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Photoluminescence from Silicon Nanostructures

25.1 Introduction

Silicon, the second-most abundant element on earth (after oxygen) having superior mechanical and electronic properties, has become the principal material of the semiconductors industry from the dawn of microelectronics, and apparently will remain dominant in the foreseen future. Silicon is a semiconductor whose electrical conductivity can be controlled over a wide range, either dynamically or permanently. Its oxidized state (SiO₂) is one of the best and most stable electrical insulator and its superior chemical and mechanical properties make silicon the ideal material for advanced materials processing. For all these reasons, silicon became essentially the sole player in electronic integrated circuits, being the basic building block of most electronic devices, from transistors and diodes to microprocessors, solar cells, wireless communication devices, and more. Yet, silicon is not a good choice for photonic applications where optically active elements are required due to its indirect energy bandgap characteristics where energy’s minima of the conduction and the valence bands do not fall at the same wavevector (i.e., the crystal Bloch momentum normalized to \( \hbar \)). The situation is schematically illustrated in Figure 25.1 where the energy-band diagram of silicon is shown and compared to that of GaAs, which is a direct bandgap semiconductor.

In a steady state, electrons (open circles) occupy the lowest energy states of the conduction band while holes (filled circles) occupy the upper states of the valence band. The emission of a photon takes place once the electron and the hole recombine radiatively, namely, conduction electrons drop down to empty states of holes in the valence band and, releasing their energy to photons of energy, \( \hbar \omega = E_g - E_v \equiv E_g \) where \( E_g \) is the bandgap energy of the semiconductor and \( \hbar \omega \) is the photon energy. Besides energy, momentum should also be conserved during the process. However, as the photon wavelength (\( \lambda = 2\pi/k \approx 1\mu m \) for silicon) is about three orders of magnitude larger than the de Broglie wavelength of the electrons (which is of the order of the lattice constant of the semiconductors \( \sim 5\AA \)), the photon momentum can be neglected relative to that of the electrons and the holes. In direct bandgap semiconductors like GaAs, both the electrons and the holes have the same momentum at the center of the Brillouin zone (\( \Gamma \)-point in Figure 25.1) and vertical radiative recombination can take place. In silicon, however, the large momentum mismatch between electrons and holes does not permit direct radiative recombination unless another entity, a phonon, for example, is involved in the recombination process. As a result, silicon is a poor emitter of light and cannot be utilized for applications where active light sources are required. In many papers and even textbooks this property of silicon is considered to be a disadvantage. However, one should remember that radiative recombination in direct bandgap semiconductors is a fast process (usually of the order of a few nanoseconds in direct bandgap semiconductors with \( E_g \sim 1-2\text{eV} \) that limits the lifetime of the carriers (mainly that of the minority carriers in the semiconductor). In silicon, the slow radiative lifetime (of the order of a few milliseconds in pure silicon) allows the minority carriers to diffuse over macroscopically large distances (a few hundreds of micrometers and more), a highly favorable property for electronic applications.
The situation is substantially different when dealing with silicon nanostructures. Generally speaking, semiconductor nanostuctures are artificially made semiconductor objects whose dimensions have been shrunk down to the nanometer length scales. They are classified according to their dimensionality, e.g., two-dimensional (2D) quantum wells, one-dimensional (1D) nanowires (or quantum wires), and zero-dimensional (0D) nanocrystals (or quantum dots), where the classification is according to the number of unconfined dimensions along which carriers (electrons and holes) are still free to move. At the nanometric length scales, quantum confinement (QC) phenomena become important. For example, one should anticipate the momentum conservation law to relax with the decreasing size of the object. In case of silicon nanostructures, for example, a 0D silicon nanocrystal of radius $R$, we may use the Heisenberg uncertainty principle to estimate the wavevector relaxation: $\Delta k \sim 1/R$. As the relaxation of the wavevector conservation law increases with the decreasing size of the nanostructure, one may expect the radiative recombination rate to considerably increase once the wavevector mismatch, shown in Figure 25.1, becomes comparable to $\Delta k$, raising the question: Can we generate active photonic elements from silicon nanostructures?

The above question has turned to be a practical subject in 1990 when Canham reported on efficient red light emission from porous silicon (PS) under UV light illumination. PS is a nanometric random network of pores and silicon prepared by electrochemical etching of a silicon substrate. Following Canham’s discovery, a very extensive investigation has been conducted by many groups, aimed at verifying the QC model. Surprisingly, while many investigations provided additional support to the QC model, a considerable number of works have reported results and properties of the PL that cannot be explained by the QC picture. This puzzle has led numerous researchers to propose alternative models and theories that do not rely on QC, the more notable ones suggesting that surface phenomena are responsible for the PL. In this picture, radiative transitions take place on the surface of the nanostructures either due to surface bonds, surface defects, imperfections, or even surface molecular species. In particular, the fact that certain properties of the PL depend on “surface chemistry,” for example, the specific way that silicon surface bonds are terminated, have led certain researchers to suggest that surface phenomena are responsible for the luminescence from silicon nanostructures.

Let us emphasize that surface phenomena are expected to play a major role in small nanostructures. To follow this, let us estimate the surface-to-volume (STV) ratio for few nanostructures of different dimensionality but having a simple geometrical form such as spheres (0D), cylinders (1D), and slabs (2D), as schematically shown in Figure 25.3.

In order to define a “volume” of the surface, we may estimate the surface’s thickness of a given nanostructure, $d$, to be about 1–3 monolayers thick. For silicon (with a lattice constant of $\sim 0.54$ nm),...
FIGURE 25.3 The surface-to-volume (STV) ratio for a 2D slab, 1D cylinder, and 0D sphere where R is the thickness of the slab, radius of the cylinder, and radius of the sphere, respectively. In all three cases, \( d \) represents the thickness of the surface.

we may take, \( d \approx 1 \) nm, to be an estimate of the surface’s thickness. Hence, for a 0D spherical nanocrystal we find, \( STV = 3(d/R) \), where \( R \) is the radius of the sphere, so that for \( R = 6 \) nm nanocrystal we get, \( STV \approx 0.5 \), meaning that 50% of the silicon atoms belong to the surface while for \( R = 10 \) nm, 33% of the silicon atoms sit on the surface of the nanocrystal. We conclude that surface phenomena become more and more appreciable with the decreasing size of the nanostructures and, on the nanoscales not only quantum size effects can affect the electronic properties of the nanostructures but also surface phenomena should carefully be considered as a possible source of interactions that may affect electronic properties of the nanostructures. This is particularly true for silicon, which is known to be material sensitive to surface termination and usually requires a special treatment for passivation.

Unfortunately, PS is not the ideal medium for the study of quantum size effects and surface phenomena at the nanoscale. PS is a random network of electrochemically etched pores and silicon that is characterized by a broad size and shapes distribution, it is chemically and mechanically unstable and it tends to change its properties with time (aging effects).\(^{15} \) Hence, to a great extent, the puzzles and discrepancies between the QC and the surface chemistry (SC) models could not be resolved despite of the extensive investigation on PS. Yet, over the last decade, alternative techniques to fabricate silicon nanostructures, with better capabilities to control their size, shape, and the host matrix in which they are embedded, have emerged.\(^{14} \) With these improved techniques, it is now possible to investigate the evolution of optical and electrical properties of silicon nanostructures versus size and dimensionality. Recent experimental results together with refined theories indicate that none of the above models alone, for example, the QC and the SC models, can explain the entire optical properties of silicon nanostructures.\(^{15-17} \) Instead, a refined comprehensive model, which takes into account both quantum size effects and surface phenomena has to be developed.\(^{18,19} \)

The purpose of this chapter is to describe these recent developments in the field of silicon nanostructures, particularly those experiments and models that provide a support and verification to the mutual role played by QC and SC in shaping the optical properties of silicon nanostructures.\(^{19} \) The interested readers are referred to earlier reviews and the rich literature in the field discussing each individual model (QC and SC) and the supporting/contradicting experimental results.\(^{7-12} \)

### 25.2 Synthesis of Silicon Nanostructures

In this section, we briefly review some of the most popular techniques to synthesize light-emitting silicon nanostructures. The simplest and the less expensive method is based on PS, which is fabricated by electrochemical etching of crystalline silicon substrates using hydrofluoric acid (HF)–based solutions. The specific conditions to obtain light-emitting PS (like the PS sample shown in Figure 25.2)\(^{20,21} \) are reviewed in detail in Refs. [22,23].

Light-emitting PS has a random, nanometric sponge-like structure with a fairly large surface area that can easily be accessed and chemically modified due to its porous characteristics. While this property of PS is of great advantage for certain applications such as chemical\(^{14,25} \) and biochemical sensing,\(^{26,27} \) it represents a major limitation for a consistent study of quantum size effects as the size, shape, and even the dimensionality of the nanocrystalline silicon objects are not well defined and can vary between samples and preparation techniques. Furthermore, as the PS matrix may contain various species such as SiO\(_2\), amorphous silicon (a:Si), and other amorphous derivatives of silicon, the exact surface termination of the nanocrystalline silicon objects cannot be determined accurately. Aging effects can be quite significant in PS and may affect both optical properties and transport phenomena. For all these reasons and despite the extensive literature on luminescence from PS, the author of this chapter is in the opinion that in practice, it is impossible to draw consistent conclusions about nanoscale phenomena from PS alone.

The first experimental report on room-temperature PL from silicon nanostructures other than PS is related to silicon nanocrystals (SiNCs) fabricated by ion implantation of silicon into SiO\(_2\) matrix.\(^{28} \) Recently after, other methods to produce SiNCs...
embedded in SiO₂ matrices emerged, including chemical vapor deposition (CVD) of sub-stoichiometric oxide (SiOₓ), RF magnetron sputtering, reactive evaporation, and plasma-enhanced CVD (PECVD). In principle, all these methods require high-temperature annealing of the deposited films to produce phase separation of the excess silicon from the SiO₂ matrix followed by crystallization of the silicon into nanocrystalline particles. The ion implantation method is quite popular due to its compatibility with the standard silicon CMOS technology (where it is routinely used to create doped silicon regions). In this technique, silicon ions are extracted from the plasma, accelerated toward the SiO₂ substrate by an electric field and losing their energy after traveling a given depth in the substrate. The thickness and the profile of the implanted layer depend mainly on the implantation dose and the ion energy. In principle, the lower the ion energy the narrower the implanted zone, however, implantation dose also decreases at lower ion energies, setting up a practical limit on the ion energy, which is typically in the range of 1–10 keV.

A similar result of forming oxide layers with excess silicon concentration has been obtained by RF magnetron sputtering. The sputtering process (sometime referred as physical vapor deposition ≡ PVD) involves a bombardment of silicon and SiO₂ solid targets by energetic ions (usually argon ions), removing atoms and molecules from the targets that are deposited on the substrate. As silicon dioxide is an electric insulator, an RF electric field is used to create the plasma between the substrate and the targets. A popular method to produce SiNCs is the co-sputtering technique in which, the two targets (usually pure silicon and quartz) are simultaneously exposed to the ions, producing a mixed layer of silicon and oxide with the excess silicon being used to create SiNCs after high-temperature annealing. The thickness and the amount of excess silicon concentration are determined by the RF power as well as by the geometry of the sputtering chamber. Usually, in order to improve uniformity, the substrate is rotated and placed far enough from the targets. In certain cases however, particularly when size-dependent phenomena are to be investigated, it is desirable to put the substrate near the targets without rotation. In this case, the excess silicon concentration along the deposited film continuously varies from one edge of the substrate to the other edge, as schematically illustrated in Figure 25.4.

The amount of excess silicon concentration can be determined by measuring the volume ratio of silicon and SiO₂ obtained from reference depositions of the single components (Si and SiO₂) under the same deposition conditions and is measured in unit of % excess silicon content in a given volume (x). In the experiments reported in Refs. [15,16], x varied from about 10% (at the edge

![Figure 25.4](image-url)
closer to the SiO$_2$ target) up to about 80% (at the edge closer to the Si target). Luminescent SiNCs are obtained after high-temperature annealing from a limited range of $10\% \leq x \leq 35\%$ where isolated nanocrystals can be observed. At higher excess silicon content, a connected network of silicon clusters is formed, the PL diminishes, and both dark- and photoconductivities from the deposited layers appear, leading Balberg et al.$^{39}$ to propose that a formation of percolating connected network of silicon clusters gives rise to mutual exclusion of the PL and the transport.$^{40}$ Annealing of the as-deposited films at high temperatures of about 1150°C–1200°C in a controlled environment (Ar or N gas) leads to phase separation and crystallization of the silicon monomers. In Figure 25.4, we present a few examples of cross-section transmission electron microscope (TEM) micrographs obtained after thinning the samples by ion milling to allow passing of the electron beam through the specimen. The images shown in Figure 25.4 are related to two different values of excess silicon content, $x \approx 18\%$ and $25\%$. Nearly spherical SiNCs can clearly be seen in both images, revealing typical silicon lattice fringes of mainly the [111] silicon crystal planes (and sometime also the [220] crystal planes). The insets to each figure show the silicon crystallographic planes obtained after spatial filtering of the images in the frequency domain for selected SiNCs marked by solid white squares. The diameter of the nanocrystals is not constant but rather varies in the range of 2–10 nm. The histograms shown in Figure 25.5 were obtained after statistical processing of numerous TEM images, identifying SiNCs and measuring their diameters for each value of the excess silicon volume content. The profile of the histograms can be fitted to a Gaussian shape size distribution with a full width at half maximum (FWHM) of approximately 2 nm at the lower content ($x \approx 10\%$) and 3 nm at the higher silicon volume content ($x \approx 30\%$), reflecting the inhomogeneous characteristics of the samples, which are typical to almost all fabrication techniques. The average diameter of the nanocrystals increases with increasing silicon content and can be fitted to the following power law (solid line in Figure 25.5b):

$$d (\text{nm}) = 2(x - x_0)^{1/3} \quad (25.1)$$

where

- $d$ is the average diameter of the SiNCs
- $x_0 = (8 \pm 2)\%$

The power exponent of 1/3 stems from the relationship between the diameter and the volume of the nanocrystals, reflecting the spherical characteristics of the SiNCs. Let us emphasize that SiNCs with a diameter smaller than 2 nm have not been observed so far, independent of the fabrication method that has been utilized, and Equation 25.1 is rather limited to the range of $10\% \leq x \leq 35\%$.

Another elegant method to produce continuous size variation of SiNCs in a single deposition run is the laser pyrolysis of silane in a gas-flow reactor, which has been reported by Ledoux et al.$^{41}$ In this technique, a pulsed CO$_2$ laser produces a molecular beam of silicon nanoparticles having a size distribution of 3–7 nm with the larger nanoparticles moving slower than the smaller ones. Using a rotating mechanical chopper synchronized with the laser pulses, size-selected nanoparticles are transmitted and deposited at different locations across the substrate. The PL image shown in Figure 25.6 reveals a color variation of the PL

![FIGURE 25.5](image-url)
A slightly narrower size distribution but a much better control of the position and the density of SiNCs has been achieved by synthesizing Si/SiO$_2$ superlattices. This method has been introduced by Lockwood et al. who have used silicon molecular beam epitaxy (MBE) system combined with ex situ UV ozone oxidation for growing alternating nanolayers of amorphous silicon (a:Si) and SiO$_2$. Later, this approach has been adopted to create alternating layers of SiNCs and SiO$_2$ using PECVD, low-pressure CVD (LPCVD) and RF magnetron sputtering in the serial sputtering mode. A key factor in all these methods is a good control of the layer’s thicknesses down to the nanometric length scales and good uniformity, particularly of the interfaces between layers. A similar approach, based on depositing alternating SiO$_2$/SiO$_2$ layers with $1 \leq x < 2$, has also been introduced where phase separation during annealing gives rise to a formation of a:Si layers that later on crystallize to create SiNCs. Results obtained by serial sputtering of silicon/SiO$_2$ superlattices are shown in Figure 25.7.

In this method, individual layers are deposited one on top of the other at deposition rates of about 2–4 nm/min to achieve a good thickness control. Cross-section HRTEM images, shown in Figure 25.7, reveal the presence of 2D alternating layers of SiNCs separated by amorphous SiO$_2$ layers. The order and the high quality of the interfaces can be appreciated from the low-magnification TEM image at the inset to Figure 25.7(a) while the higher magnification HRTEM micrograph of Figure 25.7(b) reveals 2D layers of SiNCs with average diameter of about 4.3 nm and a statistical size distribution similar to those presented in Figure 25.5. Figure 25.7(a) presents a STEM (scanning TEM) micrograph obtained after introducing high angle annular dark field (HAADF) detector into the microscope for collecting

**FIGURE 25.6** (See color insert following page 21-4.) (a) A photograph showing the PL variation along the substrate from silicon nanocrystals deposited by the laser pyrolysis technique. (b) The normalized PL spectra from different positions along the substrate. (Reprinted from Ledoux, G. et al., *Appl. Phys. Lett.*, 80, 4834, 2002. With permission.)

**FIGURE 25.7** High-resolution, cross-section TEM micrographs of serially sputtered SiNCs embedded in SiO$_2$ matrices. (a) STEM image (high z-contrast) revealing nearly spherical SiNCs (bright spots) with average diameter of 3 nm, separated by 10 nm of SiO$_2$ layers. The inset shows a lower magnification image of the superlattice. (b) HRTEM image of selected layers of SiNCs (marked by circles) having average diameter of 4.3 nm.
electrons that undergo high angle inelastic scattering to yield high z-contrast (where z is the atomic number of the element). In this image, the average diameter of the SiNCs is about 3 nm.

25.3 Luminescence Properties of Silicon Nanostructures

25.3.1 Optical Characterizations and Luminescence Bands

In general, several luminescence bands can be excited from silicon nanostructures, but most of them are not directly related to the nanostructures but rather to defects and imperfections in the host matrix. A relatively strong but misleading band is the so-called “F”-band (Fast-band) which has been observed for oxidized PS and for most silicon nanostructures embedded in SiO₂ matrices. The emission spectrum of this band extends over the blue-green (400–550 nm) range of the visible spectrum and is characterized by a fast PL decay time of several nanoseconds. This band has been observed from fully oxidized PS and from silicon nanostructures, such as silicon nanowires, with fairly large diameters and therefore, cannot be associated with the nanostructures themselves but with luminescence oxide and interface defects. Other luminescence bands that have been reported but do not relate to quantum size effects are UV bands (~350 nm) and near-IR bands of bulk silicon, unsaturated silicon bonds, and rare-earth heavy ions in the silicon matrix.

The size-dependent luminescence band, which shows a clear correlation with quantum size effects in silicon nanostructures, is called the “S”-band (Slow-band) and has been the subject of extensive investigation over the past two decades. The emission spectrum from this band can be tuned over the green–red–near IR spectral ranges (500–900 nm) and is characterized by significantly slower PL decay times (compared to the F-band) in the range of few microseconds. In a typical PL experiment, carriers (electrons and holes) are optically excited via absorption of photons of energies exceeding the energy bandgap of the nanostructures, followed by nonradiative relaxation of the photocarriers into the lowest energy levels of the nanostructures and finally, radiative recombination of the carriers that generates PL photons (see Figure 25.8).

Several complementary methods including direct optical absorption, ellipsometry, and PLE (PL excitation) have been utilized for revealing the absorption spectra from silicon nanostructures. In general, the absorption is substantially blue-shifted relative to the PL spectrum with a weak tail below 3 eV and increasing absorption above 3 eV that resembles some of the crystalline and the amorphous silicon characteristics. Therefore, it is not simple to correlate absorption data with the nanostructures themselves as contributions from silicon species, defects, and other absorbing centers in the host matrix cannot be distinguished. The photoexcited carriers undergo a fast relaxation, on timescales of several picoseconds, releasing their energy via nonradiative processes (such as phonons emission) and are trapped in the lower energy levels of the nanostructures. Hence, the luminescence spectrum, particularly the luminescence from the S-band, can directly be correlated with the silicon nanostructures to provide a direct tool for studying the size effects in these nanostructures. Two kinds of PL experiments can be performed. In continuous wave (cw) PL experiments, the system approaches a steady state where all relaxation and transient phenomena have already disappeared and a steady state PL spectrum is measured. Time-resolved PL experiments allow studying dynamical aspects of the nanocrystals where, the investigated dynamics depends on the temporal resolution of the measurement system, particularly the time resolution of the optical detection system that follows the decay of the PL signal shortly after the excitation pulse is switched off. In silicon nanostructures, the dynamics associated with interband (e.g., conduction to valence) radiative and nonradiative relaxation processes is on timescales of few microseconds and therefore, the excitation source can be either a pulsed laser or a beam of a cw laser modulated by an external light modulator (such as acousto-optical modulator).

25.3.2 CW Photoluminescence Experiments

One of the most convincing evidences for quantum size effects in silicon nanostructures comes from cw PL experiments on series of SiNCs having different diameters. The room temperature, normalized PL spectra shown in Figure 25.6 (SiNCs fabricated by laser pyrolysis of silane) and Figure 25.9 (SiNCs fabricated by co-sputtering) demonstrate this phenomenon where all PL spectra are blueshifted to higher energies for smaller nanocrystals. This behavior of the PL, e.g., a blueshift of the PL peak energy with the decreasing size of the nanocrystals, has also been observed for PS and for SiNCs fabricated by other methods. The relatively large bandwidth of all PL spectra (FWHM = 200 meV) has been...
assigned to the inhomogeneous characteristics of the samples, for example, the broad size distributions shown in Figure 25.5 for co-sputtered SiNCs.

Figure 25.10 (top) presents the variation of the PL peak energy with the increasing excess silicon volume content, $x$, in the range of $10\% \leq x \leq 35\%$ (bottom axis of Figure 25.10) and accordingly, with the decreasing average diameter of the co-sputtered SiNCs (upper axis of Figure 25.10). The solid line in this figure represents the best fit of the experimental results to an inverse power law as follows:

$$E - E_G = \frac{b}{(x - x_0)^{\delta/3}}$$  \hspace{1cm} (25.2)

where

$\delta/3 \equiv 0.45 \pm 0.1$ is the power exponent

$E_G = 1.12$ eV is the energy bandgap of bulk silicon

$x_0 \equiv (9 \pm 2\%)$ (very close to the experimental value of $x_0$ obtained for the variation of the average diameter with $x$; see Equation 25.1)

Using Equations 25.1 and 25.2, we find a relationship between the PL energy shift (relative to bulk silicon) and the diameter of the SiNCs:

$$\Delta E = E - E_G = \frac{A}{d^\delta}$$  \hspace{1cm} (25.3)

where

$\delta \equiv 1.35 \pm 0.3$

$\Delta E$ is called the “confinement energy” of the nanocrystals

A very similar inverse power law with essentially the same power exponent has been found for SiNCs fabricated by laser pyrolysis of silane,\textsuperscript{41} by PECVD,\textsuperscript{34} and by other techniques. However, this power exponent deviates from the exponent predicted from a simple QC model, e.g., a particle confined into a spherical quantum dot having infinite potential barrier. In the latter case, the quantized energy levels of the dot are given by $E_{nl} = \hbar^2 z_n^2 / (m^* d^2) \sim 1/d^2$, where $z_n$ is the $n$th root of the $n$th order spherical Bessel function and $m^*$ is the effective mass of the carriers in the bulk medium. Therefore, in such a simple effective mass model, one would expect the confinement energy to vary as $\Delta E \sim 1/d^2$. Several factors may account for the deviation of $\delta$ from this simple model. A major factor, which has been ignored so far, is the Coulomb interaction between electrons and holes to create excitons. Excitons are bound states of electron–hole pairs that are created by the Coulomb attraction between the charged carriers. In a bulk silicon crystal, the Bohr radius of the exciton is given by $a_{ex} = \hbar^2 / (e^2 \varepsilon_{Si} \mu) = 5 - 7$ nm, where $\varepsilon_{Si}$ is the dielectric constant of silicon and $\mu$ is the reduced mass of the electron–hole pairs. QC modifies this picture, particularly when the size of the nanocrystals becomes comparable to the
Bohr radius of the exciton. In this case \((d/2 \leq a_0)\), which is called the strong confinement regime, the electrostatic Coulomb energy is scaled as \(E_{\text{ex}} = e^2/\varepsilon_0 \varepsilon_r d/2 \sim 1/d^2\) as opposed to \(\sim 1/d^3\) of the effective mass model; see Figure 25.8. Thus, we can expect the power exponent to vary in the range of \(1 \leq \delta \leq 2\) with \(\delta \approx 2\) being the weak confinement limit for big nanocrystals. Indeed, recent first-principle calculations (meaning that the many-body problem of having a finite number of silicon atoms in a dot, including the specific form of surface termination bonds, has numerically been solved) such as the LCAO (linear combination of atomic orbitals) and the pseudo-potential methods, have found a power exponent of \(\delta \equiv 1.4\), in a very good agreement with the experimental results, thus providing a solid support to the QC model.

Yet, cw PL experiments provide additional information about SiNCs that cannot be easily interpreted by the QC model. Figure 25.10b shows the variation of the integrated PL intensity, which is obtained by integrating the area below the non-normalized PL spectra (inset to Figure 25.10a) versus the silicon volume content (and the average diameter of the nanocrystals). In order to obtain the actual PL yield, one should take into account the varying density of SiNCs as lower \(x\) means lower density of SiNCs. The corrected PL yield, obtained after dividing the integrated PL by \(x\), is shown in Figure 25.11. In this presentation, the precise number of photons absorbed per each unit area could only be estimated. While this quantity has not been measured directly, in several other experiments aimed at measuring the absolute value of the PL yield, it has been found that the PL yield for SiNCs having a diameter of 4–5 nm is fairly high in the range of 60%–80%. Similar values have also been found for PS. The maximum yield of 30%–50% shown in Figure 25.11 (for nanocrystals emitting their light in the 650–750 nm, red-orange spectral range) should be considered as a lower limit. However, the general trend of the PL yield, e.g., sharp increase with the decreasing diameter up to a maximum for 4–5 nm in diameter nanocrystals and a decrease of the yield for smaller nanocrystals, has been confirmed by numerous groups. This finding cannot simply be explained by the QC model. According to this model, the smaller the nanocrystals the more pronounced is the relaxation of the momentum conservation rule (as confirmed experimentally) and accordingly, a larger PL yield should be measured. Further implications of the high PL yield and its relation to the rates of radiative and nonradiative processes in SiNCs is discussed in Section 25.3.3.

Among the first experiments indicating the mutual role of QC and SC is the one reported by Wolkin et al. In this experiment, a series of PS samples having different porosities have been kept under controlled environment to avoid oxidation and to ensure that the surface of the silicon nanostructures is passivated by Si–H chemical bonds. The state of passivation has been monitored by FTIR infrared spectroscopy to exclude the presence of Si–O and Si–OH bonds. A second group of similar PS samples were exposed to air for 24 h, allowing surface oxidation and the presence of Si–O bonds. Results of room-temperature PL measurements from both series of samples are presented in Figure 25.12. Despite that the actual average size of the silicon nanostructures cannot accurately be measured for PS, it is well known that smaller silicon features appear for larger porosities of the samples. The PL spectra, shown in Figure 25.12a, show indeed a consistent blueshift with the increasing porosity for hydrogen-terminated PS samples. On the other hand, oxygen-terminated samples (Figure 25.12b) show, at first, a blueshift of the PL spectra up to the yellow (~600 nm) and then, no blueshift and even a redshift for the blue-green emitting PS samples. Clearly, this phenomenon cannot be explained by the QC model alone and the role of SC, particularly the passivation of the PS surface must be taken into account. The model proposed by Wolkin et al. assumes that some of the dangling bonds, on the silicon oxide interface, are passivated by the Si=O double bond, which is known to be more stable than other forms of surface passivation. Based on this assumption, the authors simulated the electronic band structure of SiNCs having Si=O double bonds at the silicon oxide interface. The results, shown in Figure 25.13, suggest that the QC model is valid for hydrogen-terminated SiNCs as radiative recombinations are via free excitons (e.g., excitons of the bulk nanocrystalline silicon core) for all sizes of the nanocrystals. However, for Si=O passivated SiNCs, both electrons and holes can be localized (or trapped) by the Si=O bonds where, in zone I of Figure 25.13 none of the carriers are trapped, in zone II only electrons are trapped, and in zone III both electrons and holes are trapped to form surface-trapped excitons. This model provides a nice and elegant explanation to the experimental results shown in Figure 25.12, particularly for kinetic properties associated with the joint contribution of SC and QC to the shift of the energy bandgap.

Yet, as pointed out by these authors, the intensity of the PL (which is proportional to the integrated PL) increases by few orders of magnitude up to the orange emitting samples and then, diminishes for higher porosity samples emitting in the blue-green; quite similar to the PL yield presented in Figure 25.11 for co-sputtered
SiNCs. Hence, dynamical characteristics of the nanocrystals still require sufficient explanations, particularly as the PL decay time from the blue-green PS samples have been reported to be much faster (0.07 μs in the blue) than those of the red samples (∼2 μs) and therefore, according to the QC model, should exhibit higher PL yield. Further discussion of this topic will be given in Section 25.4.2 after presenting the vibron model.

25.3.3 Time-Resolved Photoluminescence Experiments

The PL decay process from silicon nanostructures has been intensively investigated over the recent years, both from PS and from SiNCs embedded in SiO2 matrices. In a typical setup, a train of short laser pulses excites the carriers to their lowest excitonic state from which they radiatively recombine to generate PL photons. The PL decay time is measured shortly after the pump laser is switched off using, for example, a gated photon-counting system that is mostly suitable for SiNCs since the relevant dynamics occurs on timescales of sub-microseconds up to few milliseconds.

A typical room-temperature, time-resolved PL decay curve from co-sputtered SiNCs with x = 18% (average diameter of ∼4.5 nm) and at a PL energy of 1.65 eV (PL wavelength of ∼750 nm), is shown in Figure 25.14. The temporal behavior of the decay function (Equation 25.4). The inset shows the PL decay curves at various low temperatures.

**FIGURE 25.12** Room-temperature PL spectra from PS with different porosities (a) kept in Ar atmosphere, (b) after exposure to air. (Reprinted from Wolkin, M.V. et al., Phys. Rev. Lett., 82, 197, 1999. With permission.)


**FIGURE 25.14** Room temperature, time-resolved PL decay normalized to the initial PL intensity taken at PL photon energy of 1.65 eV for the x = 18% sample (average diameter of 4.5 nm). The solid line represents the best fit of the experimental data (symbols) to the stretched-exponential decay function (Equation 25.4). The inset shows the PL decay curves at various low temperatures.
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PL does not follow a simple exponential decay function \[ I/I_0 = \exp(-t/\tau); \] notice the semilogarithmic scale of Figure 25.14, but rather a stretched-exponential decay function of the form:

\[
I(t) = I_0 \exp \left( -\left( \frac{t}{\tau} \right)^{\beta} \right)
\]

where 
- \( \tau \) is the characteristic PL lifetime,
- \( 0 < \beta \leq 1 \) is the dispersion exponent of the PL decay function.

This form of the PL decay function has been observed for many classes of silicon nanostructures and is frequently assigned to disordered characteristics of systems where dispersive transport takes place, particularly migration and trapping–detrapping (or release) of photoexcited carriers. This topic is directly related to transport phenomena in PS and SiNCs where disperse transport has been observed and discussed but will not be reviewed here. The solid line in Figure 25.14 represents the best fit of the experimental data to Equation 25.4, yielding a PL lifetime of about \( \sim 40 \mu s \) and \( \beta \sim 0.85 \). As opposed to the dispersion exponent that is approximately independent on the PL energy, the PL decay time decreases with the increasing PL energy, from about \( 100 \mu s \) at 1.4 eV to few \( \mu s \) at 2 eV. This is rather important as it indicates, again, about the inhomogeneous nature of the PL spectrum, in accordance with the inhomogeneous size distributions of the nanocrystals shown in Figure 25.5. According to the QC model, the smaller the SiNCs (and therefore, the breakdown of the \( k \)-conservation rule), the larger the radiative transitions rate and the faster the radiative lifetime. We will follow this picture, assuming that each wavelength in the PL spectrum probes a different size of the nanocrystals, as suggested by the QC model. In addition, let us denote the substantial dependence of the PL decay time (at a given PL energy) on temperature, shown at the inset to Figure 25.14. The lower is the sample temperature the longer is the PL decay time, approaching fairly slow PL lifetimes of about only few milliseconds at low temperatures (below 50 K). The variation of the PL lifetime with temperature, for several PL energies, is presented in the Arrhenius plot (semilogarithmic scale versus the inverse temperature) of Figure 25.15.

We can identify two distinct temperature regimes in Figure 25.15: a low-temperature regime (below 60 K) where the PL lifetime is essentially independent of temperature and a high-temperature regime (above 60 K) where the PL lifetime gets shorter with the increasing temperature. To follow these characteristics of the PL lifetime let us briefly describe the exchange-splitting model that has originally been proposed by Calcott et al. for PS, and later on adopted for other classes of silicon nanostructures. In typical semiconductors the lowest excitonic state is composed of conduction electrons having a total angular momentum of \( J = 1/2 \) (the sum of \( L = 0 \) orbital angular momentum of the conduction band and spin \( 1/2 \) of the electrons) and heavy holes states having \( J = 3/2 \) \((L = 1 \) of the valence band and spin \( 1/2 \)). Hence, the total angular momentum of the exciton can be either 1 or 2. Of course, QC makes this picture much more complicated as different bands can be mixed and the spherical symmetry of the ideal dot can be distorted (in fact, the spherical symmetry of the dot is always slightly distorted when constructed from a cubic crystal). Therefore, Calcott et al. treated the exciton as composed of two spin \( 1/2 \) particles assuming that only the spin components of the total angular momentum are conserved. In this case, the total spin of the exciton can be either \( S = 1 \) (triplet) or \( S = 0 \) (singlet). The Coulomb exchange interaction between electrons and holes lifts the singlet–triplet degeneracy. To follow the role of the exchange interaction, let us point out that, according to the Pauli principle, a singlet state (which is antisymmetric with respect to exchange of the electron–hole spins) has to be symmetric with respect to exchange of the electron–hole orbital states, while the spin-triplet state has to be orbitally antisymmetric with respect to this exchange. Hence, the Coulomb energy associated with the exchange interaction is always larger for the spin-singlet state \( (S = 0) \) relative to the spin-triplet state \( (S = 1) \). The situation is schematically illustrated at the inset to Figure 25.15 where \( k \) is the singlet–triplet exchange splitting energy. In a bulk silicon crystal, the splitting energy is fairly small, of the order of \( \sim 150 \mu \text{eV} \); however, since the exchange interaction is proportional to the overlap between the electron and the hole states, it can significantly be enhanced by confining the exciton into small nanostructures. This picture explains very well the behavior of the PL lifetime. Denoting the lifetimes of the upper singlet and the lower triplet states by \( \tau_u \) and \( \tau_l \), respectively, and taking the population of the two states to be in thermal equilibrium (which is a reasonable assumption as relaxation processes between these neighboring states should very fast, of the order of few picoseconds), we find the following expression for the PL radiative lifetime:
The solid lines in Figure 25.15 represent the best fit of the PL lifetimes to Equation 25.5. The appearance of two temperature regimes can be understood now as follows. At low temperatures (where $kT < \Delta$), only the lower triplet state of the exciton is populated and the PL decay time is dominated by the long lifetime of the triplet state. At higher temperatures, the upper singlet state becomes populated. If the radiative lifetime of this state is much faster than that of the lower triplet state, it will dominate the PL decay time at high temperatures, giving rise to exponentially faster lifetimes (versus the inverse temperature), which is in a very good agreement with the results shown in Figure 25.15. The upper state lifetime is expected to be (relatively) short since the spin singlet is an optically active state (e.g., radiative recombination of the exciton into the ground state of no exciton is allowed) as opposed to the lower triplet state, which is optically forbidden state according to the spin selection rules. The spin–orbit interaction can mix the singlet–triplet states, making the triplet state weakly allowed. However, this interaction is fairly weak in silicon so that the lifetime of the triplet state is expected to be quite long.

Before discussing the application of this analysis to the various SiNCs samples (of variable silicon volume content), let us denote the contribution of nonradiative relaxation processes to the measured PL decay time. In principle, the measured (inverse) PL decay time is the sum of radiative and nonradiative relaxation rates, $\frac{1}{\tau} = \frac{1}{\tau_R} + \frac{1}{\tau_{NR}}$, where $\tau_{NR}$ is the nonradiative relaxation time. Yet, as will be further explained hereafter, at high temperatures the measured PL decay time is dominated by radiative processes and we may take, $\tau_{NR} \approx \tau_S$ (where $\tau_S$ is the singlet lifetime). At low temperatures, the contribution of nonradiative processes cannot be neglected; thus we have $\tau^{-1} = \tau^{-1}_R + \tau^{-1}_{NR}$, with $\tau_R$ being the triplet (radiative) lifetime.

The above analysis, which yields the upper level lifetime, the lower level lifetime, and the exchange-splitting energy for each of the PL energies, has been exploited to the entire set of SiNC samples having different average diameters. The results are presented in Figure 25.16 for selected samples. Let us emphasize again that each of these samples is characterized by inhomogeneous, approximately Gaussian, size distribution of the nanocrystals (see Figure 25.5). The PL energy probes a given size (or diameter) of the nanocrystals within this distribution. This is schematically illustrated at the bottom of Figure 25.16, where a smaller PL energy is linked to a larger nanocrystal with a scale of diameters (based on Equation 25.3—the relationship between the PL energy and the diameter of the nanocrystals). For a given size distribution, the PL intensity varies across the PL spectrum yielding more photons near the average size of the nanocrystals.
SiNCs. Nevertheless, according to the QC model the PL lifetime should be independent of the size distribution but rather characteristic of a given nanocrystal’s diameter. In other words, according to the QC model, the PL lifetime should vary with the PL energy but should be independent of the size distribution of the nanocrystals. The results shown in Figure 25.16a for the upper state (singlet) lifetime and in Figure 25.16b for the exchange-splitting energy, remarkably follow the QC model. The upper state lifetime, $\tau_u$, decreases by an order of magnitude (from about 40–50μs down to 2–3μs) with increasing PL energy, in agreement with the QC model where larger relaxation of the $k$-conservation rule is expected for smaller nanocrystals. Furthermore, all the results for $\tau_u$ from different samples having different average diameters, collapse into a single line (the blue line in Figure 25.16a) independent of the size distributions of the samples. The PL energy probes a lifetime of nanocrystals having the same diameter, which should be independent of how many nanocrystals of that size appear at a given distribution. A similar conclusion holds for the exchange-splitting energy. The smaller the nanocrystal, the larger the exciton confinement and the bigger the splitting energy. Here again, as the splitting energy is a size-dependent property of the nanocrystals, this energy should be independent of the size distribution and the results for all samples should collapse into a single line.

So far, we have found the upper state (singlet) lifetime and the exchange-splitting energy to provide a solid support to the QC model. However, a completely different behavior appears for the lower state (triplet) lifetime, $\tau_s$. The lower state lifetime is essentially independent of the PL energy and therefore, is not a size-dependent property of the nanocrystals. In contrast, $\tau_s$ depends on the excess silicon content ($x$), and accordingly, on the average diameter of the SiNCs. Thus, the lower state lifetime cannot be assigned to radiative relaxation from the triplet state but rather to nonradiative relaxation processes that depend on the environment of the SiNCs, e.g., the amount of excess silicon in the host matrix and, as will be explained later, on the SC (or passivation) of the SiNCs. These findings suggest that QC is responsible for the relatively fast radiative transitions rates from SiNCs, while SC is responsible for the fairly slow nonradiative relaxation processes in these nanocrystals. Yet, both processes are responsible for the PL yield, $\eta$ (see Section 25.3.2), which is derived from the competition between radiative and nonradiative recombination rates, as schematically illustrated at the inset to Figure 25.11, and is given by the following expression:

$$\eta = \frac{\tau_{\text{R}}}{{\tau_{\text{R}}} + {\tau_{\text{NR}}}} = \frac{\tau_{\text{NR}}}{{\tau_{\text{R}}} + {\tau_{\text{NR}}}} = \frac{\tau}{\tau_{\text{R}}}$$ (25.6)

where $\tau^{-1} = {\tau_{\text{R}}}^{-1} + {\tau_{\text{NR}}}^{-1}$ is the total (measured) PL decay time. For high-yield samples (average diameter in the range of 4.5–5.5 nm), the PL decay time varies by more than two orders of magnitude over the 50–300 K temperature range (see Figure 25.15), while the integrated PL is approximately constant over the same temperature range (it varies by less than a factor of 2; see Figure 25.17).

**FIGURE 25.17** The variation of the integrated PL as a function of temperature for various samples having different average diameters.

Both experiments (Figures 25.16 and 25.17) suggest that over the 50–300 K temperature range, the PL decay time is dominated by radiative transitions of the exciton where, $\tau_s \ll \tau_{\text{NR}}$. In this range, we find $\eta \equiv \text{constant}$, in a good agreement with the high yield measured for these SiNCs. At this temperature range, radiative transitions are dominated by the upper-state lifetimes, $\tau \equiv \tau_U \sim 2–50\mu$s, which should be compared to the nonradiative lifetimes, $\tau_{\text{NR}} \sim 1–3\text{ ms}$. Notice that nonradiative rates have been measured at low temperatures and, in general, one should expect faster nonradiative lifetimes at higher temperatures. Nevertheless, all experimental results indicate that $\tau_s \ll \tau_{\text{NR}}$ over the entire temperature range, up to room temperature.

Based on the assignment of radiative lifetime to the upper (singlet) state, we can estimate now the oscillator strength for optical transitions from this state. The oscillator strength, $f_{\text{var}}$, is a dimensionless parameter that measures the strength of a dipole-allowed optical transition from a given jth state to another jth state, relative to all other dipole-allowed transitions from the same (ith) state. The oscillator strength is normalized so that the sum over all oscillator strengths originated from the same level, is equal to 1, a property which is known as the $f$-sum rule$^{29}$ (or the Thomas–Reiche–Kuhn sum rule). The relationship between the oscillator strength and the (spontaneous) radiative lifetime of the singlet state is given by$^{18}$

$$f_{\text{GR}} = \frac{2\pi mc^3h^2\epsilon_0}{E^2e'n} = \frac{1}{\tau_U}$$ (25.7)

where

- $m$ is the electron mass
- $n$ is the refractive index of the medium
- $E$ is the photon energy

In Figure 25.18, we have plotted the oscillator strength for optical transitions, from the upper singlet state, versus the confinement energy, $\Delta E$. Here again, all results from samples having
QC plays a major role here. For small nanocrystals, \( QC \) enhances the oscillator strength for small nanocrystals, but only to the order of \( (2-3) \times 10^{-4} \) and, apparently up to \( 10^{-3} \) for blue-emitting nanocrystals. For a comparison, in direct bandgap semiconductors, the oscillator strength for interband transitions is \( -1 \), about 3–4 orders of magnitude larger than the oscillator strength of our silicon nanostructures. A direct consequence of this result is that the efficient light emission from SiNCs is due to exceptionally slow nonradiative lifetimes in silicon nanostructures relative to direct bandgap semiconductors. However, the author of this chapter prefers not to talk about “bands” in small silicon nanostructures as we actually deal with a discrete set of levels rather than “bands.”

2. **Nonradiative Processes**: As opposed to radiative processes, QC does not play a major role here. The efficient light emission from SiNCs is due to exceptionally slow nonradiative relaxation processes in SiNCs, of the order of few milliseconds. While this result explains very well the high quantum yield from SiNCs, it raises another fundamental question. The measured nonradiative lifetimes of few milliseconds are typical for the purest silicon wafers, with impurity levels of about \( 10^{13} \)–\( 10^{14} \) cm\(^{-3} \) (e.g., one impurity atom per more than a billion of silicon atoms).\(^1\) It is well known that higher density of impurities enhances nonradiative relaxation rates, for example, in p-type silicon crystals with boron concentration of about \( 10^{16} \) cm\(^{-3} \), the minority carriers’ lifetime is about 0.1–1 \( \mu \)s; adding \( 10^{17} \) cm\(^{-3} \) Au impurities into the crystal gives rise to nonradiative lifetimes as short as 10\(^{-10} \) s. The high PL yield and the slow nonradiative relaxation times in SiNCs seem to be a universal property of SiNCs, essentially independent of the method of fabrication (see Section 25.2). Yet, these fabrication methods are not necessarily “clean” and free of imperfections, defects, and impurities. In fact, the quality of interfaces between SiNCs and the host matrices cannot be compared to those obtained by epitaxial growth methods; their shape and symmetry are less regular than nanocrystals synthesized by colloidal chemistry and the level of impurities and defects is far from those obtained by advanced silicon crystal growth techniques. Considering all these facts, one would expect to find much faster nonradiative relaxation times in SiNCs, at least a considerable variation of the PL yield among the various preparation techniques. It seems that SC plays a major role in excluding nonradiative relaxation channels.

\[ f_{OS} = f_0 \exp \left( \frac{\Delta E}{E_{OS}} \right) \]  

(25.8)

where

\[ E_{OS} = 0.4 \pm 0.1 \text{ eV} \]

is the characteristic oscillator strength energy

\[ f_0 = (3.5 \pm 1) \times 10^{-3} \]

is the oscillator strength of the bulk crystal (no confinement)

The above analysis of the PL characteristics seems to adequately explain most of the experimental findings but, at the same time, open up other fundamental questions concerning the origin of the PL. Let us briefly summarize these findings and the most relevant questions\(^3\):

1. **Radiative Processes**: QC plays a major role here. For small silicon nanostructures, QC gives rise to a blueshift of the bandgap energy, up to the visible range of the spectrum, according to the power law of Equation 25.3. At the same time, the increasing bandgap energy gives rise to shorter radiative lifetimes since \( \tau \sim 1/E^2 \) (without taking into account the effect of confinement on the oscillator strength, which will be discussed hereafter). A second contribution of QC to radiative processes comes from the breakdown of the \( k \) - (or momentum) conservation rule. However, the effect of confinement on the rate of radiative transitions has been overestimated by many researchers over the years. Our estimate of the oscillator strength for the case of no confinement is, \( f_0 \sim 10^{-3} \), in a fairly good agreement with the poor optical emission and the fairly slow radiative lifetimes (210 ms) from bulk silicon. QC enhances the oscillator strength for small nanocrystals, but only to the order of \( (2-3) \times 10^{-4} \) and, apparently up to \( 10^{-3} \) for blue-emitting nanocrystals. For a comparison, in direct bandgap semiconductors, the oscillator strength for interband transitions is \( -1 \), about 3–4 orders of magnitude larger than the oscillator strength of our silicon nanostructures. A direct consequence of this result is that the efficient light emission from SiNCs is due to exceptionally slow nonradiative lifetimes in silicon nanostructures relative to direct bandgap semiconductors. However, the author of this chapter prefers not to talk about “bands” in small silicon nanostructures as we actually deal with a discrete set of levels rather than “bands.”
in SiNCs. Understanding what possible mechanism could give rise to remarkably slower nonradiative relaxation rates is a major issue in the field and is expected not only to explain the origin of the efficient PL, but also to explore novel aspects of SC at the nanoscales. A possible mechanism that could prevent nonradiative relaxation processes at these length scales, and is related to SC, is presented and discussed in the following section (the vibron model). In principle, understanding this mechanism may open up new horizons concerning surface engineering of nonradiative processes at nanoscales.

25.4 The Vibron Model: The Relationship between Surface Polar Vibrations and Nonradiative Processes

The purpose of this section is to discuss basic properties of SiNC surfaces, particularly the silicon–SiO₂ interface (Section 25.4.1) as most experimental data reported so far are related to SiNCs embedded in silicon dioxide matrices. The “vibron” model (Section 25.4.2), which correlates surface relaxation at the silicon–SiO₂ interfaces to nonradiative processes, is proposed as a specific mechanism that passivates the nanocrystals against nonradiative relaxation channels. Such a mechanism can explain the role of SC and its influence on nonradiative relaxation processes in SiNCs. Finally, in Section 25.4.3, we describe recent experimental results that seem to support the vibron model.

25.4.1 The Silicon–Silicon Dioxide Interface

The silicon–SiO₂ interface is one of the most studied interfaces due to the vital role it plays in microelectronics, particularly in the MOS (metal-oxide-semiconductor) technology. In general, it is well known that thermally grown oxide on top of a crystalline silicon substrate has amorphous structure down to distances of about 1–3 nm away from the interface. The common picture of the interface is that of 1–2 monolayers of non-stoichiometric SiOₓ (with 1 < x < 2), followed by 1–2 nm of strained SiO₂ and a remaining layer of stoichiometric, strain-free amorphous SiO₂.

The Si–SiO₂ interface plays a major role in the MOS technology as it can permanently trap charges (interface charges) acting as a source of voltage that shift the electrical characteristics of MOS devices. The amount of surface traps can be as high as 10¹⁵ cm⁻² (meaning that essentially all surface atoms can trap charges); however, after hydrogen annealing that passivates most of surface dangling bonds, the amount of surface traps can be reduced to a level of ~10¹⁰ cm⁻² or less. The electronic properties of bulk silicon crystals are almost insensitive to these imperfections due to the very small STV ratio of bulk materials (see, Figure 25.3). However, for small SiNCs, the circumstances are substantially different as the number of atoms (or molecules) belonging to the surface of the nanocrystal is similar to the number of silicon atoms of the “bulk” nanocrystal.

Several theoretical and experimental investigations have been conducted for exploring the nature of the interface transition region, of about 1–3 nm, where the structure changes from a perfect order of crystalline silicon to a disordered structure of amorphous SiO₂. Numerous reports have shown that the interface may include few monolayers of compressed crystalline, epitaxial-oxide phase in the form of either cristoblite, quartz, or even tridymite. After few monolayers of strained crystalline oxide, the stress is released and amorphous phase of SiO₂ appears. A quite remarkable demonstration to the presence of crystalline SiO₂ phase at the Si–SiO₂ interface has been reported by Cho et al.86 using thermally oxidized SOI (silicon-on-insulator) substrates to create a thin crystalline silicon layer embedded in between relatively thick amorphous SiO₂ (a 2D silicon quantum well). The cross-section HRTEM images of these structures, which can be considered as 2D analogous of 0D SiNCs, are shown in Figure 25.19a and b. Despite that the exact crystalline phase of SiO₂ could not be identified in this experiment, these images demonstrate the possibility of creating crystalline SiO₂ at the Si–SiO₂ transition region. Notice also that the model of surface passivation by Si=O double bonds (see Section 25.3.2) proposed by Wolkin et al.17 has been shown to be consistent with the presence of cristoblite phase at the transition region of the interface.86 The remarkable point about the TEM images shown in Figure 25.19a and b is the fairly thick crystalline-oxide layer, of ~2–3 nm, which may contain more than 10 monolayers of crystalline SiO₂. The situation is much more complicated when dealing with nonplanar surfaces such as the spherical surface of SiNCs. The EFTEM (energy filtered TEM) image of a single SiNC, shown in Figure 25.19c, was taken from Ref. [86] and is one of the best images of a single nanocrystal ever been reported. Daldosso et al.86 provided clear evidences to the existence of a Si–SiO₂ spherical transition region, of about 1 nm in thickness, which is marked by the dashed lines in Figure 25.19c. While the signature of crystalline SiO₂ is absent in this image, it is worth noting that such a signature from few monolayers of a crystalline phase, thinner than 2 nm, has not been observed even for planar surfaces and definitely not for the much more challenging spherical surfaces discussed here. The presence of a spherical transition region made of crystalline SiO₂ is not a prerequisite for the vibron model to be discussed in Section 25.4.2. Yet, the existence of such a surface would provide a supplementary support to the model as coherent vibrations across the SiNCs surface, are expected to enhance the vibron effect (see Section 25.4.2) as compared to noncoherent vibrations. The presence of such a surface would also help to understand the analogy between the “classical” polaron problem and the vibron model as “phonons.”

THE VIBRON MODEL: NONRADIATIVE PROCESSES AT NANO SCALES

The vibron model is a specific mechanism that passivates the nanocrystals against nonradiative relaxation processes; it can be explained as a specific surface relaxation mechanism that prevents nonradiative relaxation processes at the nanoscale. The vibron model can be described as a specific mechanism that passivates the nanocrystals against nonradiative relaxation processes; it can be explained as a specific surface relaxation mechanism that prevents nonradiative relaxation processes at the nanoscales.
are natural vibrations of a crystalline SiO$_2$ phase. However, this is essentially a technical point and the vibron model can be justified even in the absence of a crystalline SiO$_2$ shell.

### 25.4.2 The Vibron Model

Following the conclusions of Section 25.3, particularly the conclusion that the high PL efficiency is due to the inhibition of nonradiative relaxation in SiNCs, we should look for a specific mechanism, associated with SC, which can “passivate” the nanocrystals against nonradiative relaxation processes. Such a mechanism has been proposed in Refs. [18,19,87,88] and is called the “vibron” model. Let us briefly explain this model that assigns the inhibition of nonradiative channels to a resonant coupling between electronic states of the nanocrystals and surface vibrations of the silicon–oxygen bonds. These vibrations can be either noncoherent, e.g., vibrations associated with the Si=O and/or the Si-O bonds on the surface of the SiNCs, or coherent vibrations of a spherical crystalline SiO$_2$ shell that wraps the inner crystalline silicon core of the nanocrystals.

In general, a major source of scattering and relaxation in any semiconductor is the electron scattering from lattice vibrations of its own crystal, known as phonons. The phonon dispersion relation (e.g., the relation between the frequency and the wavevector of the phonons) consists of two branches: an acoustic branch (where $\omega$ goes to zero as $\vec{k}$ approaches zero) and an optical branch of phonons that can interact with light (with non-zero value of $\omega$ at $\vec{k} \to 0$). In addition, each of these branches is divided into longitudinal and transversal phonon modes where, for longitudinal modes (LO and LA), the atoms vibrate parallel to the propagation direction while for transversal modes (TO and TA), the atoms vibrate perpendicular to the propagation direction of the phonons. In polar semiconductors (such as GaAs), where ions constructing a unit cell of the crystal carry positive and negatives (ionic) charges, longitudinal vibrations of the crystal generate a long-range polarization field. The polarization field is an electric field produced by the electric dipole moment of the vibrating ions, which is responsible for the strong interaction between LO phonons and charged carriers (electrons and holes) in polar semiconductors, and is a major source of scattering and energy dissipation in these semiconductors. In silicon, however, the situation is quite different as silicon is a covalent semiconductor having the same atoms in a unit cell of the crystal that do not carry a net charge. Therefore, neither longitudinal nor transversal phonon vibrations in silicon generate a polarization field, giving rise to significantly slower phonon scattering rates compared to polar semiconductors. The presence of charged impurities, vibrating bonds, or any other source of oscillating electric dipoles (or charges) on the surface of silicon could generate electric field that interacts with the charged carriers. However, these are small surface effects that have minor impact on the electronic properties of bulk silicon crystals.

The situation is substantially different when dealing with low-dimensional silicon nanostructures, particularly small SiNCs. In these nanocrystals, the surface can no longer be treated as a small perturbation since a significant portion of the atoms sit on the surface of the nanocrystals (see Figure 25.3). While vibrations of the core silicon crystal cannot produce a polarization field, polar vibrating bonds on the surface of the nanocrystals can generate a polarization field, in the vicinity of the nanocrystals, that interacts with the charged carriers. This is the basic mechanism that stands behind the vibron model. Some readers may argue that this picture seems to contradict our goal, e.g., finding a mechanism that will allow to passivate the nanocrystals against nonradiative processes. Indeed, the smaller are the nanocrystals the bigger is the surface area giving rise to larger amount of nonradiative relaxation channels. This is also the case for SiNCs with a diameter larger than 10 nm. However, for smaller SiNCs with a diameter less than 10 nm, a new mechanism of resonant coupling between surface vibrations and electronic states appears and allows passivating the nanocrystals against nonradiative channels.

To follow the origin of this mechanism, let us consider the SiNC schematically illustrated in Figure 25.20, which consists
of (approximately) spherical nanocrystalline silicon core terminated with silicon–oxygen bonds on its surface. Traditionally, finding the electronic levels and the vibrational modes of a bulk semiconductor have been treated as two independent problems (the so-called adiabatic approximation) as the electronic energies are of the order of few eV while vibrational (or phonon) energies are an order of magnitude smaller. At present, we will follow this picture, but later on we will reexamine this assumption. The SiNCs spectrum of electronic levels has been calculated by several groups using various techniques such as tight-binding,\(^5\) pseudo-potential,\(^9\) and effective mass.\(^2\) Most reports have focused on the lowest unoccupied conduction level (called the LUMO state) and the highest occupied valence level (the HOMO state) as these levels are involved in interband optical transitions contributing to the PL. However, the vibron model requires some knowledge about higher excited states of the system. In direct bandgap semiconductor nanocrystals, it is convenient to classify the electronic levels according to their orbital symmetry using the standard atomic orbital notations, e.g., \(S, P, D, \) etc.\(^1\) Several factors make the classification for SiNCs more complex. First, the anisotropic effective mass of conduction electrons (with a transverse mass of \(0.19m_0\)) and longitudinal mass of \(0.92m_0\) may give rise to a splitting of the levels with lower energy levels associated with the heavier mass. Secondly, the six minima degeneracy of the conduction band in bulk silicon (near the X-point, along the family of (100) directions; see Figure 25.1), which should be preserved for an ideal spherical dot, will be lifted by any deviation from a perfect spherical symmetry. In addition, a unique splitting into two groups of levels that are symmetric/antisymmetric under inversion (e.g., \(\vec{k} \rightarrow -\vec{k}\)) are expected for small SiNCs due to intervalley couplings.\(^9\) Finally, mixing between different bands is expected in small SiNCs.

For the purpose of our model, we will ignore most of these fine splitting and mixing features, referring to the lowest two sublevels of each band as 1\(S\) and 1\(P\) for conduction electrons (1\(S\) and 1\(P\) for holes), as schematically illustrated on the left side of Figure 25.21. \(E_g\) is the effective energy bandgap (the energy difference between the 1\(S\) and the 1\(S\) states) and \(\Delta E_C\) and \(\Delta E_V\) are the energy differences between lowest conduction and valence sublevels, respectively. On the right side of Figure 25.21, we schematically illustrate the configuration space diagram for the Si=O surface bonds (e.g., the variation of the potential energy versus the length of the Si=O bond) with a ground vibrational state and a first excited state having a vibrational energy of \(\hbar \omega_{VB}\) (a common approximation here is taking the potential energy to be parabolic and the quantized vibrational levels and energies being the levels of a simple harmonic oscillator). The vibrational energies are measured upward for conduction electrons and downward for valence holes. Notice that vibrational energies are size independent (e.g., independent on the diameter of the nanocrystal), depending only on the type of bonding used to terminate the surface of the nanocrystal. On the other hand, the quantized electronic levels of the nanocrystal are size dependent and should increase with the decreasing diameter of the SiNCs. Hence, for (relatively) big SiNCs, one expects the conduction/valence energy differences to be fairly small compared to vibrational energies. With the decreasing size of the

\[\Delta E_c \quad \Delta E_v\]

**FIGURE 25.20** Schematic illustration of a spherical silicon nanocrystal terminated with silicon–oxygen bonds. The dashed area represents a surface region where a crystalline SiO\(_2\) shell could be formed. The inset illustrates the Si–O–Si asymmetric stretching mode of vibration.
nanocrystals, $\Delta E_\text{c}$ (and $\Delta E_\text{p}$) increases until, for a given diameter of the nanocrystals, the two energies (electronic and vibrational) coincide. This is the condition for a resonant coupling between surface vibrations and the electronic states of the nanocrystals via a polarization field of the vibrations.

The above model should slightly be modified when dealing with surface phonons of a crystalline $\text{SiO}_2$ shell, but the main conclusion concerning resonant coupling between electronic states and surface phonons, remains valid.* In this case, we will focus our attention on LO phonons as these phonons generate a considerably large polarization field. In general, the dispersion relation of the phonons should be taken into account (e.g., the dependence of the phonon energy on the phonon wavevector, $\vec{q}$), but, to a first order approximation we may take the LO phonon energy to be dispersionless and equal to $\hbar \omega_{\text{LO}}$. When the condition for a strong coupling is fulfilled, $\Delta E = \hbar \omega_{\text{LO}}$, the electrons and the phonons are not anymore in the weak coupling regime where scattering and energy dissipation occur. Instead, the strong coupling between electrons and phonons gives rise to a creation of virtually everlasting mixed electron–phonon modes, called polarons. In polar semiconductor quantum dots, these polarons are due to strong coupling between the electrons and the LO phonons of the same crystalline core while in the vibron case, a similar coupling occurs between surface phonons of the crystalline shell and the core electrons. These surface polarons “passivate” the surface against nonradiative relaxation processes. Let us emphasize that this process of creating surface polarons (vibrons) is expected to be particularly important in silicon where, as opposed to polar semiconductors, only surface phonons (or vibrations) can produce a polarization field explaining the crucial role of SC in SiNCs.

The polaron state of nanocrystals can be viewed as a “dressed” state of the electron–phonon system. A simple illustration of a polaron state is depicted in Figure 25.22 where the negatively charged electron produces a local disturbance to the polarization field of the lattice (which is created by longitudinal lattice vibrations). In the vibron case, the surface polaron is a “dressed” state of the surface, meaning that the electron and/or the hole are coupled to the surface of the SiNC. This provides a direct explanation and a specific mechanism to the model of Wolkin et al.17 of surface-trapped electrons/holes/excitons discussed in Section 25.3.2. Here again, resonant coupling to surface vibrations can produce a localized (or trapped) electron-surface vibrations, hole-surface vibrations, or a localization of the entire exciton as suggested by Verzelen et al.94 Another important characteristic of the polaron problem, which can be utilized for experimental verification of the model, is the polaron energy splitting due to confinement. To follow this phenomenon, one needs to solve the entire polaron Hamiltonian including the electron-polaron interaction, finding the new eigen-energies of the polaron that becomes a mixed state of the electrons (or the holes) and the phonons. While the exact algebra is quite complicated and tedious, a simplified model has been proposed by Mahdouani et al.95 by limiting the interaction into the subspace of the $|1S_{\text{el}}, 1q\rangle$ and $|1P_{\text{el}}, 0q\rangle$ uncoupled states, which are composed of the electronic ground state ($1S_{\text{el}}$) + 1 phonon state ($1q$), and the first excited electronic state ($1P_{\text{el}}$) + 0 phonon state ($0q$), respectively. In this subspace, the electron–phonon interaction Hamiltonian (known as the Fröhlich Hamiltonian96) takes the following form:

$$H_{\text{POL}} = \begin{pmatrix} E_\text{el} + \hbar \omega_{\text{LO}} & W \\ W^* & E_\text{p} \end{pmatrix}$$

where

- $E_\text{el}, E_\text{p}$ are the electronic energies of the 1S and the 1P sublevels, respectively
- $\hbar \omega_{\text{LO}}$ is the LO phonon energy

The off-diagonal electron–phonon interaction term is given by

$$W = \langle 1S_{\text{el}}, 1q | H_{\text{el-ph}} | P_{\text{el}}, 0q \rangle$$

The solution to this problem (e.g., diagonalization of the Fröhlich Hamiltonian) yields the mixed electron (hole)–phonon states of the vibron and the energies of the vibron, which are schematically illustrated in Figure 25.23.

The lower energy branch ($E_\text{el}$) has a phonon-like behavior ($E_\text{el} \approx \hbar \omega_{\text{el}}$) for small SiNCs and behaves as an electronic state (1P) for large SiNCs (with $E_\text{p} \approx \Delta E_\text{c} \approx 1d$; see Equation 25.3). The upper branch ($E_\text{p}$) is electronic-like for small SiNCs and phonon-like for

* For the sake of simplicity, we have ignored the effect of confinement on the spectrum of phonons and their dispersion relation. However, this topic could lead to additional novel phenomena that have not been studied so far.

**FIGURE 25.22** Schematic description of the polaron formation mechanism. On the left, the polarization field from the unperturbed lattice of charged ions is shown while on the right, the perturbed field (e.g., the polaron) created by a negatively charged electron (dotted circle) is presented.
that these are optical transitions between sublevels coming from the same band and therefore, having the same Bloch wavefunction (for example, the same conduction Bloch state for both the $|1S_c\rangle$ and the $|1P_c\rangle$ sublevels). Hence, dipole matrix elements for optical transitions between these sublevels are reduced to dipole matrix elements between envelope states of these sublevels. Thus, the $|1S_c\rangle \rightarrow |1P_c\rangle$ transition is a dipole allowed optical transition (with the oscillator strength for this transition being close to 1) that can be measured by infrared absorption spectroscopy. Let us emphasize that ISL optical transitions are a direct manifestation of QC as these sublevels do not exist in bulk semiconductors. In addition, according to the vibron model, these sublevels are expected to interact with surface polar vibrations yielding modified energy spectra similar to those presented in Figure 25.23. Therefore, this experiment should be sensitive to both QC and SC in SiNCs.

The experimental setup for measuring ISL transitions in SiNCs includes a visible pump laser exciting electron–hole pairs (excitons) and a weak, tunable IR probe beam measuring the photinduced absorption (PIA) spectra. Both the photinduced transmittance, $\Delta T$, and the linear IR transmittance, $T$, are measured (by modulating the pump laser beam in one experiment and the probe beam in a second experiment using a lock-in detection method) to obtain PIA: $\Delta T/T = T/T_0$. The same set of co-sputtered SiNC samples, with varying average diameter (and silicon volume content; see Figure 25.5), which were used for the PL experiments (see Figures 25.9 through 25.11), have also been exploited for PIA measurements to allow investigation of possible correlation between these experiments.

Figure 25.24 presents the linear IR absorption (dashed line) and the PIA (solid line) spectra for SiNCs having an average diameter of 4.5 nm.

**FIGURE 25.23** Schematic presentation of the vibron energies (solid lines) as a function of the nanocrystal diameter. The dashed lines represent the vibrational energy, which is not affected by the confinement (horizontal line), and the electronic energy ($\Delta E_C$), which depends on the diameter of the nanocrystal. Large SiNCs. However, the most interesting behavior occurs for $\Delta E_C = \hbar \omega_{LO}$ (the resonant coupling condition), where the polaron states are mixed states of the form $|\psi_{pol}\rangle = a_1|1S_c, 1q\rangle + b_1|1P_c, 0q\rangle$ (with $|a_1|^2 + |b_1|^2 = 1$). Similar results can be obtained for the hole–phonon coupling and for the exciton–phonon coupling. In principle, the same formalism can be applied to noncoherent surface vibrations with $h\omega_{ph}$ replacing $h\omega_{LO}$. Yet, this problem requires further investigation as the application of the Fröhlich Hamiltonian for coupling to surface vibrations and/or amorphous phases has not been investigated so far. Finally, let us point out that measuring the vibron energies can provide a direct verification to the model. This is the subject of Section 25.4.3.

**25.4.3 Experiments Supporting the Vibron Model**

At first, let us mention several reports about polar optical phonons of the silicon–SiO$_2$ planar interfaces, which have been theoretically predicated and experimentally observed. In these planar Si–SiO$_2$ interfaces, polar optical phonons of the oxide layer give rise to enhanced scattering and energy dissipation, from charged carriers moving in the adjacent silicon channel of MOS devices and bipolar transistors having SiO$_2$ spacer layers. In this case, the interaction with polar optical phonons causes a lower mobility of the carriers and a degradation of the current–voltage characteristics. As discussed in the previous section, this is the regime of weakly coupled electrons–phonons that is reflected by energy dissipation and enhanced nonradiative relaxation rates.

Among the first experiments providing direct evidence for vibrons in SiNCs is the one reported in Refs. 87 through 88. In this experiment, the aim was to measure inter-sub-level (ISL) optical transitions between the quantized sublevels of SiNCs, for example, the $|1S_c\rangle \rightarrow |1P_c\rangle$ and the $|1S_c\rangle \rightarrow |1P_c\rangle$ ISL transitions between the quantized states of the conduction and the valence bands, respectively (see Figure 25.21, left). Ignoring band mixing, let us indicate

**FIGURE 25.24** Room temperature PIA (symbols and a solid line) and linear IR absorption (dashed line) spectra for the sample with average diameter of 4.5 nm.

* Since our SiNCs are essentially undoped, the carriers must optically be induced. Once a technology to introduce dopants into SiNCs will emerge, it would be interesting to investigate direct ISL transitions from SiNCs having a single type of carriers.

† The linear and the photinduced transmittance are given by $T = T_0 e^{-\alpha d}$ and $\Delta T = T_0 [e^{-\alpha d} - e^{-(\alpha - \Delta\alpha)d}]$, where $\alpha$ is the linear absorption coefficient and $\Delta\alpha$ is the photinduced absorption coefficient. Hence, we find $\Delta T/T = 1 - e^{-\Delta\alpha d}$ for $\Delta\alpha d < 1.$
of 4.5 nm ($x = 18\%$). The linear IR absorption spectrum includes a single absorption band, at about 130–150 meV (1050–1210 cm$^{-1}$ in terms of wavenumbers), of the Si–O asymmetric stretching mode of vibration,$^{102,103}$ schematically illustrated in Figure 25.20. Similar linear IR absorption spectra have been obtained for all SiNCs embedded in SiO$_2$ matrices. The PIA spectrum reveals two photoinduced absorption bands; a relatively strong and narrow band at $\sim 135$ meV and a fairly broad, high-energy band at about 280 meV. The broadening of the PIA bands is expected here as absorption measurements average over all sizes of nanocrystals according to the size distribution of each sample (see Figure 25.5). In fact, the fairly narrow linewidth of the low-energy band (FWHM of $\sim 20$ meV) is quite surprising taking into account the size distribution. As the PIA technique is not sensitive to the polarity of the carriers, we may use the effective mass approximation for assigning the low-energy PIA band to valence-ISL (VISL) transitions and the high-energy band to conduction-ISL (CISL) optical transitions.$^{91-95}$ However, another explanation of assigning both bands to CISL transitions is possible, where the $1P_s$ state of the conduction splits into two sublevels, mainly due to differences between longitudinal and transversal conduction effective masses.$^{95}$ In the following, we follow the first scenario but the main conclusions of this experiment remain valid for the second scenario as well.

Next, in Figure 25.25, we show the PIA spectra for a series of SiNCs having variable average diameter, from 4 up to 6 nm. This is also the range of diameters where the two PIA bands could be resolved from the noise. Surprisingly, while the high-energy CISL absorption band shows a remarkable redshift with the increasing size of the nanocrystals, the low-energy VISL band presents a significantly weaker shift to the red, with the energy of the VISL transition (120–140 meV) being fairly close to the energy of the Si–O asymmetric stretching mode of vibration ($\sim 135$ meV).

To correlate the results with the vibron model, we present in Figure 25.26 the PIA peak energies for both ISL bands ($\Delta E_{\text{C}}$ and $\Delta E_{\text{V}}$) versus the confinement energy, $\Delta E$ (defined here as $\Delta E = E_{\text{PL}} - E_{\text{c}}$ with $E_{\text{PL}}$ being the peak PL energy of the sample). The CISL energies display a linear dependence on $\Delta E$ as expected from the QC model (where both $\Delta E$ and $\Delta E_{\text{c}} \sim 1/d^6$ according to Equation 25.3). On the other hand, the VISL energies show a sub-linear dependence on $\Delta E$, approaching the vibrational energy of the Si–O stretching mode of vibration. The dashed line in Figure 25.26 represents the expected dependence of the VISL energies on $\Delta E$ according to the QC model (i.e., $\Delta E_{\text{V}} \sim \Delta E$). This line crosses the vibrational energy of the Si–O vibration, which is independent of the size of the nanocrystals, and is represented by the horizontal dashed-dotted line in Figure 25.26. Hence, the anti-crossing of the VISL energies and the vibration energies, which resembles the anti-crossing shown in Figure 25.23 (the vibron model), suggests that electronic states of the valence band are resonantly coupled to Si–O surface vibrations to create vibrons.

Notice also that the amplitude (or the strength) of the PIA bands increases with the decreasing size of the nanocrystals, up to a diameter of $\sim 4.5$ nm and then, decreases until the PIA spectra could not be resolved for SiNCs smaller then 2.5 nm. These results provide additional support to the vibron model. The correlation between the integrated PIA (e.g., the area below the VISL absorption bands shown in Figure 25.25) and the integrated PL, which is presented in Figure 25.27, suggests that the same mechanism, e.g., the formation of vibrons, is also responsible for the high PL efficiency. For SiNCs having a diameter in the range of 4–4.5 nm, the energy difference between the lowest valence sublevels becomes comparable to those of the Si–O surface vibrations. As a result, long-lived vibrons are created giving rise to slow nonradiative relaxation rates that, in turn, enhance

![Figure 25.25](image-url)  
**FIGURE 25.25** PIA spectra for selected samples of different average diameters from 4 up to 6 nm. The dashed lines indicate the remarkable redshift of the CISL band and the much weaker shift of the VISL band.

![Figure 25.26](image-url)  
**FIGURE 25.26** The measured ISL energies (left axis-CISL, right axis-VISL) versus the confinement energy. The horizontal dashed line indicates the energy of the Si–O asymmetric stretching mode of vibration.
the PL efficiency. This mechanism, which takes into account the mutual role of QC and SC, also explains the correlation between the PIA and the PL shown in Figure 25.27. Finally, let us point out that the Si–O asymmetric vibration is related to a “longitudinal” mode of vibration where the oxygen atom vibrates back and forth along the line joining the axis of the two silicon atoms (see Figure 25.20). This vibrational mode is expected to generate a strong polarization field relative to other Si–O vibrations\(^ {103}\) such as the symmetric stretching mode (at about 810 cm\(^{-1}\)), which can be seen in the linear IR absorption spectrum but without any correlation to the PIA spectra, and the Si–O rocking mode of vibration at \(\sim 450\) cm\(^{-1}\). Notice that, it has been suggested that the asymmetric lineshape of the Si–O stretching mode at \(\sim 1100\) cm\(^{-1}\) (see Figure 25.24) is due to the two “quasi-phonon” modes of the amorphous SiO\(_2\) medium.\(^ {104}\) with the AS\(_1\) (first asymmetric stretching) mode at \(1076\) cm\(^{-1}\) being related to “in-phase” motion of adjacent oxygen atoms while the AS\(_2\) mode at \(1250\) cm\(^{-1}\) is related to “out-of-phase” motion of adjacent oxygen atoms.\(^ {103}\) Clearly, only the AS\(_2\) mode is expected to generate a long-range polarization field, a result that can explain the strong asymmetry of the VISL band (see Figure 25.24), once approaching the high-energy shoulder of the linear Si–O stretching vibration.

Additional experimental results supporting the vibron model come from a single quantum dot spectroscopy of SiNCs fabricated by the laser pyrolysis technique (see Section 25.2). Martin et al.\(^ {105}\) have succeeded to dissolve SiNCs (surrounded by SiO\(_2\)) and disperse them in polymer matrices and to spin-coat the nanocrystals on glass substrates for a single silicon nanoparticle spectroscopy. The PL spectra, shown in Figure 25.28 for two different sizes of nanocrystals, reveal vibronic features of low-energy PL satellites, at about 130–160 meV below the high-energy peaks. These satellite peaks have been interpreted as (surface) phonon-assisted optical transitions where the high-energy PL band is related to a zero-phonon transition (having homogeneous linewidth of \(\sim 100\) meV) and a low-energy PL shoulder that is related to a phonon-assisted transition. Notice that phonon-assisted optical transitions (both interband\(^ {106}\) and ISL\(^ {98}\)) have been predicted for SiNCs; however, in most cases the bulk phonons of silicon have been considered rather than polar surface vibrations (which could be either Si–O surface vibrations, or AS phonons of amorphous-SiO\(_2\) or LO phonons of a crystalline SiO\(_2\) shell). A similar phenomenon of vibronic satellites in the PL spectrum has also been reported for PS particles.\(^ {107}\) In another work, vibronic features due to surface-oxide absorption band using ellipsometric measurements\(^ {108}\) have been reported. Seraphin et al.\(^ {109}\) have shown that modifying the surface passivation of SiNCs does not alter the PL spectrum and only the PL intensity is changed, apparently due to modification of the surface bonds with a higher PL intensity associated with the more polar surface bonds.

Finally, let us discuss the recent magneto-PL experiment reported by Godefroo et al.\(^ {110}\) In this experiment, pulsed magnetic fields up to 50 T have been applied to SiNCs and the corresponding energy shift of the PL has been measured. The high magnetic field acts to further confine the exciton with \(\ell_B = \sqrt{\hbar/eB}\) being the magnetic confinement length. Hence, free excitons of bulk nanocrystals are expected to show a blueshift in response to high enough B-fields, while localized or trapped excitons are not expected to show a similar shift. Indeed, no blueshift of the PL has been measured for SiNCs embedded in SiO\(_2\). The authors have interpreted these observations as a PL originated from defect centers in the oxide layer that wraps the nanocrystals. However, according to the vibron model, surface-localized vibrons should not present a blueshift either. In another experiment, the authors annealed the samples in hydrogen, at temperatures low enough to avoid the creation of hydrogenated a:Si. In this experiment a blueshift of the PL has been observed, thus confirming the experimental results of Wolkin et al.\(^ {17}\) where H-terminated SiNCs have shown monotonic blueshift of the PL with the decreasing size of the nanocrystals (or with the increasing B-field in the case of the Godefroo experiment\(^ {110}\)). The topic of hydrogen-terminated SiNCs remains a puzzle that has not been addressed in this chapter for the very simple reason
that no reliable methods to produce stable, H-terminated SiNCs have been reported so far. Yet, the Si–H bonds are expected to be considerably more polar than the Si–O bonds. Hydrogen atoms are highly mobile ions that can easily penetrate over few nanometers into the nanocrystalline silicon core. Even small amount of hydrogen in the silicon core is expected to produce considerable polarization field of the “core” nanocrystal. This topic calls for further investigation as the current knowledge about H-terminated SiNCs is insufficient for drawing any reliable conclusions.

25.5 Concluding Remarks

This chapter has covered one specific topic from the much broader, rapidly expanding field of silicon nanostructures and their applications, focusing on the question about the origin of the PL and the specific role of QC and SC in the eluding game played by the luminescence. Yet, this specific question is an excellent example to a situation where small is really different. Namely, not a property of matter that scales down in proportion to the size of the material, but rather a truly new phenomenon that appears at, and only at the nanometric length scales. The PL from silicon nanostructures appears to be such a property. The role of QC and SC is another fascinating example to the case where physics meets chemistry and both disciplines of science merge together into one, multidisciplinary field of nanoscience.

The questions regarding the origin of the PL from silicon nanostructures are far from being fully resolved. Many open questions still exist, some have been discussed in this chapter, some did not, and most likely, some new fundamental questions and puzzles will emerge soon. Yet, the basic direction in attempting to merge QC and SC, rather than choosing one as a sole winner, seems to be the proper approach. It is just a matter of time to see if this subjective opinion of the author of this chapter is indeed correct or not.

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