# Photoluminescence of as-grown and thermal annealed $SiO_x/Si$ -nanocrystals heterolayers grown by reactive rf sputtering

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 $SiO_x/Si$ -nanocrystals (Si NCs) heterolayers were fabricated employing a rf magnetron sputtering system. The synthesis process, through modification of the oxygen partial pressure of the plasma, promotes the synthesis of stoichiometric  $SiO_2$  layers and affect the Si NCs layer giving place to  $SiO_x/Si$  NCs (1.64 < x < 2) interfaces. All as-grown samples showed strong photoluminescence (PL) bands in the visible and near-infrared regions; transmission electron microscopy measurements confirmed the presence of Si NCs. Thermal annealing at 1100 °C promoted the SiO<sub>2</sub> stoichiometry in the interface and the crystallization of more Si NCs. The results allow us to clearly identify the origin of the PL bands; indicating that the near-infrared emission is related to the nonstoichiometric oxide while the red and green bands are originated in Si NCs. © 2010 American Institute of Physics. [doi:10.1063/1.3506424]

# **I. INTRODUCTION**

The photoluminescence (PL) from silicon nanocrystals (Si NCs) has been subject of considerable interest due to its potential applications in optoelectronic and display devices.<sup>1,2</sup> The growth of Si-rich SiO<sub>x</sub> (x < 2) films followed by thermal annealing is one of the most popular fabrication approaches for Si NCs because it is inherently a contaminant-free deposition method. The techniques to produce Si-rich oxide include chemical vapor deposition,<sup>3</sup> sputtering,<sup>4,5</sup> evaporation,<sup>6</sup> and pulsed laser deposition.<sup>7</sup> Despite that PL features have been widely reported, the fundamental mechanism in Si NCs PL is still unclear, primarily due to a lack of studies showing a clear distinction between luminescence originated from matrix defects and from NCs. Until now, most of the synthesis methods employed to grow Si NCs produce a broad distribution of size and a lot of oxygen-related defect centers in the oxide matrix; consequently the PL spectra of such materials are composed of broad bands.<sup>5–9</sup> In addition, the unsaturated bonds existing in the  $SiO_x/Si$  NCs interfaces reduce significantly the effective band gap and create localized states.<sup>10,11</sup> Therefore, the composition of the matrix surrounding the NCs plays a role of capital importance in the PL emission characteristics.

Previously, we have reported a novel approach employing reactive radio frequency sputtering to produce lightemitting semiconductor NCs embedded in a  $SiO_x$  matrix without the need to employ an additional process of thermal annealing.<sup>12</sup> In the present study, we use that methodology to study the properties of SiO<sub>x</sub>/Si NCs (1.64 < x < 2) heterolayers. All the as-grown samples showed strong PL emission in the visible and near-infrared (IR) regions; transmission electron microscopy (TEM) confirmed the presence of Si NCs. The characteristics of the PL spectra are well correlated with the presence of Si NCs and the particular SiO<sub>x</sub> stoichiometry in each sample. In order to identify clearly the origin of the PL bands, the samples were annealed at 1100 °C during 60 min in an Argon atmosphere. The annealing process promotes the SiO<sub>2</sub> stoichiometry of the oxide layers and the nucleation of Si NCs preferentially oriented in the (111) direction. The diminishing of the IR PL bands intensity along with the achievement of SiO<sub>2</sub> stoichiometry clearly indicated that their origin is associated to recombination in oxygen related defects. The weak dependence of the red band with the annealing indicates that it is mainly originated by recombination in Si NCs. After the annealing, a strong green emission shows up in the PL spectra, which is associated to the nucleation of Si NCs with  $d \sim 4$  nm.

## **II. EXPERIMENTAL DETAILS**

A set of  $SiO_x/Si$  NCs heterolayers was synthesized employing a radio frequency magnetron sputtering system. The samples were grown from a polycrystalline silicon target and deposited on Si (100) substrates heated at 400 °C. The silicon oxide layers were grown by reactive sputtering of the silicon target employing a plasma mixture of oxygen (O<sub>2</sub>) and argon (Ar); the Si layer was deposited whereas the oxy-

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gen flow was shutting off. The total gas pressure in the chamber was kept constant at 15 mTorr during the deposition process. The oxygen partial pressure (OPP) was determined with respect to the total gas pressure. After the deposition of each layer, the plasma was turned off and the chamber was evacuated to  $10^{-7}$  Torr, then the initial OPP condition was recovered for a second SiO<sub>r</sub> layer. The rf power applied to the target was 200 W. We prepared five samples employing different OPP to grow the silicon oxide layers: 25% (sample OPP25), 33% (sample OPP33), 50% (sample OPP50), 66% (sample OPP66), and 75% (sample OPP75). When the growth was finished, the samples were maintained inside the system until room temperature was attained. After the characterization, the as-grown samples were annealed inside a quartz tube furnace under a continuous Ar flux. We employed a heating rate of 3 °C/s until reach 1100 °C. The samples were annealed during one hour and then the system was turned off to allow a freely cool down under the inert atmosphere.

TEM observations were done using a TITAN system, equipped with a field emission electron gun operated at 300 kV. Scanning electron microscopy (SEM) images were obtained (with retrodispersed electrons) using a JEOL JSM-7401F, equipped with a cold cathode field emission gun operated to 2 kV. The crystallographic properties of the samples were studied by x-ray diffraction carried out in a Siemens D5000 system employing the Cu  $K_{\alpha}$  wavelength; with a grazing incidence angle of 3°. The IR spectra were obtained with a Nicolet 750 Fourier transform infrared (FTIR) system. PL measurements were carried out employing a lock-in standard technique, using a 275 M Acton single spectrometer equipped with a 1200 lines/mm grating blazed at 500 nm and a GaAs(Cs) Hamamatsu photomultiplier as detector, the width of both monochromator slits were set to 50  $\mu$ m; a 473.8 nm wavelength laser was employed as excitation source. A closed-cycle helium cryostat was used for low temperature measurements. The obtained PL spectra were corrected for the spectral sensitivity of the system.

#### **III. RESULTS AND DISCUSSION**

#### A. As-grown samples

The Fig. 1(a) shows a representative x-ray diffractogram (XRD) of the as-grown heterolayers; peaks were indexed using the powder diffraction file 271 402 for cubic silicon. The diffraction patterns confirm the presence of Si crystallites in all samples, as indicated by the presence of peaks corresponding to the (111), (220), and (311) planes. These planes have been previously observed though a two step thermal recrystallization process of a SiO<sub>2</sub>/Si superlattice.<sup>13</sup> In our case, the nucleation of as-grown crystals is promoted by the rough topography of the oxide films acting as a template.<sup>12</sup>

The  $SiO_x$  stoichiometry of the samples showed a clear dependence with the growth conditions. The as-grown sample OPP75 is the most representative for the discussion of this work: its growth process promotes the synthesis of Si NCs embedded within the oxide layers with the major departure from the SiO<sub>2</sub> stoichiometry. Figure 2(a) shows the TEM bright field micrograph of the as-grown sample OPP75,



FIG. 1. Representatives XRDs of (a) the as-grown and (b) the annealed samples.

it clearly shows the presence of Si NCs (black spots) embedded in an amorphous background. The statistical analysis of the particle diameters [Fig. 2(b)] shows a Gaussian distribution of sizes centered on 6 nm. These grain sizes are sufficiently small to observe quantum confinement (QC) effects but the associated energy levels change with the theoretical model selected.<sup>8,14,15</sup> Note that the high band gap of SiO<sub>2</sub> and the wide separation between Si NCs avoids the overlap of exciton wave functions.<sup>11</sup> High resolution TEM (HRTEM) allowed us to appreciate the structural characteristics of the Si NCs; as shown in Fig. 2(c) for a 9 nm Si NC, where the



FIG. 2. (a) TEM bright field image of the as-grown sample OPP75; it shows the presence of Si-NCs embedded in the SiO<sub>x</sub> matrix. (b) Size distribution of the nanocrystals obtained from Fig. 1(a). (c) HRTEM image of a Si-NC. (c) SEM image of the sample OPP75 after the thermal annealing.



FIG. 3. Oxygen composition x of the SiO<sub>x</sub> matrixes as obtained from the peak associated to the asymmetric Si–O–Si stretch transverse optical vibration in silicon dioxide IR spectra. The inset shows the shift in the transverse optic peak of the sample OPP75; from 1056 cm<sup>-1</sup> in the as-grown sample to 1080 cm<sup>-1</sup> in the annealed sample.

crystalline planes and the mismatch of different orientations are observed. It is worth to emphasize that the approaches employed up to date to obtain Si NCs embedded in an oxide host require the use of thermal annealing.<sup>3–5,9,16–19</sup> The approach reported here allows to produce Si NCs in a singlestep procedure. Fast Fourier transform (FFT) of the Fig. 2(c) (not included here) allowed to identify the (2–20), (220) and (400) planes of cubic silicon, with [001] as the axis zone. The FFT also showed weak spots related to Si (111) planes. It is worth to mention that the orientation of the NCs observed by the HRTEM coincides with the XRD results, suggesting that the film topography also influence the crystal grain orientation with respect to the substrate plane.

We employed FTIR spectroscopy to study the chemical composition of the samples. It is known that Si-O-Si groups give rise to several IR absorption signals due to different vibration modes. In particular, the stretching vibration of the oxygen atom in SiO<sub>2</sub> involves a strong band located on 1080 cm<sup>-1</sup>. Because of the strong electronegativity of the oxygen atom, this absorption frequency is a function of the oxygen content in SiO<sub>x</sub>.<sup>20</sup> We considered the relation x=(v-940)/70 between the frequency of the band, v, and the oxygen content x; the obtained values are plotted in Fig. 3. It is clear that the oxygen composition of the as-grown heterolayers decreases with OPP increase. It is worth to mention that an IR spectroscopy characterization of a set of oxide films, deposited under the same OPP conditions employed to grow the heterolayers, indicated the growth of SiO<sub>2</sub> samples independently of the OPP employed. Thus, indicating that, increasing OPP during the growth process of the heterolayers interacted directly with the Si NCs layer, giving place to lower x values in the  $SiO_x/Si$  NCs interface and consequently to more oxygen-vacancy defects around the Si NCs. Our results indicate that nearly stoichiometric interfaces can be achieved up to an OPP of 25%.

The continuous lines in Fig. 4 present the room temperature PL spectra of the as-grown samples. In order to clearly show the changes in the emission features, all spectra are normalized to its maximum intensity ( $I_{max}$ ). All samples



FIG. 4. Room temperature PL spectra of the as-grown (continuous line) and annealed (dashed lines) samples. (a) OPP25, (b) OPP33, (c) OPP50, (d) OPP66, and (e) OPP75. The dotted lines in (e) correspond to three Gaussians curves employed to fit the PL spectrum of the as-grown sample OPP75.

showed broad spectra dependent on the growth conditions; they become wider and its  $I_{max}$  position shifted to the IR region as OPP increase. A first analysis would suggest that as OPP increases the size of NCs becomes larger, as would be predicted by QC models;<sup>8,14,15</sup> nevertheless, XRD and TEM results discards definitely such interpretation.

A detailed study of the emission shows that all spectra are comprised of three Gaussian bands with different relative intensities, named peaks A, B, and C, respectively. As an example, the dotted lines in Fig. 4(e) show the Gaussians employed to fit the spectrum of sample OPP75. We found that the A and B contributions remain located at the same energy for all spectra. In contrast, the Gaussian C shifts its energy and its intensity gets stronger as the OPP increase. This behavior shows the presence of two physical mechanisms of emission in the spectra: a common mechanism to all samples responsible for the emission in the visible region and an OPP-dependent contribution that stimulate the broadening of the spectra toward the IR.

It is clear that the *C* band of the spectra grew up with the OPP until it gets strongest for sample OPP75. Besides, the energy position found for the *C* band show a systematical shift from 1.75 to 1.58 eV as *x* decrease from 2 to 1.64. Consequently, this band can be related to defects due to non-saturated Si bonds even though some authors have estables.



FIG. 5. Low temperature (14 K) PL spectra of the as-grown (continuous line) and annealed (dashed lines) samples. (a) OPP25, (b) OPP33, (c) OPP50, (d) OPP66, and (e) OPP75. The dotted lines in (e) correspond to three Gaussians curves employed to fit the PL spectrum of the as-grown sample OPP75.

lished that the PL emission related to defects have a range of energies only between 1.4 and 1.6 eV.<sup>21,22</sup> Contrary to the *C* band, the visible emission of the samples is not dependent of the composition of the SiO<sub>x</sub> matrix, consequently it is originated by a different physical mechanism. We have related the *A* and *B* contributions to QC effects in Si NCs. In agreement with this assumption, the spectrum of sample OPP25 is composed basically by *A* and *B* bands. A correlation between the PL features and the NC diameters will be discussed at the end of Sec. III B. Note that in contrast with previous reports,<sup>21,22</sup> the intensities of bands related to defects and NCs are comparable; indicating a relatively small quantity of defects in the samples.

To add further support to our assignation of the PL origin, we carried out PL measurements as function of temperature; the results are summarized in Figs. 5 and 6. The continuous lines in Fig. 5 correspond to the PL spectra of the as-grown samples obtained at 14 K. The spectra are normalized to its maximum intensity. The study of the low temperature (LT) spectra shows that they are comprised of the Gaussians bands A, B, and C; see for instance dotted curves in Fig. 5(e). The PL strength of each band is a function of temperature; as result the shape of the PL spectra changes as the temperature decreases. The ratio of the intensity of one band at low temperature to its intensity at room temperature



FIG. 6. The ratio of the intensities of the bands at low temperature to their intensities at room temperature is a measure of the change in strength with the temperature. (a) Values of  $R_i$  for the bands in the as-grown samples, (b) PL spectra of the As-grown OPP75 sample at different temperatures, (c) values of  $R_i$  for the bands in the annealed samples, and (d) PL spectra of the annealed OPP75 sample at different temperatures.

 $(R_i=I_{max} \text{ at } LT/I_{max} \text{ at } RT)$  allow describe the changes in its strength. The values obtained of  $R_i$  for each band are shown in Fig. 6(a). It is clear that the strength of the band *C* does not change notably, it is reflected in the magnitude of  $R_i$  close to the unity for all spectra; this behavior indicates an origin related to defects.<sup>23,24</sup> As shown in Fig. 5, at low temperature the strength of the bands *A* and *B* increases notably becoming the dominant contribution to the PL spectra. This behavior is characteristic of a PL emission due to QC in Si NCs.<sup>25,26</sup> As it is expected, the increase in  $R_i$  for the bands *A* and *B* as the OPP increase reveals the presence of a higher number of Si NCs in the more nonstoichiometric oxides.

Two mechanisms of radiative recombination in Si NCs are accepted to explain the PL emission. After the creation of the electron-hole pair inside the Si NC, radiative recombination can occur either within the NCs (QC) or at the NC surface in a defect state.<sup>27</sup> Recombination at defect states does not produce a shift in the PL peak as a function of sample temperature, while QC will produce a shift to higher energies.<sup>24,27</sup> Figure 6(b) shows the PL spectra of the asgrown sample OPP75 obtained at different temperatures. The dotted lines allow us to follow the shift in the bands A and B. The shift toward higher energies is related to the increase in the band gap energy via the electron-phonon interaction<sup>24,27</sup> and corroborates the origin of this PL band to QC in Si NCs. The absence of an energy shift in the C band is in accord to an origin related to defects. It is observed that from 300 to 100 K the shape of the spectra does not present significant changes. The strong increase in intensity of the bands A and *B*, mainly below 100 K, is in accord with a excitonlike recombination in Si NCs.<sup>25,26</sup> The higher yield emission of the band A, associated to the smaller NCs, can be associated to the stronger spatial localization of the electron and hole wave

functions in the dot.<sup>28</sup> The Fig. 6(b) also reveals that the intensity of the band *C* is reduced with the temperature while the *A* and *B* band increase in intensity. The behavior of the intensity of the PL bands observed in our samples indicates that the intensity of the band *C* is quenched when the recombination yield inside NCs augment. It can be observed in Fig. 6(a) that for all samples the  $R_i$  of the band *A* are larger than those of band *B*, thus indicating a higher recombination yield in the smaller Si NCs. This is explained because the smaller NCs have a larger surface to volume ratio.<sup>10</sup>

## **B.** Annealed samples

In order to get more details about the origin of PL emission, the whole set of samples was thermally annealed in an Ar atmosphere at 1100  $^{\circ}$ C for 60 min. We employ this temperature and a relatively long annealing time in order to get a major crystallization of the Si in the samples and to avoid the presence of defects in the oxide matrix.

After annealing, the XRD patterns of the whole set of samples presented only the Si diffraction peak related to the (111) plane; a representative diffractogram is shown in Fig. 1(b). The results indicate that the thermal treatment promotes the silicon nucleation with a sort of preferential grain orientation relative to the substrate plane. It is known that the classical nucleation theory predicts the lowest nucleation energy for the (111) facet; however, the picture of a unidirectional arrival of atoms in this model is not applicable for the three directional growth of NCs embedded in an oxide host.

Figure 2(d) shows a SEM micrograph of the annealed sample OPP75; the uniform layer corresponds to oxide layers. It can be observed the presence of a high density of Si NCs with a maximum size around 20 nm and a large amount of NCs with an average diameter of 14 nm. Note that the annealing process promoted the formation of well defined individual Si NCs (i.e., without coalescence); such phenomenon could be explained by the wide separation between NCs observed in the as-grown sample [Fig. 2(a)] and the low diffusivity of Si in SiO<sub>2</sub>.<sup>13</sup> The spherical shape of the thermally crystallized NCs is due to a competition between surface and volume tension.<sup>13</sup> It has been established that the (111) oriented crystal grains are almost spherical while other crystal orientations exhibit a strongly elongated shape.<sup>29</sup> As a result, the nucleation of individual NCs allow to preserve its spherical shape, that in turn inhibit the nucleation of those facets oriented in diverse directions.

The inset in Fig. 3 shows the IR spectra obtained from sample OPP75, as-grown and annealed. The shift in the stretching mode after annealing makes evident a change in stoichiometry in the  $SiO_x$ . Moreover, the composition of the whole set of annealed heterolayers corresponds to that of  $SiO_2$ , regardless of the growth conditions. As a consequence, the presence of defects in the interface is removed, especially in the more nonstoichiometric samples (i.e., those grown under the higher OPP values). In addition, the IR spectra show that the silicon in excess has nucleated to create more Si NCs. It is widely accepted that the nucleation process fol-

lows the relation  $\text{SiO}_x \rightarrow (x/2)\text{SiO}_2 + (1-x/2)\text{Si.}^{30}$  According to this expression, it is expected that more Si NCs grew in the more nonstoichiometric samples.

The dashed lines in Fig. 4 correspond to the PL spectra obtained from the annealed samples. According to the previous results, the annealing has a stronger influence on the luminescence of samples grown under the higher OPP values. First, note that the absence of the C band in all the spectra together with the IR spectroscopy results confirm that this band is originated by recombination in defects related to oxygen-vacancies. Figure 4(a) makes evident that even the spectrum of the as-grown OPP25 contains a slight contribution of defects (represented by the small peak around 1.75 eV), that is eliminated as consequence of the long annealing process. Furthermore, the spectra of the samples grown with the lower OPP values (characterized by the B contribution) do not present significant changes after the process. The stability of band B supports our interpretation of an origin related to Si NCs. Note that the *B* contribution is still present in all spectra despite the dominance of a new green contribution for samples grown with the higher OPPs. It is clear, from the IR results, that the PL bands around 2.2 eV are originated in Si NCs nucleated from the nonstoichiometric matrices. As expected, the strength of the bands associated with these new NCs is larger for those samples in which there was more silicon excess in the matrix.

The dashed lines in Fig. 5 present the PL spectra of the annealed samples obtained at 14 K. As expected, the band C related to defects is not present. The samples OPP33 and OPP50 show a PL band at 1.75 eV that due to its high  $R_i$ value can be attributed to recombination due to QC in Si NCs, despite that they are located in the zone of the band C. This feature of the PL spectra shows that the annealing process promotes the nucleation of new NCs even in the lower OPP samples. The vertical line in Fig. 5 allow us to follow the shift in the band A toward higher energies as OPP increases; the shift corroborates that the annealing process promotes the synthesis of smaller Si NCs in the more nonstoichiometric samples. The values of  $R_i$  obtained for each band are included in the Fig. 6(c). The  $R_i$  values are lower than those obtained for the as-grown samples as result of the absence of defects around the NCs after annealing.

Figure 6(d) shows the PL spectra of the annealed sample OPP75 obtained at different temperatures. The absence of the band *C* allows to observe clearly the evolution of the bands related to emission in NCs. The dotted lines allow us to follow the shift in the bands *A* and *B*. The fact that the PL spectrum just shifts in energy without change its shape suggests that the temperature dependence of the energy emission is the same for all NCs sizes.

A correlation of the luminescence data with the Si grain size is not easily accomplished because even when PL emission related to QC is observed, Si NCs without the right orientation with respect to the electron beam or Si NCs smaller that 1.5 nm cannot be detected by TEM.<sup>9,16</sup> There are several theoretical models proposed to obtain the energies of the quantum states associated to the PL emissions observed in Si NCs. Figure 7 presents the emission energy as a function of NCs size, as obtained with three highly cited QC



FIG. 7. Three QC models found in the literature (a) QC in crystalline silicon (Ref. 14), (b) QC in amorphous silicon (Ref. 15), and (c) QC in Si NCs assuming a size and shape distribution (Ref. 8). The PL spectra of the as-grown (continuous line) and the annealed (dashed line) sample OPP75 are superimposed to the figure for comparison effects.

models.<sup>8,14,15</sup> In order to make a direct comparison between the observed energies in the PL spectra and the chosen models we included the PL spectra of sample OPP75. According to the effective mass theory, the PL energy from QC can be modeled as:  $E = E_g + \hbar^2 \pi^2 / 8 \mu d^2$ , where  $E_g$  is the bulk Si band gap, d is the particle diameter, and  $\mu$  is the reduced mass of the electron-hole pair in Si. Because the lower value of  $E_g$  employed to obtain curve in Fig. 5(a),<sup>14</sup> the model predicts energies small enough to assign the C band of the spectra to quantum recombination at the bigger NCs observed by TEM, even when it has been clearly related to defects. The experimental evidence has suggested that to calculate correctly the emission energy of recombination at NCs it is necessary to employ an  $E_g$  value closer to that of the amorphous Si effective gap (1.6 eV), consequently the predicted PL emission energies are increased [curve in Fig. 5(b)].<sup>15</sup> Finally, a model that takes into account the randomness in size and shape of the NCs predicts higher QC energies [curve in Fig. 5(c)].<sup>8</sup> Considering the different models, it can be established that the best model to describe the emission in our samples is that represented by curve in Fig. 5(c).

As mentioned before, the theoretical model is in agreement with the interpretation that the annealing process promotes the nucleation of the silicon excess, giving place to the formation of luminescent Si NCs with sizes smaller than 4 nm.

#### **IV. CONCLUSIONS**

We presented here a successful single-step process which allows the production of  $SiO_x/Si$  NCs heterolayers with emission of light observable at room temperature. TEM analysis has demonstrated that as-grown samples contain Si NCs with diameters between 3 and 11 nm. The IR spectroscopy studies showed that the stoichiometry around of the NCs can be varied in the 1.64 < x < 2 range. The results allow identifying two different contributions of the PL: an IR band due to recombination processes in oxygen-vacancy defects and a red band originated in Si NCs. The thermal annealing of the samples promoted the stoichiometry of the matrix toward  $SiO_2$ , decreasing the PL emission related to oxygen vacancy defects. Additionally, the thermal treatment increased the size of the as-grown NCs and promoted the nucleation of more Si-NCs from silicon dispersed within the nonstoichiometric silicon dioxide matrix.

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