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Photoluminescence properties of size-controlled silicon nanocrystals at low temperatures

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This study attempts to clarify the origin of the temperature dependence of the photoluminescence (PL) spectra of silicon nanocrystals (Si-ncs) embedded in SiO2 from 5 to 300 K. For this purpose, size-controlled Si-ncs with a narrow size distribution were fabricated, using the SiO/SiO2 multilayer structure. The PL intensity is strongly temperature dependent and presents a maximum at around 70 K, depending on the Si-nc size and on the excitation power. The origin of this maximum is first discussed thanks to PL dynamics study and power dependence study. The evolution of the PL energy with temperature is also discussed. In bulk semiconductors the temperature dependence of the gap is generally well represented by Varshni’s law. Taking into account the quantum confinement energy, the PL energy of Si-ncs follows very well this law in the range 50–300 K. Below 50 K, a strong discrepancy to this law is observed characterized by a strong increase in the PL energy at low temperature, which is dependent on the Si-nc size distribution. This temperature dependence of the PL energy is correlated with a decrease in the radiative rate at low temperature and is explained by a preferential saturation effect of the bigger Si-ncs. © 2009 American Institute of Physics. [DOI: 10.1063/1.3169513]

I. INTRODUCTION

Nanostructured Si has allowed overcoming the poor optical properties of bulk Si, by showing an enhancement of its radiative emission. This has led to a new interest in this material, to achieve the integration of silicon-based photonic devices with electronic ones on the same Si chip. The question of the origin of the light emitted by silicon nanocrystals (Si-ncs) of size lower than 5 nm has been involved in a great amount of investigation. It has largely been observed that the PL energy is a decreasing function of the Si-nc size, in agreement with the quantum confinement model.1–3 In the same way, it was observed that the radiative lifetime is also an increasing function of the Si-nc size, as a consequence of the k-vector selection rule relaxation, which is more pronounced as the Si-nc size decreases.2,4 If it is commonly accepted that the quantum confinement plays an important role in the high radiative emission yield as well as in the emission at higher energy than the Si band gap energy, a debate still exists on the origin of the PL, which could implicate surfaces states as suggested in several works.5–8 In this study, the temperature dependence of the PL characteristics is addressed. The Si-nc related PL decay time is generally strongly temperature dependent with a strong increase in the decay time at low temperature, which can be attributed to the low temperature increase in the radiative decay time. This behavior is well described by the thermal equilibrium of the lifetime of the excitonic triplet and singlet states due to the electron-hole exchange interaction, as proposed by Calcott et al.9 In this description, the normally forbidden triplet transition becomes slightly authorized, thanks to the spin-orbit interaction, but gives rise to a lifetime of the excited state greater than 1 ms, whereas the singlet state is in the range of 10 μs. These two states are separated by some tens of meV. The upper state, the singlet one, is thermally activated so that at low temperature, only the triplet state is populated. As this state has a much longer radiative lifetime than the upper singlet state, the radiative lifetime is larger at low temperature than at high temperature. This temperature dependence of the radiative decay time has an influence on the internal quantum efficiency, defined by the ratio between the radiative decay rate value and the total decay rate value. Hence, the existence of a maximum at around 100 K in the temperature dependence of the PL intensity was often related in materials containing Si-ncs such as porous silicon10 or Si-ncs obtained by ion implantation of Si in SiO2.11 A maximum at 150 K was also observed in Si-ncs obtained from laser breakdown of silane12 or by plasma enhanced chemical vapor deposition.13 The decrease in the PL intensity above 70–150 K is generally ascribed to a thermally activated nonradiative process. In particular, in porous silicon, it was suggested that the carriers can reach nonradiative centers such as dangling bonds, because the thermally activated transport of photogenerated carriers through the nanocrystallite network becomes important.14 However, the decrease in the PL intensity below 70 K is not fully understood. Some groups explained this decrease by a tunneling escape of carriers15,16 whereas Kovalev et al.17 suggested that this behavior is purely artificial and is due to a saturation of the PL, involved by the increase in

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the radiative decay time. In a first part, this paper tries to clarify the origin of the existence of such a maximum in the temperature dependence of the PL intensity.

On the other hand, the study of the evolution of the PL energy with the temperature generally gives an indication to know if the recombination is dominated by the quantum confinement, or if the recombination occurs at the interface of the Si-ncs. The temperature dependence of the semiconductor bandgap energy is well described by the phenomenological Varshni’s law, which explains the decrease in the gap as the temperature increases. For bulk silicon, an energy gap decrease of around 60 meV is obtained for a temperature increase from 10 to 300 K. This energy dependence is correlated with the cumulative effect of mechanisms of electronic phonon interaction and thermal lattice expansion.\textsuperscript{19} Pässler\textsuperscript{20} precisely studied this evolution in the case of bulk silicon. In the case of Si-ncs, a few studies relate the evolution of the photoluminescence (PL) energy as a function of temperature, in particular, below 50 K. Brongersma \textit{et al.}\textsuperscript{11} observed a decrease in the PL energy equal to 60 meV as the temperature increases from 12 to 300 K. This evolution, mainly attributed to the decrease in the band gap energy of the Si-ncs with temperature, suggests that the PL comes from quantum confinement. Heitmann \textit{et al.}\textsuperscript{21} also obtained a shift of the PL peak position from 1.472 to 1.427 eV as the temperature increases from 4.5 to 300 K. Moreover, they observed a significant deviation to the evolution reported by Brongersma \textit{et al.}\textsuperscript{11} below 50 K. This deviation is attributed to an additional mechanism taking into account the migration of the excitons from Si-ncs to Si-ncs, but the existence of such a mechanism in this kind of material is still a subject of controversy.\textsuperscript{22–24}

In this study, we focus our attention on the temperature dependence of the PL properties of Si-ncs embedded in SiO\textsubscript{2}, in the range 5–300 K. The Si-ncs are fabricated from SiO/SiO\textsubscript{2} multilayers, which is an approach that allows the control of the Si-nc size and the obtention of a narrow size distribution, as previously shown by Zacharias \textit{et al.}\textsuperscript{25} The evolution of the PL intensity as a function of the temperature shows a dependence on the Si-nc size and on the excitation power. Moreover it is shown that the temperature dependence of the energy follows Varshni’s law from 40 to 300 K, i.e., the behavior is similar to that of bulk Si, with an energy shift due to the quantum confinement. Below 40 K, a clear discrepancy to Varshni’s law is observed, characterized by a strong increase in the PL energy by decreasing the temperature. This behavior is dependent on the size distribution, with a more pronounced energy increase for the large size distribution. The temperature dependence of the PL energy below 40 K is attributed to a size distribution effect and to a preferential saturation effect of the bigger Si-ncs.

\section*{II. EXPERIMENT}

SiO/SiO\textsubscript{2} multilayers were prepared by successive thermal evaporation of SiO powder and evaporation of fused silica glass performed by an electron-beam gun. The deposition rate is controlled by a quartz microbalance system and is equal to 0.1 nm s\textsuperscript{-1}. The thickness of the active layer was varied from 2 to 5 nm, whereas the SiO\textsubscript{2} barrier thickness was maintained constant and equal to 5 nm. The silicon substrates were maintained at 100 °C. For each sample, the total film thickness was around 200 nm. The samples were then annealed at 1050 °C during 5 min under vacuum with a pressure equal to 10\textsuperscript{-6} Torr. Both continuous-wave (CW) and time-resolved (TR) PL experiments were performed. For the cw experiments, the excitation was obtained with a 30 mW He–Cd laser using the 325 nm line. The samples were inserted in a cryostat equipped with fused silica windows with 92% transmission at the laser wavelength. Given the excitation area, the laser power reaching the sample gives rise to a photon flux equal to 1.8 × 10\textsuperscript{18} s\textsuperscript{-1} cm\textsuperscript{-2}. The excitation power can be varied using neutral density filters. For the TR-PL experiments, the sample was pumped by the 355 nm line of a frequency-tripled yttrium aluminum garnet (YAG):Nd laser. The laser pulse frequency, energy, and duration were typically equal to 10 Hz, 50 µJ, and 20 ns, respectively. The PL signal was analyzed by a monochromator equipped with a 600 grooves/mm grating and by a photomultiplier tube cooled at 190 K. The rise time of the detector is equal to around 10 ns. The response of the detection system was precisely calibrated with a tungsten wire calibration source. The cryostat is equipped with a He flux and the temperature is controlled with an accuracy of 0.2 K. For the experiments, the cryostat was first cooled down to 5 K then heated step by step up to 300 K.

The anneal of the film at 1050 °C leads to the formation of three dimensionally confined Si-ncs, coming from the dissociation of SiO into Si and SiO\textsubscript{2}. Due to the existence of the stable SiO\textsubscript{2} barrier, their size is limited and then controlled by the SiO layer thickness.\textsuperscript{26} The transmission electron microscopy study of our samples has been presented in detail in a previous work.\textsuperscript{27} The size distribution is narrow for the sample with Si-nc size up to 4 nm. The Si-ncs’ mean diameter and the full width at half maximum of the size distribution are reported in Table I. It is important to note that, despite the control of the mean crystallite size, a size dispersion of the Si-ncs exists. This size dispersion is an increasing function of the SiO thickness. In particular, a full width at half maximum of the size distribution equal to 4.6 nm is obtained for a SiO thickness equal to 5 nm. Beyond this SiO thickness, the Si-ncs’ size is not controlled anymore and the size distribution becomes multimodal.

\begin{table}[h]
\centering
\caption{Values of the SiO layer thickness, the Si-nc mean size, and the size dispersion for the different studied samples.}
\begin{tabular}{llll}
\hline
Sample & SiO thickness & Mean size & FWHM \\
(µm)  & (µm)     & (µm)    & (µm)  \\
\hline
S2     & 2        & 1.8     & 1.2     \\
S3     & 3        & 3.2     & 1.3     \\
S4     & 4        & 4.1     & 1.7     \\
S5     & 5        & 4       & 4.6     \\
\hline
\end{tabular}
\end{table}

\section*{III. RESULTS AND DISCUSSION}

\subsection*{A. Temperature dependence of the decay time}

As previously shown, a blueshift of the PL energy is clearly obtained from 1.45 to 1.67 eV, as the size is reduced...
from 4 to 2 nm, showing that a confinement effect occurs in the samples.\(^27\) The PL energy is very similar for the SiO layer thicknesses equal to 4 and 5 nm. The PL transient was first studied as a function of the wavelengths. Figures 1(a) and 1(b) show this dependence for sample S4 at room temperature and at 5 K, respectively. The shape of the PL transient is clearly multieponential, which is a well-known characteristic of Si-ncs.\(^{28-30}\) In agreement with the quantum confinement model, the decay time is a decreasing function of the wavelength both at room temperature and at 5 K. Indeed, for the low wavelength, the PL signal is preferentially due to the small Si-ncs, which present the lower decay time, while at a larger wavelength the larger Si-ncs are measured. The dependence of the decay time on the wavelength is then mostly a consequence of the size distribution. At room temperature and at 5 K, the characteristic decay times are in the range 10 \(\mu\)s and 1 ms, respectively.

The temperature dependence of the PL decay time, measured at the maximum of the PL intensity, is shown in Fig. 2, for the different Si-nc sizes. The TR-PL decay was fitted by a stretched exponential decay and only the characteristic time \(\tau\) is presented here. As already observed in literature, the decay time is a decreasing function of the temperature with a more pronounced decrease from 5 to 50 K. If nonradiative processes are more efficient than the radiative ones, the measured decay time is lower than the radiative decay time. In this case the PL intensity is governed by the nonradiative channels. The decrease in the decay time with temperature involves the decrease in the PL intensity, as it is the case in the temperature range between around 100 K and room temperature, where both PL intensity and decay time are decreasing functions of the temperature (Figs. 2 and 4). However, below 100 K, the increase in the decay time cannot be attributed to an increase in the nonradiative decay time, because if that were the case, the PL intensity would increase monotonically by decreasing the temperature. As this is not observed, this suggests that the increase in the decay time below 100 K is due to an increase in the radiative lifetime. Thus, we conclude that at low temperature, the dependence of the decay time is controlled by the radiative processes. Qualitatively, the model proposed by Calcott et al.\(^9\) describing the temperature dependence of the radiative decay time, satisfactorily explains the temperature dependence of the decay time. However, the calculation of the values of the radiative decay time of the triplet and singlet states is difficult because the experimentally measured decay time also takes into account the nonradiative recombination channels, which as said before appear more likely for the high temperatures.

B. Temperature dependence of the PL intensity

CW PL experiments were performed on each sample from 5 to 300 K with a particularly weak temperature step to obtain a high precision on the evolution of the PL properties. Figure 3 shows the PL spectra for sample S4 for different temperatures, to present a typical evolution of the spectra with temperature, and with an excitation flux equal to 1.8 \(\times 10^{18}\) s\(^{-1}\) cm\(^{-2}\). This evolution is very similar for the other Si-nc sizes. In the next, the integrated intensity and the energy of the maximum of the PL peak will be presented as a function of the temperature. The spectra were first measured using a filter with 10% transmission of the He–Cd laser excitation, leading to a photon flux equal to 1.8 \(\times 10^{17}\) s\(^{-1}\) cm\(^{-2}\). The influence of the excitation power will then be discussed.

The temperature dependence of the PL intensity is shown in Fig. 4 for the different Si-nc sizes, and for an excitation flux equal to 1.8 \(\times 10^{17}\) s\(^{-1}\) cm\(^{-2}\). For all the Si-nc sizes, the temperature dependence of the PL intensity presents a maximum that appears at around 70 K. This maximum appears at a slightly lower temperature for sample S2. The decrease in the PL intensity at high temperature is generally explained by a temperature-activated nonradiative process. As said before, at low temperature, the decrease in the PL intensity needs to be discussed taking into account the radiative decay time. Assuming the Si-ncs can be represented by a quasi-two-level system, the following rate equation can be written:
\[
\frac{dN^e}{dt} = \sigma \varphi (N - N^e) - \frac{N^e}{\tau},
\]

where \(N\), \(N^e\), \(\sigma\), \(\tau\), and \(\varphi\) are the total number of the Si-ncs, the number of the Si-ncs in the excited state, the Si-nc absorption cross section at 325 nm, the lifetime of the Si-nc excited state, and the excitation photon flux, respectively. If the PL intensity is defined by

\[
I_{PL} \equiv \frac{N^e}{\tau_{rad}},
\]

where \(\tau_{rad}\) is the Si-nc radiative lifetime, solving Eq. (1) for steady state conditions involves the following expression of the PL intensity:

\[
I_{PL} \equiv \frac{1}{\tau_{rad}} \frac{\sigma \varphi \tau}{1 + \sigma \varphi \tau} N.
\]

For low power conditions, i.e., for \(\varphi \ll 1/\sigma \tau\),

\[
I_{PL} \text{ can be approximated by}
\]

\[
I_{PL} \equiv \frac{1}{\tau_{rad}} \sigma \varphi \tau N.
\]

For a constant flux, the PL intensity is proportional to the decay time. This equation shows that for the high-temperature range (beyond 70 K) where the PL intensity is a decreasing function of the temperature, the decrease in the PL intensity is well explained by the decrease in the decay time, in agreement with the fact that the nonradiative processes play an important role in the PL efficiency in this temperature range. However, at low temperature, if we assume that the decay time is mainly governed by the radiative process, \(\tau \approx \tau_{rad}\) and, therefore, the PL intensity should become nearly independent of the decay time and of the temperature, as shown by Eq. (5). Hence Eq. (5) cannot explain the decrease in the PL intensity at low temperatures. Consequently, studying the influence of the excitation power is needed because expression (5) is the consequence of approximation (4), which is likely to become wrong at low temperature due to the PL decay time increase by at least one order of magnitude at low temperature.

The influence of the laser power on the PL intensity was investigated for different temperatures. The PL intensity of the maximum is presented in Fig. 5 as a function of the laser power for 5, 80, and 300 K, for sample S4. The data are normalized with respect to the PL intensity measured at the maximum of the laser power used. The lines represent the fit of the data according to expression (3) of the text.
At room temperature, the PL intensity increases almost linearly with the photon flux. When the temperature is lowered at 80 K, this evolution is no more linear. This nonlinear behavior is even more pronounced at 5 K. The power dependence shows that for the low-temperature measurement, approximation (4) becomes wrong. Hence expression (3) was used to fit the experimental data. As shown in Fig. 5 by the continuous lines, this expression satisfactorily fits the data, allowing us to extract the product $\sigma \tau$. It is found that the Si-nc cross section, measured at 325 nm, is equal to $3 \times 10^{-15}$ cm$^2$. For $T=5$ K, the inverse of the product $\sigma \tau$ is equal to $3 \times 10^{-17}$ cm$^{-2}$ s$^{-1}$, which is of the same order of magnitude than the photon flux. This clearly shows that approximation (4) is not valid at low temperature for the range of excitation power used in this study, even for the experiments performed with 10% of the laser power. At room temperature, $1/\sigma \tau$ is equal to $3 \times 10^{18}$ cm$^{-2}$ s$^{-1}$ and for the experiments performed with 10% of the laser power ($\varphi=1.8 \times 10^{-17}$ cm$^{-2}$ s$^{-1}$), the low power approximation can be used. These results concerning the power dependence of the PL intensity implicates the use of Eq. (4) in agreement with the major role played by the radiative decay time, which is an increasing function of the size. For example, the decay time is equal to 350 $\mu$s at 100 K for sample S4. The same decay time is obtained at lower temperature, i.e., 40 K for sample S2. Thus, the saturation effect appears at lower temperatures for sample S2, leading to a less pronounced decrease in PL intensity.

**C. Temperature dependence of the PL energy**

The temperature dependence of the energy $E_{PL}(T)$ of the PL peak maximum is presented in Fig. 7 for the different Si-nc sizes. The PL energy is a decreasing function of the temperature with a stronger evolution for temperatures below 40 K. In bulk semiconductors, the evolution of the gap with temperature is generally well described by the phenomenological Varshni’s law

$$E_g^{\text{bulk}}(T) = E_g^{\text{bulk}}(0) - \frac{\alpha T^2}{T + \beta},$$

where $\alpha$ and $\beta$ are characteristic parameters. This law was modified by Vinâ et al. and by Pässler who obtained the following law:

$$E_g^{\text{bulk}}(T) = E_g^{\text{bulk}}(0) - \frac{\alpha}{2} \left[ p \sqrt{1 + \left( \frac{2T}{\Theta} \right)^p} - 1 \right],$$

where $\alpha$, $p$, and $\Theta$ are empirical model parameters. The advantage of this phenomenological law is that the quasiquadratic low-temperature asymptote and the linear high-temperature asymptote of the evolution of the Si gap with temperature are well described. The best values that fit the experimental data on bulk silicon are $E_g^{\text{bulk}}(0)=1.17$ eV, $\alpha = 0.5176$ meV/K, $p=2.33$, and $\Theta=405.6$ K. Taking into account the quantum confinement energy $E_g^{\text{conf}}(T)$, the law becomes

![Graph showing temperature dependence of PL intensity for two different excitation photon fluxes, for sample S4.](image)

**FIG. 6. Temperature dependence of the PL intensity for two different excitation photon fluxes, for sample S4.**
The fits of our experimental results with this law are shown in Fig. 7 and the parameters of the fits are given in Table II. The energy shift between the value given by Pässler’s law (Ref. 19) and the Si-nc PL energy at 5 K is shown for each sample.

\[
E_{g}\text{Si-ncs}(T) = E_{g}\text{bulk}(T) + E_{g}\text{conf}(T).
\]

For the evolution with temperature of the \(E_{g}\text{conf}(T)\) value, we can show that a constant value can be used. Indeed, with a characteristic size of the Si-ncs equal to \(L\), and assuming infinite barrier heights, the confinement energy is proportional to \(L^{-2}\) and the shift of the confinement energy due to the thermal expansion of the nc can be overestimated by

\[
|\Delta E_{g}\text{conf}| \leq 2E_{g}\text{conf}(T = 0\text{ K}) \cdot \frac{\Delta L}{L},
\]

where \(\Delta L\) is the size variation between 300 and 4 K. Assuming a constant thermal expansion coefficient of silicon with temperature equal to \(2 \times 10^{-5}\) K\(^{-1}\), we obtain \(\Delta L/L = 6 \times 10^{-4}\). With a confinement energy equal to 240 meV, which is the value given for a nc with a diameter equal to 3 nm, the overestimated confinement energy shift is equal to 0.28 meV.

Due to this very low value, below the detection sensitivity, our data were fitted by the following expression:

\[
E_{PL}(T) = E_{g}\text{conf} + E_{g}\text{bulk}(0) - \frac{\alpha}{2} \sqrt{1 + \left(\frac{2T}{\Theta}\right)^{p}} - 1.
\]

The fits of our experimental results with this law are shown in Fig. 7 and the parameters of the fits are given in Table II. The values \(E_{g}\text{conf}\) correspond to the difference between the PL energy value and the gap of bulk silicon at 300 K. The dependence of the PL energy on temperature is very well described by Pässler’s law in the temperature range 40–300 K. Moreover, the confinement energies are in good agreement with the already published results. Note that the sample that gives closer parameters to bulk Si for the Pässler law is sample S2, which has the narrower size distribution. The origin of the evolution of these parameters for the other samples is still not clear but could be assigned to the larger size distribution of these samples. However, a strong discrepancy of the temperature dependence of the PL energy on Pässler’s law appears below 40 K. That law predicts that the gap energy remains almost constant and equal to the gap value at 4 K. However, we obtain a strong increase in the PL energy below 40 K. Such an evolution has already been related by two authors. In the work of Brongersma et al., the PL energy decreases with temperature in the measured range 12–300 K. A stronger decrease from 12 to around 40 K seems to be visible, but is not commented. Heitmann et al. observed a clear dependence of the PL energy on temperature. In the range 40–300 K, their values were well fitted by the type expression of Viña et al. Below 40 K, a strong discrepancy with this expression was observed and discussed in terms of a migration process of excitons. In this case, it was said that a thermalization process of the excitons could occur, which would lead to a preferential migration from small to big nc. At low temperature, beyond 50 K, this process becomes weaker and weaker and each nc contributes like an exciton trap. Then smaller crystals contribute to the PL signal, which could explain the strong increase in the PL energy at low temperature. A debate still exists as far as the migration of excitons in the Si-ncs is concerned. In porous silicon, some authors have proposed that a migration process could happen between nc, which could be at the origin of the stretched exponential decay of the PL intensity. However, some experimental and recent theoretical works strongly suggest that no carrier migration exists.

In this present work, we demonstrate that the temperature dependence of the PL energy below 40 K can be interpreted without taking into account the contested migration process. Indeed, as shown above, the very long radiative lifetime at low temperature was induced in a saturation phenomenon. Moreover, the radiative lifetime is a decreasing function of the energy. As shown in Table I, the size distribution is narrow but still presents a dispersion, which probably contributes to the existence of a wide PL peak. The size distribution also involves a distribution of the radiative decay time because the quantum confinement energy is size dependent. Hence the saturation effect that appears at low temperature.
does not affect the small crystals as much as the large ones, as shown by the results obtained by the study of the temperature dependence of the PL intensity. At a given temperature, the large crystals feel a stronger saturation effect than the smaller ones, due to their larger lifetime. When the temperature decreases, the PL intensity of the large crystals decreases more rapidly than the PL intensity of the smaller ones. Consequently, when the saturation effect becomes strong, i.e., below around 40 K, the PL signal comes essentially from the smaller ncs and the PL band shifts toward the higher energies, due to the preferential saturation effect. The strong increase at low temperature of the PL energy compared to the prediction of Pässler’s law was obtained for all the studied samples, as demonstrated in Fig. 7. Moreover, the deviation with respect to this law is an increasing function of the size distribution. This energy increase is equal to 6 and 18 meV for samples S2 and S5, respectively. This difference can be explained by the fact that, the larger the size dispersion is, the larger the dispersion on the lifetime is and the more pronounced the preferential saturation is. The shift at low temperature due to the saturation is consequently increased by the large size dispersion.

**IV. CONCLUSIONS**

In summary, the temperature dependence of the PL properties of Si-ncs was studied for different Si-nc sizes. For this purpose, size-controlled Si-ncs were obtained using SiO/ SiO2 multilayers prepared by evaporation. The temperature dependences of the decay time, the PL intensity, and the PL energy were studied from 5 to 300 K. The influence of the excitation power was also investigated. The PL intensity shows a maximum at a temperature, which is an increasing function of the power excitation. While the PL is strongly influenced by the nonradiative recombinations at temperatures higher than this maximum, the decrease in the PL intensity from 70 to 5 K is explained by a saturation effect, which is due to the strong increase in the PL radiative lifetime at low temperature. This saturation effect is more pronounced for the large Si-ncs because of their higher radiative lifetime.

The PL energy of the Si-ncs is a decreasing function of the temperature, which presents a stronger decrease from 5 to 40 K. Taking into account the quantum confinement energy, the PL energy follows very well Varshni’s law in the range 40–300 K. Below 40 K, the strong discrepancy to this law was interpreted by a preferential saturation effect of the Si-ncs that appears at low temperature. The small clusters present a smaller lifetime than the larger ones. Hence they do not feel the saturation effect as much as the larger ones, which induces a preferential decrease in the PL intensity in the low-energy part of the PL spectrum and therefore a shift of the spectrum toward the high energies.

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