

## Bulk silica-based luminescent materials by sol-gel processing of non-conventional precursors

J. A. Rodríguez, C. Fernández-Sánchez, C. Domínguez, S. Hernández, and Y. Berencén

Citation: *Appl. Phys. Lett.* **101**, 171908 (2012); doi: 10.1063/1.4764561

View online: <http://dx.doi.org/10.1063/1.4764561>

View Table of Contents: <http://apl.aip.org/resource/1/APPLAB/v101/i17>

Published by the [American Institute of Physics](#).

---

### Related Articles

Three-photon near-infrared quantum cutting in Tm<sup>3+</sup>-doped transparent oxyfluoride glass ceramics  
*Appl. Phys. Lett.* **101**, 171108 (2012)

Debye-diffraction-based concentric energy analysis on two-photon photoluminescence imaging of gold nanorods under radial polarization illumination  
*J. Appl. Phys.* **112**, 083106 (2012)

Atomic-scaled investigation of structure-dependent luminescence in Sialon:Ce phosphors  
*Appl. Phys. Lett.* **101**, 161904 (2012)

From fabrication to mode mapping in silicon nitride microdisks with embedded colloidal quantum dots  
*Appl. Phys. Lett.* **101**, 161101 (2012)

Vanadium bound exciton luminescence in 6H-SiC  
*Appl. Phys. Lett.* **101**, 151903 (2012)

---

### Additional information on *Appl. Phys. Lett.*

Journal Homepage: <http://apl.aip.org/>

Journal Information: [http://apl.aip.org/about/about\\_the\\_journal](http://apl.aip.org/about/about_the_journal)

Top downloads: [http://apl.aip.org/features/most\\_downloaded](http://apl.aip.org/features/most_downloaded)

Information for Authors: <http://apl.aip.org/authors>

## ADVERTISEMENT

**Universal charged-particle detector  
for interdisciplinary applications:**

- > Non-scanning Mass Spectrometry
- > Non-scanning Ion Mobility Spectrometry
- > Non-scanning Electron Spectroscopy
- > Direct microchannel plate readout
- > Thermal ion motion and mobility studies
- > Bio-molecular ion soft-landing profiling
- > Real-time beam current/shape tuning
- > Diagnostics tool for instrument design
- > Compact linear array for beam lines

Contact **OI Analytical**: +1-205-733-6900



## Bulk silica-based luminescent materials by sol-gel processing of non-conventional precursors

J. A. Rodríguez,<sup>1,a)</sup> C. Fernández-Sánchez,<sup>2,a)</sup> C. Domínguez,<sup>2,a)</sup> S. Hernández,<sup>3</sup> and Y. Berencén<sup>3</sup>

<sup>1</sup>Facultad de Física, Universidad de La Habana, San Lázaro y L, 10400 Habana, Cuba

<sup>2</sup>Instituto de Microelectrónica de Barcelona, IMB-CNM(CSIC), Campus UAB, Bellaterra, 08193 Barcelona, Spain

<sup>3</sup>MIND-IN2UB, Dept. Electrònica, Universitat de Barcelona, Martí i Fanquès 1, 08028 Barcelona, Spain

(Received 11 September 2012; accepted 15 October 2012; published online 25 October 2012)

The sol-gel synthesis of bulk silica-based luminescent materials using innocuous hexaethoxydisilane and hexamethoxydisilane monomers, followed by one hour thermal annealing in an inert atmosphere at 950 °C–1150 °C, is reported. As-synthesized hexamethoxydisilane-derived samples exhibit an intense blue photoluminescence band, whereas thermally treated ones emit stronger photoluminescence radiation peaking below 600 nm. For hexaethoxydisilane-based material, annealed at or above 1000 °C, a less intense photoluminescence band, peaking between 780 nm and 850 nm that is attributed to nanocrystalline silicon is observed. Mixtures of both precursors lead to composed spectra, thus envisaging the possibility of obtaining pre-designed spectral behaviors by varying the mixture composition. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4764561>]

The old dream of developing an all-silicon integrated optoelectronic circuit begun to be considered a real possibility after the discovery of a visible photoluminescence (PL) radiation in porous silicon.<sup>1</sup> The radiation was related to quantum confinement effect taking place in silicon nanostructures (nanocrystals or nanoclusters, Si<sub>nc</sub> here after) embedded in a native silicon oxide matrix (Si<sub>nc</sub>/SiO<sub>2</sub>). However, the importance of defects in the interface between Si<sub>nc</sub> and SiO<sub>2</sub>, acting as radiative centers in a silicon rich silicon oxide layer there situated, was further established in this phenomenon.<sup>2</sup> In the last few years, the development of silicon-based optoelectronics has received a decisive improvement with the fabrication of different Si<sub>nc</sub>/SiO<sub>2</sub>-based light emitting diodes (LED)<sup>3–5</sup> and the observation of light amplification in Si<sub>nc</sub>,<sup>6</sup> opening a route towards a silicon injection laser.

Si<sub>nc</sub> embedded in a SiO<sub>2</sub> matrix may be obtained through a variety of techniques such as implantation of Si ions in thermal SiO<sub>2</sub>, co-sputtering, chemical vapor deposition, laser ablation, etc. In particular, sol-gel technique promises obtaining such a nanocomposite material in thin films as well as in bulk structures of any required shape with adequate structural and optical properties for light sources. Several papers have reported on the synthesis of this material by sol-gel with *in situ* (bulk<sup>7</sup> and thin film<sup>8</sup> configurations) and *ex situ*<sup>9–12</sup> formation of Si<sub>nc</sub>. However, the use of hazardous chemical precursors, such as the traditional triethoxysilane (TREOS), in the first case, and the complexity of the technological process, in the second one, are some of the difficulties these works have faced. Moreover, the absence of information about important aspects such as the low density of *in situ* formed nanostructures, that lead to luminescent radiation with low absolute intensity as well as the difficulties with the conservation of physical integrity during drying, cure, and

annealing, especially in thin films, is a common fact in most of published papers.

In the present work, the development of bulk luminescent materials based on the synthesis of silicon rich silicon oxides by sol-gel technique followed by one hour thermal treatment in inert atmosphere at temperatures in the range of 950 °C–1150 °C is reported. The possibility to obtain materials with pre-designed PL spectra by varying the parameters of the technological process is established. The main results as well as a general idea of the fundamentals are presented and discussed.

The starting material is obtained by the combined hydrolysis and condensation reactions of two different innocuous alkoxidisilanes: hexaethoxydisilane and hexamethoxydisilane. The idea is to obtain either silicon excess or oxygen defect (radiative) centers in this material, since both chemicals have a silicon-silicon bond in their structural units.

One set of samples was prepared for each of the two above-mentioned precursors. To prepare the *sol* solution, either the hexaethoxydisilane (C<sub>12</sub>H<sub>30</sub>O<sub>6</sub>Si<sub>2</sub>; Hexaet) (set 1) or hexamethoxydisilane (C<sub>6</sub>H<sub>18</sub>O<sub>6</sub>Si<sub>2</sub>; Hexamet) (set 2) was mixed with ethanol (EtOH/Hexaet(Hexamet), 2/1 in volume) and subsequently diluted in acidic water (pH = 5; H<sub>2</sub>O/Hexaet(Hexamet), 2/1 in volume). The resulting solution was vigorously stirred at room temperature in a sealed disposable beaker for two hours. During this step, the material started to condense. After that, small holes were open in the lid of the beaker, and the polymer material was left to further condense and dry for at least two days at room temperature, until a solid was obtained. Finally, the sol-gel material was dried in a furnace at 80 °C for 48 h. Other samples were also synthesized by using mixtures of both precursors (different proportions, Hexamet/(Hexaet + Hexamet), in volume) (set 3). For all sets, the resulting bulk materials were annealed in a N<sub>2</sub> atmosphere for one hour at temperatures in the range of 950 °C–1150 °C. The raising and decreasing temperature rates were 5 °C/min from and up to room temperature, respectively. As-synthesized samples exhibit a somewhat

<sup>a)</sup>Authors to whom correspondence should be addressed. E-mails: jar@fisica.uh.cu, cesar.fernandez@imb-cnm.csic.es, and carlos.dominguez@imb-cnm.csic.es.

different external appearance for sets 1 and 2. For the former, samples look like a hard, dense, and translucent solid, whereas those ones from hexamethoxydisilane (set 2) exhibit a white, more opaque and in some cases (depending on the original product lot), dust-like aspect. After annealing, the differences persist and Hexaet-based material exhibits a dark-red color, which predominates in the mixtures and is lightened when using very low proportions of this precursor. In all cases, as-synthesized samples are quite brittle and may lose its physical integrity during cure and annealing. Therefore, great care must be taken, especially with thin samples, during these processes. However, this is not the case after annealing, when a mechanically stable ceramic material is obtained.

Figures 1–3 depict room temperature PL spectra corrected with the spectral response of the setup of sets 1–3 materials, respectively, for different annealing temperatures and compositions. They were obtained by means of an Ocean Optics QE65000 spectrometer with an integration time of 1 s, unless otherwise stated. Continuous wave excitation was accomplished by using the 325 nm line of a 30 mW He-Cd laser. A 350 nm long pass filter (please observe the shoulder at about 390 nm in most of PL curves) was utilized to eliminate laser radiation from the emergent beam, which was collected by a lens system and directed to a microscope objective coupled to a 1 mm silica core optical fiber. PL spectra show very interesting features as well as important differences for both precursors utilized, depending on the thermal process parameters, as will be described and justified below.

As-synthesized material emits luminescent radiation, which is especially high for sets 2 and 3 (see Figures 1–3),

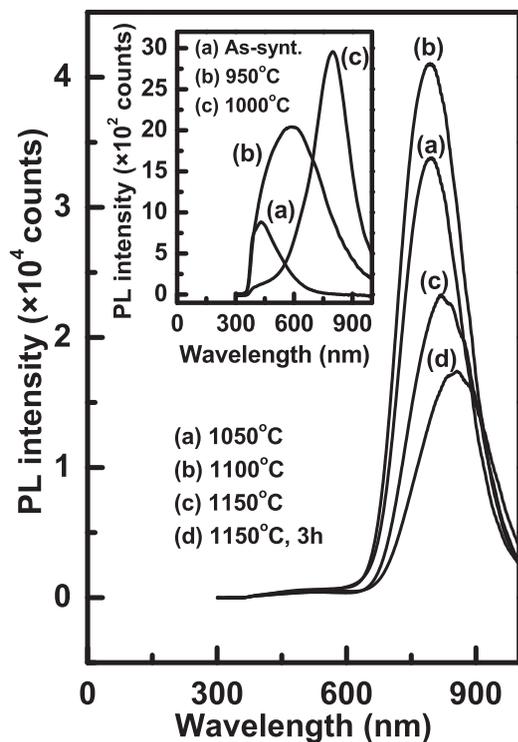


FIG. 1. PL spectra for hexamethoxydisilane-based samples (set 1), annealed during hour (if not specified), at different temperatures. Low intensity curves are separately shown in the inset for clarity.

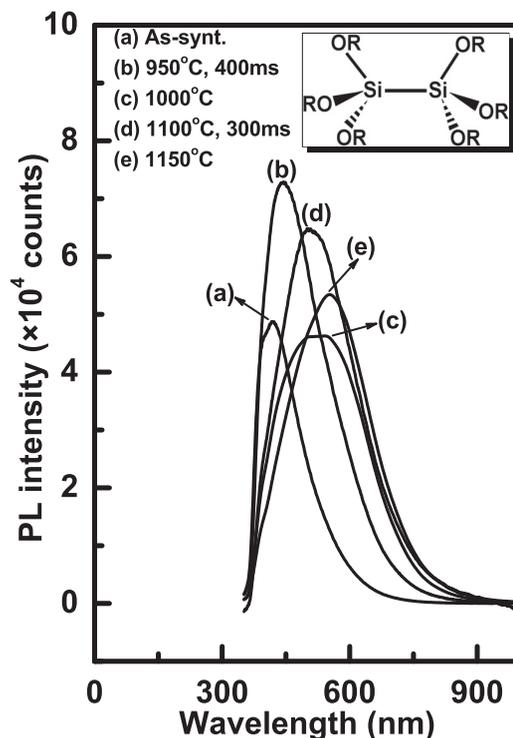


FIG. 2. PL spectra for hexamethoxydisilane-based samples (set 2) annealed at different temperatures. Integration time is one second unless otherwise stated. Inset shows the structural basic unit of both alkoxydisilanes.

with approximately the same spectral line-shape. This result apparently contradicts previously published works,<sup>8</sup> where no appreciable PL emission was observed in this case. It suggests a low density of non-radiative recombination centers in

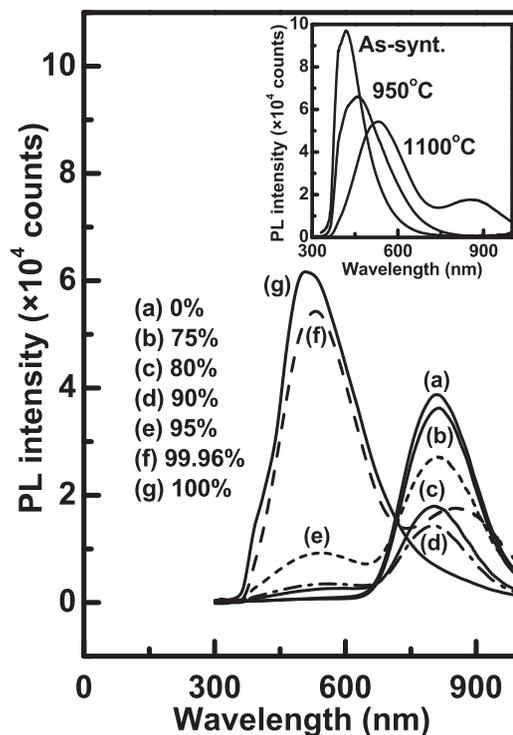


FIG. 3. PL spectra for samples prepared with mixtures of both alkoxydisilanes (set 3), annealed at 1100 °C. Samples are denoted according to their % Hexamet content in respect of the total volume. Inset shows PL spectra for 99.96% Hexamet, as-synthesized and annealed at 950 °C and 1100 °C.

our materials, even before annealing. This fact could be of significant practical importance since losing of physical integrity during annealing at high temperatures may be, in our opinion, one of the most important drawbacks of sol-gel materials, especially in thin film configuration. The luminescent behavior of as-synthesized samples can be understood by referring to the structural basic unit of hexaethoxydisilane and hexamethoxydisilane, which is generically shown in the inset of Figure 2. It represents silane monomers of the type  $(OR)_3SiSi(OR)_3$ , where  $OR-$  is a hydrolysable alkoxy groups and R is either an ethyl or methyl group, respectively.

The kinetics of the hydrolysis and condensation reactions strongly depends on the solution pH.<sup>13</sup> At the acidic pH used in this work, the ethoxy or methoxy group could be protonated, so that a water molecule could react with the silane and carry out a nucleophilic substitution with one of these groups, thus liberating an ethanol or methanol molecule and generating a silanol group (Si-OH). Further, during the condensation reaction of the hydrolyzed monomers, the formation of the Si-O-Si bonds (and, consequently, of the silicon oxide matrix) from the reaction of two silanol groups occurs, thus liberating a water molecule. Si-Si bonds are still present in the matrix and might be the basis of the observed blue PL band (at around 420 nm), in the form of neutral oxygen vacancy or other oxygen-deficient radiative centers.<sup>14</sup>

Very important differences appear in PL spectra for sets 1 and 2 (Figures 1 and 2, respectively) in the analyzed annealing temperature range. Inset of Figure 1 shows the PL intensity rise and the significant evolution of spectral line-shape for samples of set 1 annealed at 950 °C in respect of the as-synthesized material. Likewise, special attention deserves the curve for 1000 °C. Its shape and peak position suggest the presence of Si<sub>nc</sub> embedded in a SiO<sub>2</sub> matrix.<sup>15</sup> Moreover, in Figure 1, a drastic increase in PL intensity is observed by rising annealing temperatures up to 1050 °C (the same spectral line-shape and position as for 1000 °C), with a maximum for 1100 °C, and a decrease of intensity as well as a redshift of the PL maxima for a further increase of thermal budget (curves for 1150 °C one hour annealing, and 1150 °C three hours annealing). All these circumstances clearly suggest the presence of a luminescence mechanism by quantum confinement effect in nanometer-sized silicon crystals embedded in silicon oxide matrix (Si<sub>nc</sub>/SiO<sub>2</sub>).<sup>15</sup> Indeed, as annealing temperature increases, initially the segregation of the exceeding silicon occurs, leading to the formation of Si<sub>nc</sub>, the density of which rises (curves for 1000 °C–1100 °C), thus producing a rise of PL intensity. A further increase of annealing temperature (or time) leads to the growth of largest Si<sub>nc</sub> at expense of smallest ones (the so called “ripening” phenomenon), giving rise to a redshift in qualitative agreement with quantum confinement model and a decrease of PL intensity. The presence of silicon nanocrystals in Hexaet-based (set 1) samples was verified by Raman spectroscopy and high resolution transmission electron microscopy (HRTEM). Raman measurements were accomplished in a Horiba Jobin-Yvon LabRaman microsystem by using the 532 nm line of a double harmonic of a Nd:YAG continuous wave laser. HRTEM micrographs were obtained in a JEM 2011 microscope (Jeol Ltd., Japan) at 200 kV acceleration voltage and 0.18 nm resolution. Figure 4 depicts

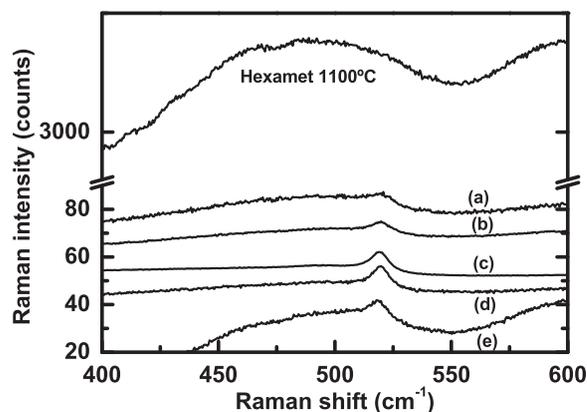


FIG. 4. Raman spectra for samples of all sets treated one hour (if not specified) above 1000 °C. Curves (a)–(d) correspond to Hexaet-based samples (set 1) treated at 1050, 1100, 1150, and 1150 °C (3 h), respectively. Curve (e) is from a mixture with 95% Hexamet (set 3). In top of the figure a curve for Hexamet-based sample (set 2), annealed at 1100 °C, is shown.

Raman spectra for some samples of all sets treated above 1000 °C. Observe the sharp peaks at around  $518\text{ cm}^{-1}$ – $520\text{ cm}^{-1}$  in Hexaet-based samples (curves a–d), which is an evidence of the presence of Si<sub>nc</sub> embedded in a SiO<sub>2</sub> matrix.<sup>7,16</sup> Moreover, the peaks are more pronounced for increasing annealing temperature and time, in accordance with the precedent analysis. On the other hand, nanocrystals with diameter of about 3–5 nm and interplanar distances of 0.30–0.33 nm, attributed to (111) planes of crystalline silicon, were also observed by HRTEM in samples of this set, annealed one hour at 1100 °C (image not shown for shortness).

The characteristics of PL spectra for Hexamet-based (set 2, Figure 2) samples differ significantly from the ones described above. For all annealing temperatures, a very intense PL radiation is obtained, which is observed to naked eye under daylight conditions, with a maximum for 1100 °C. Besides, PL spectra peak in the range of 400–600 nm depending on the annealing temperature and extended to longer wavelengths. We believe that this behavior should not be associated to quantum confinement in Si<sub>nc</sub>. Rather, they should be the consequence of activation and deactivation of definite radiative recombination mechanisms associated to different oxide matrix defects, as well as the annealing out of non-radiative recombination centers, taking place during thermal processing.<sup>17</sup> Two other experimental results further confirm the precedent hypothesis. On the one hand, the presence of Si<sub>nc</sub> in Hexamet-based samples was observed neither by Raman spectroscopy nor by HRTEM, even for the highest thermal budget (annealing treatment at 1150 °C for 3 hours). On the other hand, time-resolved PL (TR-PL) measurement for samples of sets 1 and 2 lead to PL decay time constants, which are typical of the proposed luminescent mechanisms. Indeed, TR-PL measurements for these samples were carried out by using the third harmonic of a 5-ns pulsed Nd:YAG laser ( $\lambda = 355\text{ nm}$ ) and a repetition rate of 10 Hz. The temporal evolution was detected by a GaAs PMT with a temporal resolution of 10 ns and recorded by a 500 MHz digital oscilloscope. For a Hexaet-based sample treated at 1100 °C, PL decay curve, centered at 780 nm, follows a double exponential function with time constants of 70 and 9  $\mu\text{s}$ . For a Hexamet-derived one, the decay

curve, measured at 550 nm, also fitted a double exponential, but with time constants of 17 and 31 ns. Since the width of the excitation pulse is 5 ns and the time response of the detector is of the same order of magnitude, we can barely confirm that the PL decay time constants for these latter samples are of the order of nanosecond. Therefore, PL decay times of the order of  $\mu$ s and ns are obtained for samples of sets 1 and 2 annealed at 1100 °C, respectively. This is a clear indication that the emission is associated to quantum confinement in Si<sub>nc</sub> embedded in SiO<sub>2</sub> matrix and radiative recombination by oxide defect centers for sets 1 and 2, respectively, in accordance with other authors.<sup>9</sup>

We believe that the differences observed in PL behavior for samples of set 1 and 2, annealed in the range of 950 °C–1100 °C, are due to differences in the evolution of the composition and microstructure of as-synthesized samples during the first stages of the annealing process. Indeed, for Hexaet-based material, the formation of nucleation and growth centers takes place during this process, thus favoring the segregation of exceeding silicon and the formation of Si<sub>nc</sub>. This is not the case for Hexamet-based samples, for which, on the contrary, the breaking of Si-Si bonds may occur. The origin of this different behavior may be associated with differences in the kinetics of the hydrolysis and condensation reactions taking place during the polymer formation for Hexaet and Hexamet-based materials, leading to differences in composition and microstructure of as-synthesized materials. A just concluded full study of these aspects is out the scope of the present space limited Letter and will be published soon.

Finally, Figure 3 shows the PL spectra for samples synthesized from mixtures of both alkoxidisilanes, annealed at 1100 °C. Very interesting features are observed. For Hexamet content from 0% to about 75%, PL spectra reproduce exactly the behavior corresponding to Hexaet-based material, i.e., a unique maximum at around 800 nm, due to quantum confinement luminescent mechanism, is observed. For values higher than 75%, measured spectra exhibit a composed line-shape, each part of which could be associated to a component of the mixture independently (even though the effect of hexaethoxydisilane predominates for Hexamet contents as high as 95%). This fact suggests the simultaneous presence of both radiative recombination mechanisms, i.e., recombination by quantum confinement in Si<sub>nc</sub> (typical for Hexaet-derived material) and by oxide defect centers (typical for Hexamet-based samples). The sharp maximum in the Raman spectrum corresponding to this last composition can be observed in Figure 4, thus denoting the presence of Si<sub>nc</sub>. Besides, TR-PL measurements were carried out in this sample. The PL decay curves obtained at 550 and 820 nm maxima fitted exponential and double exponential functions with time constants of 10 ns and 9–80  $\mu$ s respectively, which further confirm the proposed statement. An extreme composition was necessary (99.96% Hexamet, the limit composition that was possible to measure with adequate accuracy in our laboratory) to observe the predominance, in PL spectrum, of Hexamet behavior. We believe that even an extremely small proportion of hexaethoxydisilane in the mixture would be high enough to produce nucleation and growth centers, through which the exceeding silicon due to hexamethoxydisilane could be segregated.

An additional observation should be made. Since irregular bulk samples have been measured, some variations in the relative intensity of both maxima may be observed when the laser beam falls on different points of the sample. This is due to the effect of self-absorption. In Figure 3, the spectra with the highest intensity in the low wavelength peak, for the same sample, are reported. This drawback should be eliminated when working with thin films.

Lastly, the inset of Figure 3 shows the PL spectra for samples synthesized from a mixture with 99.96% hexamethoxydisilane, as-obtained and annealed at 950 °C and 1100 °C. It can be observed that for the two former cases, the PL behavior is the one corresponding to Hexamet-based material. Therefore, annealing at temperatures about or higher than 1000 °C is necessary to produce the silicon segregation and, consequently, to obtain the composed PL spectra.

In conclusion, two innocuous silicon alkoxidisilanes have been used, separately and as a mixture, to synthesize bulk silica-based luminescent materials through a sol-gel route. Their excellent luminescent properties, in particular the PL spectra, can be engineered in a wide property range by suitable selection of synthesis and thermal treatment parameters. The possibility of using these materials in bulk or in thin film configurations to develop silicon-based light sources, opto-chemical transducers and so on is envisaged.

The authors acknowledge the financial support of CSIC project, PIE, ref. 200950I197 and Spanish MINECO-DGI project, ref. TEC2010-17274. They are also grateful to Professor B. Garrido for supporting TR-PL measurement. Y.B. acknowledges financial support from the Subprograma de Formación de Personal Investigador FPI-MICINN (TEC2009-08359).

<sup>1</sup>L. T. Canham, *Appl. Phys. Lett.* **57**, 1046 (1990).

<sup>2</sup>L. N. Dinh, L. L. Chase, M. Balooch, W. J. Siekhaus, and F. Wooten, *Phys. Rev. B* **54**, 5029 (1996).

<sup>3</sup>A. Irrera, D. Pacifici, M. Miritello, G. Franzo, F. Priolo, F. Iacona, D. Sanfilippo, G. Di Stefano, and P.G. Fallica, *Physica E* **16**, 395 (2003).

<sup>4</sup>R. J. Walters, G. I. Bourianoff, and H. A. Atwater, *Nature Mater.* **4**, 143 (2005).

<sup>5</sup>J. Barreto, M. Perálvarez, J. A. Rodríguez, A. Morales, M. Riera, M. López, B. Garrido, L. Lechuga, and C. Dominguez, *Physica E* **38**, 193 (2007).

<sup>6</sup>L. Pavesi, L. Dal Negro, C. Mazzoleni, G. Franzo, and F. Priolo, *Nature* **408**, 440 (2000).

<sup>7</sup>G. D. Soraru, S. Modena, P. Bettotti, G. Das, G. Mariotto, and L. Pavesi, *Appl. Phys. Lett.* **83**, 749 (2003).

<sup>8</sup>G. Das, L. Ferraioli, P. Bettotti, F. De Angelis, G. Mariotto, L. Pavesi, E. Di Fabrizio, and G. D. Soraru, *Thin Solid Films* **516**, 6804 (2008).

<sup>9</sup>J. Dian, J. Valenta, K. Luterova, I. Pelant, M. Nikl, D. Muller, J. J. Grob, J. L. Rehspringer, and B. Hönerlage, *Mater. Sci. Eng. B* **69–70**, 564 (2000).

<sup>10</sup>E. Borsella, M. Falconieri, S. Botti, S. Martelli, F. Bignoli, L. Costa, S. Grandi, L. Sangaletti, B. Allieri, and L. Depero, *Mater. Sci. Eng. B* **79**, 55 (2001).

<sup>11</sup>A. Dima, F. G. Della Corte, C. J. Williams, K. G. Watkins, G. Deardena, N. O'Hare, M. Casalinob, I. Rendinab, and M. Dima, *Microelectron. J.* **39**, 768 (2008).

<sup>12</sup>K. Luterová, K. Dohnalová, V. Svrcek, I. Pelant, J. P. Likforman, O. Crégut, P. Gilliot, and B. Hönerlage, *Appl. Phys. Lett.* **84**, 3280 (2004).

<sup>13</sup>J. D. Wright, N. A. J. M. Sommerdijk, "Sol-gel materials chemistry and applications," in *Advanced Chemistry Text Series, Vol. 4*, edited by Taylor & Francis Group (CRC, FL, 2000).

<sup>14</sup>Salh and Roushdey, "Defect related luminescence in silicon dioxide network: A review," in *Crystalline Silicon—Properties and Uses*, edited by S. Basu (InTech, Rijeka, 2011), pp. 135–172.

<sup>15</sup>F. Iacona, G. Franzo, and C. Spinella, *J. Appl. Phys.* **87**, 1295 (2000).

<sup>16</sup>S. Hernández, A. Martínez, Y. Lebour, P. Pellegrino, E. Jordana, J.-M. Fedeli, and B. Garrido, *J. Appl. Phys.* **104**, 044304 (2008).

<sup>17</sup>Z. Songand and X. M. Bao, *Phys. Rev. B* **55**, 6988 (1997).