The structural and optical properties of supercontinuum emitting Si nanocrystals prepared by laser ablation in water

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Laser ablation of Si(100) targets immersed in deionized water at room temperature was studied by applying the second harmonic of a ns pulsed Nd:YAG laser and by employing different methods for characterization of the resulting nanocrystals (NCs). Spontaneous Raman scattering showed first order Raman spectra of the Si NCs, which varied in their Raman shift and width. The Raman data were analyzed using a phonon confinement model, involving three-dimensional confinement and lognormal size distributions for the nanocrystallites constituting the samples, indicating the presence of particles greater than ~2 nm diameter. High-resolution transmission electron microscopy and electron diffraction of the as-prepared samples showed NCs with diameters greater than ~1.75 nm and quantum dots, corresponding to Si/SiOx. The optical properties of the Si NCs were studied with cathodoluminescence (CL) spectroscopy for sample temperatures in the 50–300 K range, which exhibited a supercontinuum emission ranging from the near ultraviolet to the red regions. The emission is characterized by four major emission bands, peaked at 1.88, 2.18, 2.64 and 3.44 eV, which practically remain at the same positions as the temperature is varied. These bands are assigned to excitonic recombination in the Si NCs, whose electron/hole transition energies are consistent with the quantum confinement of carriers in four size-dispersed groups of Si NCs. The influence of electron beam irradiation on the passivation of the NCs was examined, showing quenching of the CL as a function of electron-beam exposure time. This quenching is attributed to desorption of hydrogen, disruption of the NC surface passivation, and formation of nonradiative recombination channels involving surface states in the gap. The approach used in this study demonstrates the possibility of growing nano-scale Si crystals with the potential for incorporation into optoelectronic devices or for use in biomedical applications.

I. INTRODUCTION

Nanoparticles attract considerable interest since they might exhibit properties that can differ extensively from those of materials in bulk and particularly lead to fascinating potential applications. This is due to the fact that the small size nanoparticles can result in unique size-dependent properties, including magnetic, electrical, optical and chemical, which cannot be achieved by bulk materials. For instance, bulk silicon is an extremely inefficient light emitter and therefore can play only a minor role in optoelectronics. On the other hand, since the discovery of the visible (red) photoluminescence (PL) from porous silicon, silicon-based nanostructures with controlled composition and dimensions are increasingly being studied for novel applications in optoelectronics, including lasers, light emitting diodes (LEDs), and solar cells as well as for biological applications like cellular and molecular imaging, cell labeling and tracking, multiplexed analyses, and DNA detection.

A variety of methods have been used for the preparation of silicon nanoparticles with specific tailored properties, including chemical synthesis, chemical vapor deposition (CVD), pulsed laser deposition, laser ablation in liquid (LAL), as well as other methods. While LAL is considered to provide new avenues for preparation of nanostructures with various compositions (metals, alloys, oxides, carbides, hydroxides, etc.) and morphologies (nanoparticles, nanocubes, nanorods, nanocomposites, etc.) it has been only rarely used for preparation of Si nanocrystals (NCs). For instance, blue luminescent Si NCs were prepared by nanosecond (ns) pulsed laser (355 nm) ablation in de-ionized water at room temperature and atmospheric pressure. These particles exhibited a distribution of diameters ranging from 2 to 50 nm with mean aggregate sizes of 20 nm. Yang et al. have shown that the size of Si crystals prepared by the fundamental of a ns Nd:YAG laser (1064 nm) can be controlled by choosing different liquid media, where those prepared in pure ethanol showed average diameters of 3–7 nm and were significantly smaller than those prepared in water. Very recently, small Si NCs (3–5 nm diameter) were fabricated in a two step process, including ns laser (355 nm) ablation of a silicon target in chloroform and ultrasonic post-treatment of the Si nanoparticles in HF.

The above examples show the potential of LAL, but also the effect of different parameters, including laser wavelength, laser energy, solvent, etc., on the produced Si NCs sizes and characteristics. Here we will use ns LAL of a silicon target, immersed in deionized water, which is moreover
considered as a contamination-free green preparation method. A 532 nm beam with pulses of relatively low fluence was focused on the target with the goal of fabricating sufficiently small Si NCs (i.e., possessing diameters less than $\sim 5$ nm), so as to exhibit quantum confinement effects. In comparison to previous LAL studies, we observed four distinct size-dispersed groups of Si NCs that were analyzed with a unique combination of structural and optical characterization methods, which enabled the application of a Raman confinement model and a carrier recombination model.

II. EXPERIMENT

A. Laser ablation in liquid

Preparation of Si nanoparticles was achieved by using the system displayed in Fig. 1. The beam of the second harmonic of a ns pulsed Nd:YAG laser (Continuum, Powerlite 8010) (532 nm, 10 Hz, $\sim 6$ ns) was focused onto the wafer surface by a cylindrical lens of 6 cm focal length (f.l.), resulting in laser pulse fluence of $\sim 136$ J/cm$^2$. The Si(100) wafer was immersed in 2.6 ml of high purity deionized water and held at the bottom of a 100 ml glass container. There is an advantage of using water as a solvent, since its vapor pressure is generally lower than that of most organic solvents. The laser beam irradiated the target at room temperature and at ambient pressure for three and half hours, resulting in an exposure of $\sim 130$ 000 pulses. The container was translated during the ablation process to avoid continued irradiation of the same position of the target and to reduce crater formation. A persistent plasma plume on the Si target surface could be observed during the laser ablation. The focusing conditions were determined not only by the target position with respect to the focusing lens but also by the water layer thickness above the surface.

During the course of the laser ablation, identical conditions were maintained by fixing both the target—lens distance, the water thickness, laser spot size, and the fluence of the incident beam. The target translation in the $x$, $y$ directions was achieved by two motorized stages (Thorlabs, TDC001), and controlled by our LabVIEW code. Following the ablation, different quantities of the colloidal dispersion (Si-NCs in water) were taken and applied on different substrates for characterization by Raman spectroscopy, cathodoluminescence (CL), and transmission electron microscopy (TEM). In particular for Raman spectroscopy, four drops of 8 $\mu$l colloidal solution were applied sequentially on the same small area of a glass microscopic slide and dried at ambient conditions. Similarly, for CL, 60 drops of 8 $\mu$l of the colloidal dispersion were applied on a copper substrate and for TEM, 1 drop of 5 $\mu$l was applied on a carbon grid (Tedpella, 01824TN).

B. Raman microspectroscopy

Raman spectra of the original target and films were monitored using a confocal Raman microscope (Jobin Yvon, Labram HR UV) with excitation by a diode laser at 784.79 nm of about 10 mW power, injected via a 50/0.75 objective. The back scattered light was then directed via a sharp long wavepass filter into a 0.8 m dispersive spectrometer equipped with a 1800 grooves/mm grating and combined with an air cooled charged coupled device, consisting of 1024 $\times$ 256 pixels. Successive recordings of Raman spectra from the Si samples, prepared by LAL, allowed monitoring of the characteristic Raman shifts at about 1 $\mu$m spatial resolution. The definition of the measurement parameters and measuring control was done by the LABSPEC 4.04 software. The time for each measurement was 20 s.

C. Transmission electron microscopy

TEM images and electron diffraction (ED) patterns of nanoparticles deposited on carbon grids were recorded on an electron microscope (JEOL 2100F Field Emission Electron Microscope). The TEM images were produced by the DigitalMicrograph—image acquisition and processing software.

D. Cathodoluminescence spectroscopy

The CL experiments were performed on a modified JSM-5910 scanning electron microscope (SEM). The CL detection system has been described previously in detail. An electron-beam ($e$-beam) energy ($E_b$) of 25 keV and beam currents ($I_b$) of 50 pA to 2 nA were used to excite and create excess carriers in the Si NCs. A UV multialkali photomultiplier tube operating in the 185 to 850 nm spectral range enabled photon counting of the luminescence emitted by the Si NCs which was dispersed by a monochromator with a 0.25 m f.l. The spectral resolution was set to $\sim 1$ nm. The samples were mounted in the SEM on a variable temperature and vibrationally isolated cold stage that was cooled with a closed-cycle cryo-cooler and were maintained at temperatures ranging from 50 to 300 K. The CL spectra were acquired while the $e$-beam was raster scanned over various regions of the sample with areas fixed at $128 \times 96$ $\mu$m$^2$. Exposure of the $e$-beam was observed to quench the luminescence from the Si NC samples. The quenching of the CL emission intensity and the influence on the spectral lineshape were studied as a function of $e$-beam current and $e$-beam exposure time.
III. RESULTS AND DISCUSSION

A. Raman spectroscopy of the Si nanoparticles

Raman spectra were measured and analysed for obtaining information about the size distribution of the Si NCs produced by LAL. As can be seen from Fig. 2, the Raman spectrum shows besides the first-order characteristic peak of crystalline Si at 520.7 cm\(^{-1}\) (scattering of a transverse optical (TO) phonon mode), two additional weaker and broader features, centered around 960 and 300 cm\(^{-1}\). These bands correspond to the second-order optical phonon (2TO), and the second-order transverse acoustic phonon mode (2TA) (the two phonons must have equal but opposite wave vectors to fulfill momentum conservation). Since the second-order Raman signals are quite weak, the following measurements were focused only on the first-order Raman peak.

Taking advantage of the spatial resolution provided by the Raman microscope (~1 \(\mu\)m), the Si NCs, fabricated by LAL, were characterized by measuring the Raman spectra in different regions of the samples [see Fig. 3(A)]. Their measurement is possible, even if their size is much smaller (see below) since they aggregate, leading to Si polycrystallines. Thus, a particular Raman spectrum is measured by sampling many NCs at a specific position in a sample. When the sample is \(x,y\) translated, additional spectra at other positions in the polycrystalline or in the sample can be measured.

Representative Raman spectra, measured at various positions in the Si samples, are shown in Fig. 3(B). As observed in the figure, they differ one from the other and, for instance, by measuring the Raman spectra at different positions of the Si polycrystalline, shown in Fig. 3(A)(ii), the red, black, magenta, and cyan spectra were obtained. It can be immediately seen, that the peaks, corresponding to the TO phonon mode, are characterized by different shifts and widths, a behavior that was attributed to the phonon confinement effect. In particular, in a bulk crystal, the first-order Raman scattering probes the frequency of the optical phonon at the \(\Gamma\)-point in the Brillouin-zone, due to the \(\Delta k = 0\) selection rule. However, as the crystal dimensions are reduced, this selection rule is lifted, and the frequency distribution of the scattered light includes a broader interval in \(k\)-space around \(\Gamma\).

In recent years, a few models describing the effect of Si NCs on Raman spectra\(^{27-34}\) were developed, and it was found that the size distribution has a little effect on the Raman...
frequency shift, but greatly affects their width and shape. We chose to employ the model of Ke et al.\textsuperscript{35} for analyzing the measured Raman spectra. This model is an expansion of the model of Faraci et al.\textsuperscript{36} which was shown to be most sensitive to Si NC size distribution. By accounting for the size distribution of the Si nanoparticles, the resulting intensity of the Raman scattering could be calculated and compared to the measured spectra. By fitting the results of the calculated model to the experimental spectra, we were able to determine the size distribution for the various Si NC samples. A simulation code, was written in MATLAB, and it provides as an output the best fit spectrum, as compared to a particular measured spectrum, while accounting for the most probable diameter of the Si NCs, D\textsubscript{0}, and the size distribution. The parameters a and b of the model (see below) correspond to the smallest and largest particles in the polycrystals, respectively.

The intensity of the Raman scattering ensuing from the Si nanoparticles is given by the following expression:\textsuperscript{35}

\[
I(\omega, D) \propto \int_{a}^{b} \frac{1}{4\pi} \frac{\left| C(q, D) \right|^2 q^2 dq}{\left( \omega - a'(q) \right)^2 + \left( \frac{\omega}{\Gamma} \right)^2} \times \exp \left( - \frac{\ln \left( \frac{D}{D_0} \right)^2}{2\sigma^2} \right) dD,
\]

where C(q,D) is the probability amplitude of the phonon with an initial wave vector k\textsubscript{p}, q is the wave vector in the Brillouin zone, D\textsubscript{0}(q) is the phonon dispersion curve, \Gamma is the natural Lorentzian line shape and \sigma is a parameter used to describe the size distribution width. As mentioned above, this model calculates the Raman energy shift, due to the confinement and due to the breakdown of the selection rule, for Si NCs. By analyzing the first order Raman scattering measurements, shown in Fig. 3(B) with the above mentioned code, the peak positions, size distribution width, most probable diameter, and smallest and largest parameters of the distribution were obtained and are given in Table I. As can be seen from Fig. 3(B), the measured and calculated Raman spectra agree very well and indeed, the calculated \(R^2\) for all the spectra, based on the least square approximation, was \(>0.99\).

The results of Table I show that the most probable diameter for the measured Si nanoparticles is in the 2.4–10 nm range, with the smallest distribution parameter corresponding to 2.1 nm. It is important to mention that the Raman confinement model for Si NCs is sensitive only to particles of diameters below \(\sim 10\) nm.\textsuperscript{36} For \(D_0 = 10\) nm, the calculated Raman spectrum is unaffected by size distribution and the spectrum is almost similar to that of bulk Si, mainly due to the weak phonon confinement effect in large Si NCs. The peak position for Si crystals of 10 nm diameter is calculated to be 520.70 cm\(^{-1}\) and indeed the blue Raman spectrum in Fig. 3(B) corresponds to a peak centered at 520.66 cm\(^{-1}\), implying that the diameter of the detected particles is 10 nm or above, with a natural width of 4 cm\(^{-1}\).

The results presented here show that it is possible to detect and quantify the size of Si nanoparticles by measuring their Raman spectra and analyzing them with the Raman confinement model. The comparison of the calculated spectra to the measured ones enabled a determination of (i) the absolute intensity of the Raman features for the Si polycrystallines and (ii) the most probable diameter and the distribution of the nanoparticles in the polycrystalline. Of particular note is the asymmetry of the Raman peak, Fig. 3(B), which increases as particles of smaller sizes become more dominant (as shown in Table I), confirming the presence of Si NCs within the samples produced by LAL.

B. Transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS) analysis

To corroborate the presence of the Si nanoparticles found by Raman spectroscopy, their morphology was also studied by TEM. The TEM micrograph in Fig. 4 shows that the sizes of the polycrystallines are in the 70–400 nm range. However, the dark field TEM image of a \(\sim 480\) nm size polycrystal, in Fig. 5 shows that it consists of many nanoparticles. Moreover, the high-resolution TEM (HRTEM) image of a \(\sim 160\) nm size polycrystal Fig. 6(i) shows that it is composed of many NCs, which can be seen from the expanded

<table>
<thead>
<tr>
<th>Measured Raman spectra</th>
<th>Peak position (cm(^{-1}))</th>
<th>(\sigma)</th>
<th>(D_0) (nm)</th>
<th>a-b (nm)</th>
<th>Measurement position</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blue</td>
<td>520.66</td>
<td>-</td>
<td>10</td>
<td>-</td>
<td>i</td>
</tr>
<tr>
<td>Red</td>
<td>520.34</td>
<td>0.2</td>
<td>7.0</td>
<td>5.5–8.5</td>
<td>ii</td>
</tr>
<tr>
<td>Green</td>
<td>519.63</td>
<td>0.3</td>
<td>4.6</td>
<td>4.0–5.2</td>
<td>iii</td>
</tr>
<tr>
<td>Black</td>
<td>519.04</td>
<td>0.1</td>
<td>4.2</td>
<td>3.3–5.5</td>
<td>ii</td>
</tr>
<tr>
<td>Magenta</td>
<td>517.09</td>
<td>0.3</td>
<td>3.5</td>
<td>2.1–5.0</td>
<td>ii</td>
</tr>
<tr>
<td>Cyan</td>
<td>516.12</td>
<td>0.3</td>
<td>3.0</td>
<td>2.1–3.7</td>
<td>ii</td>
</tr>
<tr>
<td>Yellow</td>
<td>514.98</td>
<td>0.3</td>
<td>2.4</td>
<td>2.1–2.8</td>
<td>iii</td>
</tr>
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</table>

FIG. 4. TEM micrograph of Si polycrystallines prepared by LAL of Si targets embedded in deionized water.
portion of the rectangular area shown in Fig. 6(ii) and is characterized by groups of lattice fringes aligned in a few directions. The polycrystalline material was also analyzed at the point marked as \( a \) in Fig. 6(i), using EDS for local chemical analysis. According to the spectrum shown in Fig. 6(iii), the composition at this point corresponds to [Si] 95.43 wt. % and [O] 4.57 wt. %, implying that the polycrystal contains mainly Si, as well as some small amount of SiO\(_x\). For comparison, the EDS spectrum in Fig. 6(iv), as measured at point \( b \) of Fig. 6(i) and which represents the background in the vicinity of the polycrystal, corresponds to [Si] 37.57 wt. % and [O] 63.43 wt. %. This means that the composition of the surround background matrix differs from that of the polycrystal and exhibits a lower Si/SiO\(_x\) ratio. It is worth noting that in addition to Si and O, the EDS spectra also show peaks corresponding to Cu and C, due to a contribution from the grid. It is important to note that other NCs have shown different EDS spectra and different Si/SiO\(_x\) ratios which depend on their size and their thickness.

Moreover, an ED pattern obtained from an area, whose size is \( \sim 100 \times 100 \) nm\(^2\) is presented as an inset to the HRTEM image of Fig. 7. The pattern reveals the presence of (111), (220) and (311) crystallographic planes of crystalline Si whose interplanar spacings are 0.313, 0.194, and 0.166 nm, respectively, further confirming the formation of Si nanocrystals during the LAL process.

The representative TEM micrograph in Fig. 8 allowed for a further determination of the size distribution of the Si NCs, by using the DigitalMicrograph—image acquisition and processing software. As observed in Fig. 8, the particles are spherical in shape [panel (i)] and of small sizes [panel (ii)], particularly for those marked by the red arrows. The Si NCs sizes are in the 1.75–18.09 nm range, peaking at a size of 3 nm. This size distribution agrees very well with the findings from the Raman spectra, which showed a presence of Si NCs as small as 2.1 nm.

Figure 9(i) shows a HRTEM image of an isolated \( \sim 7 \) nm diameter Si quantum dot (QD), whose crystalline structure is revealed by the observed set of (111) lattice planes, exhibiting an interplanary spacing of 0.300 nm that characterizes bulk Si crystal. The particle has a cubic...
structure as determined from the fast Fourier transform (FFT) analysis of the interplanar spacing in the marked area of the crystals, as shown in the ED pattern of the inset. The observed strong ring patterns reveal interplanar spacings of 0.300, 0.194, and 0.163 nm, which again correspond to the (111), (220), and (311) planes, respectively, of crystalline Si.

C. Cathodoluminescence (CL) spectroscopy

A stack-plot of CL spectra is shown in Fig. 10 for various Si nanocrystal sample temperatures ranging from 50 to 300 K. In order to minimize the influence of the e-beam induced degradation, the e-beam raster scan was performed over fresh un-exposed regions of the sample, each having a 128 × 96 μm² area, for each spectrum at a fixed temperature. The relative intensity scale for each spectrum has been adjusted according to the scale factors shown to the left of each CL spectrum in Fig. 10.

The CL spectra exhibit distinct peaks and shoulders whose relative intensities are found to vary with temperature. In order to analyze the spectra and to better estimate the peak positions and widths, we have deconvolved each of the spectra into four Gaussian components, labeled P1-P4, using a nonlinear least-squares fitting procedure available in the Origin graphical software. The intensities, peak positions, and full-widths-at-half maximum (FWHM) of the Gaussian components were allowed to vary during the fit. The FWHM reflects the inhomogenous broadening of the components due to a distribution of QD sizes that form for a particular group of NCs. The results of the deconvolution are shown in Fig. 11 for temperatures of 50, 150, and 300 K. The fitting was performed for Gaussian components as a function of photon energy and is being presented as a function of wavelength in Fig. 11. In addition, a broad cubic background function (labeled B in Fig. 11), due to the possible emission from carrier recombination in the surrounding SiOₓ matrix, was added to the Gaussian components during the fit in order to account for small differences in the CL intensity baseline at wavelengths of ~200 and 800 nm. The results of the fits are shown in Figs. 12 and 13. The energy positions for Gaussian components P1- P4 as a function of temperature are shown in Fig. 12 for two cases involving beam currents of 1 and 2 nA. While small fluctuations in the peak positions are observed, most variations are within the typical error bars that are shown for each peak. The fits yielded average FWHMs of 0.75, 0.54, 0.37, and 0.14 eV for peaks P1-P4, respectively, and reflect the distribution in NC sizes which are discussed below. The relative constancy of the peak positions as a function of sample temperature also supports the notion that radiative excitonic transitions in confined levels of the four size-dispersed groups of Si NCs, represented by peaks P1-P4, are responsible for the luminescence.

In order to establish consistency between the size distribution of the Si NCs as obtained from TEM and extracted from the Raman confinement model described above, we have compared our results with those of Kim et al.,38 who have measured the PL energies for excitonic transitions in similar Si NCs embedded in a silicon nitride film as a function of NC diameter. By empirically fitting their PL results, Kim et al. determined that \( E_{\text{gap}}(D) = 1.16 + 11.8/D^2 \), where \( E_{\text{gap}} \) is the effective band gap energy for excitonic emission from Si NCs in eV and \( D \) is the diameter in nm.38 The results are shown in Fig. 14. We have likewise included our CL peak energy positions and their FWHMs (as shown with error bars) for components P1-P4 in the figure. The resulting diameters \( D \) of the Si NCs that correspond to the

![FIG. 7. HRTEM micrograph and the inset shows the electron diffraction pattern of the Si polycrystal shown in Fig. 6(i) possessing real space diameters of 0.313, 0.194, and 0.166 nm, corresponding to the (111), (220) and (311) planes of crystalline Si, respectively.](image)

![FIG. 8. TEM image of the Si nanoparticles prepared by LAL of a silicon target embedded in deionized water (i) and the corresponding size distribution (ii). The red arrows mark the position of several small nanosized crystals.](image)
emission components P1-P4 are approximately 2.27 ± 0.19, 2.83 ± 0.26, 3.41 ± 0.31, and 4.05 ± 0.20 nm, respectively, as shown in Fig. 14. These nanoparticle sizes are consistent with the size distribution observed in the TEM results of Fig. 8 and with the diameter ranges extracted from the Raman confinement model presented in Table I.

We have examined the temperature dependence of the relative CL intensity of the Gaussian components. The fraction of the integrated CL intensity, \( x_i \), for each of the peaks, \( P_i \), is plotted versus temperature in Fig. 13. The integrated CL intensities have been normalized such that \( \Sigma x_i = 1 \). Typical error bars are indicated for each peak intensity. The relative intensities of peaks P1-P3 remain approximately constant, within the uncertainties, as a function of temperature over the 50–300 K range suggesting that the excess carrier distribution among the three groups of Si NCs is also insensitive to the temperature. Since the NCs are surrounded by a SiO\(_x\) matrix, a temperature-independent carrier distribution in the NCs suggests that a negligible carrier transfer and redistribution of excess electron (\( e \)) and hole (\( h \)) populations occur among the ensemble of Si NCs contained with the polycrystalline matrix or cluster as the temperature is varied in the 50–300 K range. Due to a low carrier mobility in the amorphous SiO\(_x\) matrix, a negligible carrier transfer (and communication) between the various groups/clusters of Si NCs is expected. The relative intensity for P4 decreases for lower temperatures.
the highest temperatures approaching 300 K, suggesting that thermal activation of excited carriers into the surrounding SiOx matrix may play an important role for the largest Si NCs whose emission is in the P4 band.

The deleterious effect of e-beam exposure is unavoidable with CL, as the luminescence from the Si NCs was observed to rapidly decrease as a function of e-beam exposure time. However, in this particular study, the e-beam induced quenching of the luminescence may provide important clues regarding the nature of the surface passivation and the origin of the luminescence from the Si NCs. In Fig. 15, the intensity for each of the components P1-P4 is shown as a function of e-beam exposure time for T = 50 K. The component intensities decay rapidly and exponentially by factors ranging from ~3 to 5 in the first minute, followed by a much slower rate of decay and leveling off of the decay curves in the time range of 3 to 10 min. The luminescence decay process is irreversible, as attempts at interrupting the exposure, warming the sample to room temperature, and exposure to air failed to restore the initial CL intensity observed for initially unexposed regions of the sample.

An e-beam induced reduction of luminescence centers has been observed in related porous Si, which was synthesized using electrochemical etching. While porous Si has been studied extensively with PL, the rapid degradation caused by e-beam exposure has resulted in far fewer studies with CL. Maurice et al. have found that exposure of porous Si to high energy (20 keV) e-beam bombardment leads to a disruption of S-H bonds that correlate with the rapid decrease in the emission intensity. A similar decrease of emission intensity during e-beam exposure has likewise been observed.

![FIG. 12. The energy positions of peaks P1-P4 obtained from the fits to the CL spectra shown in Figs. 10 and 11 for various temperatures in the 50 to 300 K range. The results are shown for beam currents of 1 and 2 nA. Typical error bars are shown.](image1)

![FIG. 13. The normalized integrated CL intensity, x, for each of the peaks, P, versus temperature (i = 1–4). The intensities were obtained from the fits to the CL spectra shown in Figs. 10 and 11 for various temperatures in the 50 to 300 K range.](image2)

![FIG. 14. The measured effective band gap energy for Si nanocrystals as a function of quantum dot diameter from the results of Kim et al. (Ref. 38). The CL peak energies from the fits, the FWHMs (indicated by the error bars) for components P1-P4, and the calculated range of QD diameters for each component are shown in the graph.](image3)
associated with the desorption of hydrogen in hydrogenated amorphous silicon (a-Si:H). Since the preparation of the Si nanoparticles involves laser ablation in water, the presence of OH$^-$ and H$^+$ species, in addition to oxide formation (SiO$_x$), in the passivation of the Si nanostructures is expected. Thus, we hypothesize that persistent high-energy $e$-beam irradiation will likewise desorb hydrogen or disrupt bonds involving various hydrogen related species (e.g., Si–H$_x$, $x = 1–3$) that are essential in the passivation of the Si nanoparticles. In the absence of a well-passivated Si nanoparticle, additional nonradiative recombination channels associated with surface/interface states in the gap are expected to form and compete with the radiative recombination channels.

In order to explain the partial quenching of the CL from the Si NCs that is caused by $e$-beam irradiation, we consider two possible models that are schematically illustrated in Fig. 16. In model (a), the zero-dimensional quantum confinement of $e$-$h$ pairs gives rise to the large oscillator strength radiative channel ($\tau_R$) believed to exist in a well passivated Si QD. Several authors have explained and provided evidence for the relaxation of momentum conservation laws for optical transitions involving an indirect bandgap material such as Si for small diameter ($\sim 4–5$ nm) QDs. As explained above, persistent $e$-beam irradiation is expected to result in the removal of the hydrogen passivation layer, resulting in an electronic density of states (DOS) at the Si QD surface/interface that can exist within the gap, as illustrated in the right panel of Fig. 16(a). These surface states may participate in various nonradiative recombination channels ($\tau_{NR}$), possibly involving a combination of electrons and holes generated or captured in the QD, as schematically shown.

A second possible process is illustrated in (b) in which surface/interface states already exist as part of the encapsulation of the Si nanoparticle in the SiO$_x$ matrix and participate with carries confined in the QD to give rise to radiative transitions responsible for the current emission spectra. Subsequent $e$-beam irradiation in this model would disrupt the passivation layer, leading to a progressively diminished surface DOS that participates in radiative transitions, while leaving in its wake a surface/interface DOS in the gap that is involved in nonradiative processes. In order to decide as to which of the models best describe light emission in the current samples, we observe that the quenching of the luminescence (i.e., the occurrence of only a partial quenching of the luminescence), the model in (a) is preferred.

FIG. 15. The decay of the CL intensity components P1-P4 as a function of $e$-beam exposure time for $T = 50$ K and $I_b = 1$ nA. The $e$-beam was raster scanned over separate regions of the sample each having an area of $128 \times 96 \mu$m$^2$ for each of the decay curves shown.

FIG. 16. A schematic illustration of radiative ($\tau_R$) and nonradiative recombination ($\tau_{NR}$) channels in the Si NCs. Two possible models are shown in which radiative recombination occurs by (a) recombination of confined electrons and holes in the Si quantum dots and by (b) participation of carries in surface/interface states with confined carries in the Si QDs. An electronic surface/interface density of states vs energy ($E$) is illustrated. The irradiation with the high energy $e$-beam apparently desorbs hydrogen or disrupts Si–H bonds, resulting in the presence of nonradiative recombination channels that compete with the radiative recombination channels. Due to the persistence of the luminescence (i.e., the occurrence of only a partial quenching of the luminescence), the model in (a) is preferred.
long e-beam exposure times in Fig. 15 instead favors the existence of e-h radiative transitions ($\tau_e$) occurring in the QD which competes with nonradiative channels (caused by hydrogen desorption and Si-H bond breaking) whose participating DOS saturates with persistent e-beam exposure. Thus, we believe that the e-h quantum confinement model depicted in (a) best describes the current CL emission results.

IV. CONCLUSIONS

Si NCs have been fabricated by LAL of a Si(100) target immersed in deionized water. The properties of the prepared Si NCs were probed by Raman microscopy, TEM, and CL, where the first two methods provided information regarding their crystal structure and sizes and the CL spectroscopy on their optical properties. The first order Raman spectra showed down shifts and broadening of the Raman phonon bands relative to that observed in bulk Si, depending on the position of measurement in the sample. Analysis of these spectra by a phonon confinement model, based on three-dimensional confinement and lognormal size distributions, revealed that the produced Si nanoparticles, under the conditions of our experiment, are NCs with diameters larger than ~2 nm. These results proved to be consistent with those obtained from HRTEM and EDS analysis, which showed the presence of Si/SiOx NCs with diameters > ~1.75 nm. The HRTEM and ED analysis showed that the interplanar spacing of the crystallographic planes of the Si NCs correspond approximately to that for bulk Si crystal.

Of particular importance is the supercontinuum emission in the near UV–red range (~300–720 nm), which was revealed by the CL spectra measured at different temperatures in the 50–300 K range. Four dominant components were found, corresponding to particular groups of NCs, formed by the contribution of a distribution of QDs sizes. The extracted effective band gap energies for the excitonic confinement origin of light emission from Si NCs correlate beautifully with the empirically fitted PL results of Kim et al. We have found the diameters of the Si NCs corresponding to the CL emission components, which exhibit a good agreement with the size distributions obtained from TEM and extracted from the Raman confinement model, strongly indicate the quantum confinement origin of light emission from Si NCs. A quenching of the CL as a function of e-beam exposure time was observed and attributed to the desorption of hydrogen, disruption of the NC surface passivation, and formation of nonradiative recombination channels involving surface states in the gap. The potential for preparing silicon nanoparticles with controlled luminescent properties further opens a window into new research for improving and tailoring these properties and for testing their applicability in biomedicine and optoelectronic devices.

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37JCPDS file, No. 27-1402 (a = 0.543 nm and the space group is Fd3m).
46 For an excellent review, see A. Sa’ar, J. Nanophoton. 3, 032501 (2009).