

## Si nanocrystals obtained through polymer pyrolysis

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In this letter, we report the formation of bulk samples of silica-based glass containing Si nanocrystals (Si-ncs) by pyrolysis of a preceramic precursor. The starting precursor is a sol-gel-derived polysiloxane containing only Si-H groups which leads, after annealing in a controlled atmosphere in the range 1000–1200 °C, to the precipitation of Si-ncs. Characterization of the nanostructure was performed by x-ray diffraction and Raman scattering analyses. Room-temperature luminescence experiments show the interesting optical properties of the Si-ncs/SiO<sub>2</sub> material. © 2003 American Institute of Physics. [DOI: 10.1063/1.1587876]

Silicon photonics have the potential to continue the evolution of microelectronic devices predicted by Moore's law.<sup>1</sup> A big impediment toward this target is the lack of any practical light source based on silicon.<sup>2</sup> A possible solution is the use of silicon nanocrystals (Si-ncs) formed in a suitable matrix.<sup>3</sup> Up until now, the most widely used method to produce Si-ncs, is based on the formation of substoichiometric silica films, with a large excess of Si, followed by a high-temperature annealing.<sup>4</sup> The annealing leads to a phase separation between the two constituent phases, i.e., Si and SiO<sub>2</sub> with the formation of small Si-ncs. Here, we propose an approach based on polymer pyrolysis to form room-temperature luminescent Si-ncs.

Polymer pyrolysis allows one to obtain nanostructured multicomponent ceramics with exceptional high-temperature properties such as thermal stability up to 2200 °C (Ref. 5) and oxidation/creep resistance far better than chemical vapor deposition grade polycrystalline nitride and carbide.<sup>6</sup> The process consists of two essential steps. First, the metalorganic precursor is polymerized into a rigid plastic form, for example, in a fiber or film configuration. Second, these forms are pyrolyzed under controlled conditions to convert them into ceramics. Usually pyrolysis is conducted up to a maximum temperature of 1000 °C when an amorphous covalent ceramic is obtained.<sup>7</sup> Polymer-derived ceramics belong to two families: The silicon oxycarbide (SiCO) and the silicon-carbonitride (SiCN).<sup>8</sup> SiCO glasses are mainly obtained after pyrolysis of sol-gel-derived precursors.<sup>9</sup> By starting from silicon alkoxides containing Si-CH<sub>3</sub> and Si-H groups, it is possible to form SiCO glasses in which SiC-, C-, and Si-ncs are homogeneously dispersed.<sup>10</sup>

In this letter, the starting silica-based preceramic network containing Si-H groups was obtained by hydrolysis-condensation reactions (sol-gel method) of H-Si(OCH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub> (triethoxysilane, T<sup>H</sup>). Triethoxysilane was purchased from ABCR and used without any further purification. T<sup>H</sup> was dissolved in ethanol (EtOH) with a T<sup>H</sup>/EtOH ratio of 0.5 and hydrolyzed with acidic water (pH=4.70 by HCl) using hydrolysis ratios

$R=[\text{H}_2\text{O}]/[\text{T}^{\text{H}}]=2-3$ . Due to the high reactivity of triethoxysilane,<sup>11</sup> the hydrolysis was conducted in an ice bath. The gelling solutions were stirred for 20 min before casting into plastic test tubes. Samples were left open at room temperature. Gelation occurred in a couple of hours. Gels were then dried at room temperature for one week and then at 80 °C for an additional week. Monolithic, transparent, cylindrical samples 6 by 30 mm<sup>2</sup> were obtained in this way. From these samples, thin gel disks, 0.5–1 mm thick, were subsequently obtained by sectioning the original monolithic gels. Pyrolysis was performed in an alumina tubular furnace in flowing Ar (100 ml/min) at temperatures in the range 1000–1200 °C. Heating was performed at 5 °C/min and with holding times at the maximum temperature in the range 1–4 h. Accordingly, monolithic brown-looking Si-ncs/SiO<sub>2</sub> nanocomposites were obtained.

Fourier transform infrared (FTIR) spectra collected on the starting gel (not reported here) showed the typical pattern of a H-SiO<sub>1.5</sub> gel with an absorption band at 2250 cm<sup>-1</sup> assigned to the stretching of Si-H group in T<sup>H</sup> units.<sup>12</sup> The absence of absorption bands at 2900 cm<sup>-1</sup> (C-H stretching), at ≈1663 cm<sup>-1</sup> (H-O-H bending) and in the range 4000–3000 cm<sup>-1</sup> (O-H stretching) suggests that residual Si-OEt groups and water are not present or are below the detection limit of the technique.

FTIR spectra recorded on pyrolyzed samples display the typical absorption of silica-based glasses at 1100 cm<sup>-1</sup> (Si-O stretching), 790, and 460 cm<sup>-1</sup> (Si-O bending). They no longer show the band at ≈2250 cm<sup>-1</sup> which suggests that Si-H bonds have been completely consumed during the pyrolysis process.

X-ray diffraction (XRD) studies were carried out and analyzed by the Rietveld method, using the fully automated code RIETQUAN.<sup>13</sup> The evolution of the XRD spectra of the pyrolyzed samples as a function of the pyrolysis temperature is reported in Fig. 1. At 1000 °C, the XRD spectrum is typical of a disordered material with just a broad halo at 2Θ=22° due to amorphous silica. Starting from 1050 °C, the spectra are characterized, by broad diffraction peaks at 2Θ=28°, 48°, and 56°, beside the main halo at 2Θ=22°. These diffraction peaks indicate the presence of cubic crystalline sili-

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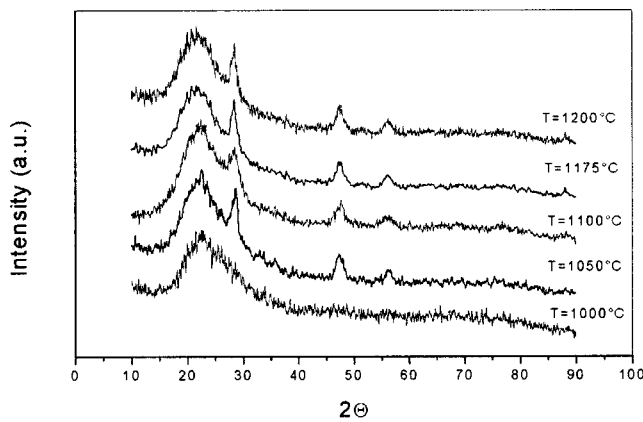


FIG. 1. XRD spectra recorded on samples synthesized with  $R=3$  and pyrolyzed in Ar for 1 h at: 1000 °C, 1050 °C, 1100 °C, 1075 °C, and 1200 °C.

con. The profile analysis by the Rietveld method indicates that the size of Si crystals is in the range of 3–5 nm, and slightly increased with the pyrolysis temperature (Table I). Hence Si-ncs have been formed. The presence of Si-ncs in the pyrolyzed glasses and their dimensions are in good agreement with the results of a transmission electron microscopy study performed on similar Si/SiOC samples.<sup>13</sup>

The formation of Si-ncs into the pyrolyzed materials was also confirmed by a Raman study (Fig. 2). Raman scattering measurements were carried out at room temperature by means of a microprobe setup consisting of an Olympus microscope (model BHS-M-L-2), equipped with an objective 100 $\times$  of numerical aperture  $N_A=0.95$ . Raman spectra of samples treated above 1000 °C show the presence of a sharp peak at about 516–519  $\text{cm}^{-1}$ , with spectral features (peak position, shape, and width) typical of Si-ncs formed in dielectric matrices.<sup>14,15</sup> These spectral features depend on the hydrolysis ratio  $R$  [Figs. 2(a) and 2(b)] and on the pyrolysis temperature [Figs. 2(b) and 2(c)]. The spectral differences of the Si-ncs peak from samples with  $R=2$  [Fig. 2(a)] and  $R=3$  [Fig. 2(b)] pyrolyzed at 1100 °C for 4 h indicate a smaller average size (peak redshift from 516.5 to 518.0  $\text{cm}^{-1}$ ) and a wider (more spread) size distribution (higher width value) of the Si-ncs for  $R=2$ . The effect of the hydrolysis ratio on the size of the Si-ncs is not understood yet. However, it shows that this is an additional parameter, besides the maximum annealing temperature and holding time, which can be used to control the Si-ncs size. Indeed, in a sample with  $R=3$ , the Raman peak moves from 518.0  $\text{cm}^{-1}$  [Fig. 2(b)] to 518.5  $\text{cm}^{-1}$  [Fig. 2(c)] when the pyrolysis temperature rises from 1100 °C to 1200 °C, while its bandwidth decreases versus  $T$ . Thus, the increase of the pyrolysis temperature seems to favor the formation of larger Si-ncs (peak blueshift) with a more homogeneous size distribution (width decrease).

A photoluminescence spectrum of a typical sample annealed at  $T=1100$  °C is reported in Fig. 3. Due to the forma-

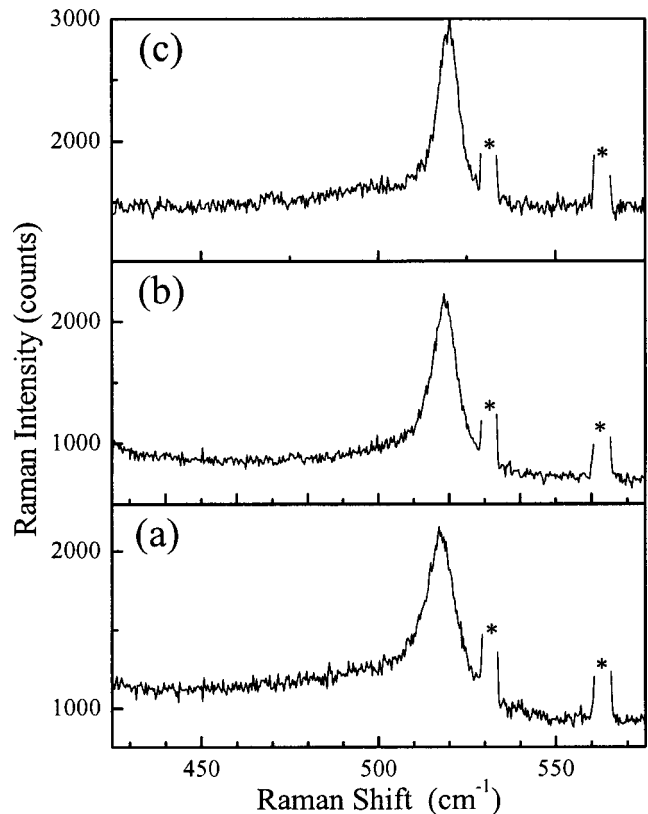


FIG. 2. Room-temperature Raman spectra carried out under excitation at 488.0 nm on samples obtained from precursors synthesized with two different hydrolysis ratio,  $R$ , and pyrolyzed at different temperature ( $T$ ): (a)  $R=2$  and  $T=1100$  °C for 4 h, (b)  $R=3$  and  $T=1100$  °C for 4 h, and (c)  $R=3$  and  $T=1200$  °C for 1 h. The asterisks (\*) label the positions of two plasma lines used as energy standards.

tion of Si-ncs a wide emission band appears at about 780 nm. This luminescence is typical of nanometer-sized Si-ncs.<sup>4</sup> The Si-ncs emission band shifts toward longer wavelengths and narrows with increasing the temperature from 1000 °C to 1200 °C (see inset of Fig. 3). The peak position is related to the size of the Si-ncs and the width to their distribution. Thus, the observed evolution confirms that, by increasing the pyrolysis temperature, the size of the Si-ncs grows and their

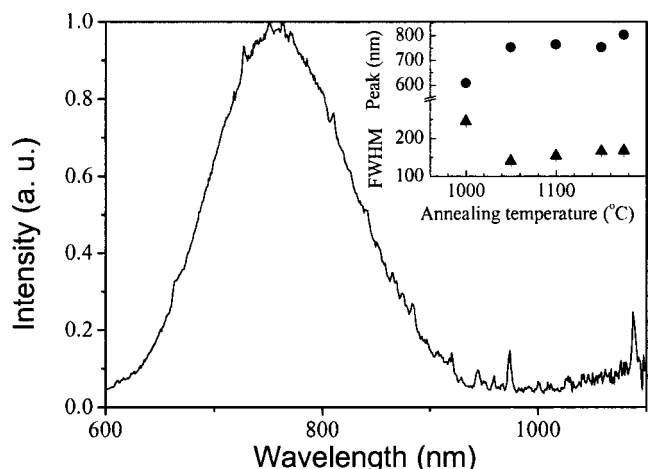


FIG. 3. Photoluminescence spectrum of a typical Si-ncs/SiO<sub>2</sub> sample annealed at 1100 °C. The inset shows the evolution with the pyrolysis temperature of the peak position and of the full width at half maximum. All of the data refer to samples synthesized with  $R=3$  and 1 h of holding time at the maximum temperature.

TABLE I. Diameter of Si-ncs as a function of pyrolysis temperature. The values are obtained from the Rietvel analysis of the XRD spectra.

Pyrolysis temperature (°C)	1000	1050	1100	1175	1200
Crystal size (nm) $\pm 10\%$	...	3.0	3.6	4.0	4.4

distribution narrows, in agreement with the XRD results.

The Si-ncs features in XRD and Raman measurements are only observed for samples annealed at a temperature higher than 1050 °C. For lower annealing temperatures, luminescence measurements show a wide emission band at 600 nm which we can tentatively attribute to either very small Si-ncs whose size is too small to be measured by XRD and Raman or to silicon–oxide related defects. XRD measurements suggest that a threshold temperature for Si-ncs formation can be estimated at 1050 °C: For lower temperature Si-ncs do not nucleate, or have extremely small sizes and density.

In conclusion, we have shown that luminescent Si-ncs embedded into a silica-based matrix can be formed through polymer pyrolysis of a preceramic network obtained via the sol–gel route. This process is highly flexible for structuring the Si-ncs samples and can be used to fabricate a wide range of components: From massive bulk layers (as reported in this letter) to thin films (by dip or spin coating on suitable substrates) or, even, to fibers. This process does not have to be restricted to the thin-film geometry as other more conventional methods. In addition, dopants can be easily introduced in the starting solution in order to form coupled systems, e.g., Si-ncs coupled to Er ions, and exploit the sensitising action of Si-ncs.

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