solid source and substrate, the temperature gradient becomes smaller and this provides a more uniform deposit. Figure 2 shows the transmittance spectra of $SiO_x$ films on quartz substrate. The $SiO_x$ films exhibit a relatively high transmittance (>80%) between 600 and 1000 nm. The absorption edge shifts towards greater wavelengths as the substrate temperature increases. The corresponding optical band gap ($E_g$) values as a function of the substrate temperature are shown in the inset of Figure 2.

Figure 3 shows the PL spectra from $SiO_x$ films deposited on silicon substrates. A wide PL spectrum, from 400 nm to 800 nm is observed for all the samples. PL spectra present a maximum emission peak centered between 534 and 678 nm depending of the Ts. A blue shift of the luminescent peak is observed when Ts decreases, coupled with an increasing of the emission intensity.

The plan-view HRTEM micrographs of $SiO_x$ films deposited at 1150, 1020 and 900 °C are shown in Figures 4 a), b) and c), respectively. All micrographs show that the $SiO_x$ matrix contains small clusters, which, on the basis of the electron diffraction analysis, can be identified as silicon nanocrystals (Si-nc).

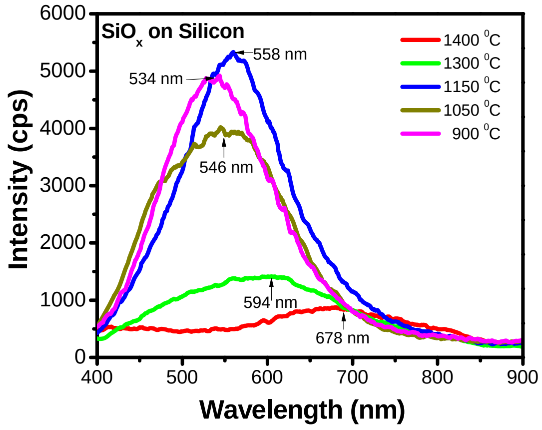


Figure 3. PL spectra of SiO$_x$ films deposited on silicon substrate for different values of Ts.

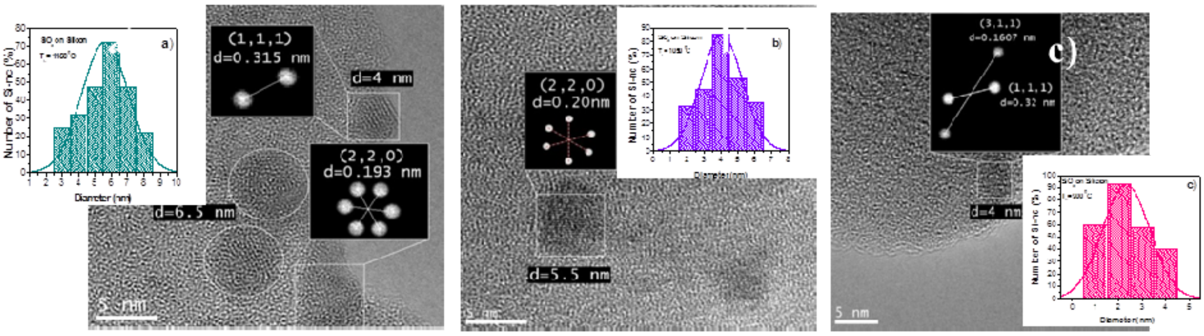


**Figure 4. The plan-view HRTEM micrographs of the SiOx films deposited at a) 1150 °C, b) 1050 °C and c) 900 °C.**

## Analysis and Discussion

PL properties of SiO$_x$ films have been studied extensively in the literature [1-2,13-14]. The two most accepted mechanisms of visible and near-infrared light emission for this type of materials are the quantum confinement effect in Si-ncs and another related with the role of defects around of the Si-ncs or defects in the SiO$_x$ matrix [1-14]. According to the first model, light emission from Si-ncs should be due to the band-to-band radiative recombination of electron-hole pairs confined within the crystals [15]. The second model attributes the PL of SiO$_x$ films to the presence of defects in the SiO$_2$ matrix and/or to surface and interface effects of the Si-ncs and SiOx films [16-17]. According to our results, we have explored the possibility of the PL signals of the SiO$_x$ films studied is originated by the quantum confinement effect in the Si-ncs. So, the PL spectra (Figure 3) were analyzed in terms of a quantum confinement model more approximate to our results and more accepted [15,18]. In this model, the energy of the Si-nc gap, E$_N$ (eV) is defined as:

$$E_N(eV) = 1240/\lambda(nm) = 1.12eV + (3.73/d^{1.39}) \qquad (1)$$

Where λ is wavelength of the Si-nc emission and d is the diameter of the Si-nc; thus the Si-nc diameter can be deduced as:

$$d(nm) = \left[\frac{3.73}{E_N - 1.12}\right]^{\frac{1}{1.39}} \qquad (2)$$

Figure 5 a) and b) shows the results of applied equation (1) and (2), where is considerate only the values of the PL maximum peak (λ) of Figure 3. These obtained values indicate a reduction of the crystal size and the enlargement of the Si-ncs band gap as the substrate temperature decreases (black's boxes). In the same Figure are shown experimental values of energy band-gap $E_N$ obtained by means of the transmittance spectra of $SiO_x$ films and using the Tauc´s law [19]. Also, are shown the size Si-nc obtained by HRTEM (red circles). The average sizes of the Si-ncs obtained with equation (2) have a value of 2.25 to 3.30 nm and they are different with respect at the experimental values of the Si-ncs obtained of HRTEM in the range from 2.5 to 6 nm as show in figure 5 b). The inset of Figure 4 shows the statistical analysis of the HRTEM images of the Si-ncs size distribution in the $SiO_x$ films. The Si-nc mean size is 2.5, 4 and 6 nm for $SiO_x$ films deposited at 900, 1020 and 1150 °C, respectively. These results obtained with equation (1) and (2) seem to be in agreement with the quantum confinement effect, which predicts the progressive blue-shift of the PL peaks with decreasing crystal size due to the enlargement of the Si-nc band gap. However, our results were calculated with equation (1) and (2) and only the peak of maximum PL value was considered, and not the others peaks of the PL spectra. These others PL peaks can to involve amorphous silicon (as Si-nps) and another related with the role of defects. Furthermore, the Si-ncs size obtained from HRTEM is very different respect with the obtained with equation (2). Therefore, this result experimentally not followed the quantum confinement effect. On the others hand, the origin of the PL bands between (400-700nm) is usually ascribed to different effects as: quantum dots, defects at the Si/$SiO_2$ interface and defects associated with oxygen in the film. A detailed PL spectra study is on course and will be published. Therefore, it is possible that the substrate temperature produces another effects due at defects in the $SiO_x$ films such as: neutral charged oxygen vacancies (NOV) (Si-Si bonds), no bridging oxygen hole center (NBOHC), positively charged oxygen vacancies (E' centres), interstitial oxygen molecules and peroxide radicals [7,8,10-12]. Some of these radiative defects such as NOV, and NBOHC can be activated with the Ts during the process, which can form Si-nps or E' centres.

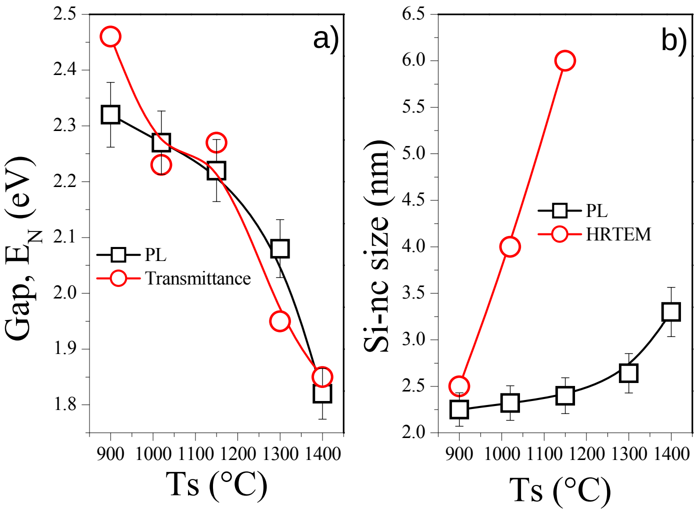


Figure 5. Experimental values of the a) Gap calculated of the equation (1) and Transmittance spectra, and b) Diameter of the Si-nc calculated of the equation (2) and HRTEM as a function of $T_s$.

## Conclusion

$SiO_x$ films deposited by HFCVD at different temperatures were studied. The results obtained of the equation (1) and (2) with the values of the PL maximum peak seem to be in agreement with the quantum confinement effect, which predicts the progressive blue-shift of the PL peaks with decreasing the Si-ncs size due to the enlargement of the Si-nc band gap. But, there are another PL peaks in the PL spectra that can to involve the role of the defects. Furthermore, the Si-ncs size by HRTEM and the gap energy of the Si-ncs obtained by transmittance spectra are different with these obtained with equation (1) and (2). Therefore and accordingly with these analysis, we proposed a combination of mechanisms to explain the photoluminescence in the films, where the dominant mechanism seem to be the quantum confinement effect in the Si-ncs with a contribution of the $SiO_x$/Si defects.

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