

Effective exponent for the size dependence of luminescence in semiconductor nanocrystallites

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The size (d) dependence of photoluminescence from nanocrystalline semiconductors is examined. The overall luminescence is determined by two distinct physical mechanisms: (i) the variation of the semiconductor gap with size d (typically $\sim 1/d^\alpha$, $\alpha > 1$), and (ii) the variation of the oscillator strength f_{osc} with size (typically $1/d^\beta$, $5 \leq \beta \leq 6$). We present an analytical framework to understand the luminescence line shape based on the above two mechanisms, taking no recourse to computational simulations. We show that the peak energy varies with the mean particle size d_0 as $d_0^{-\beta}$, where β is an effective exponent determined by the disorder in the system. Our results can explain conflicting experimental observations on the luminescence from silicon nanocrystallites. [S0163-1829(98)04623-2]

The observation of visible photoluminescence (PL) in a variety of semiconductor nanocrystallites has fueled a large body of research work in the past decade.¹ A material which has attracted considerable attention is porous silicon, which is a disordered collection of silicon nanocrystallites with varying sizes.² The photoluminescence spectra from such systems are broad, and often asymmetric about the peak energy.

To compute the parameters of emission, or, equivalently, the spectral line shape from an ensemble of semiconductor nanocrystallites, one needs to consider the distribution of crystallite sizes in the system.³⁻⁵ The luminescence depends on (i) the energy gap, (ii) the oscillator strength, and (iii) the exciton binding energy, among others. All these factors exhibit a dependence on the size of the nanocrystallite. In this work, we provide a simple theoretical framework to calculate the spectral line shape from a disordered collection of semiconductor nanocrystallites, and illustrate the consequences of disorder on earlier theoretical calculations and experimental analyses. We compare our results with the vast literature on light emission from silicon nanocrystallites, and explain conflicting experimental observations on the basis of our model.

The light emission from silicon nanocrystallites at energies higher than the bulk Si gap was attributed by several workers⁶ to quantum confinement effects. The experimental validation of the quantum confinement model has been beset with difficulties, as several groups reported conflicting results. A case in point is the shift in the PL peak with varying crystallite size. Vial *et al.*⁷ and Schuppler *et al.*⁸ reported a distinct size dependence of the PL peak, though this was refuted by other groups based on their experimental works.^{9,10} Recently, an attempt was made to explain this conflict on the basis of a size distribution of nanocrystallites, based on a computer simulation study.¹¹ Our model attempts to resolve the issues raised by these studies.

We now examine the size dependencies of individual properties in detail. The variation of the oscillator strength (f_{osc}) with the crystallite diameter d is usually assumed to be of a polynomial form such as

$$f_{osc} \sim d^{-\beta} \quad (1)$$

by effective-mass-theory (EMT)-based calculations. Hybertsen and Needels¹² as well as Khurgin *et al.*¹¹ suggested $\beta = 6$, whereas Sanders and Chang¹³ proposed a value of 5. Local-density-approximation-based calculations on silicon clusters, however, showed a nonmonotonic variation of the oscillator strength with crystallite diameter.^{14,15}

Within a simple effective-mass theory, the energy upshift due to quantum confinement can be expressed as

$$\Delta E = \frac{c}{d^x}, \quad (2)$$

where $x=2$. However, both *ab initio* as well as semiempirical electronic structure calculations on silicon clusters⁶ suggest values of x in the range 1.4–2.

The exciton binding energy in semiconductor nanocrystallites is of a much smaller magnitude than the emission energy. Consequently, the effect of its size dependence on the spectral line shape is small. Factors such as the presence of nonradiative centers on the crystallite surface also affect luminescence, but theoretical calculations¹⁶ indicate that (i) even the presence of a single nonradiative center can kill luminescence in a nanocrystallite; and (ii) given the small surface area, the probability of there being a nonradiative center is small, as indicated by the high luminescence efficiency. To preserve the simplicity of the model and bring out the essential physics in the system, we focus on the oscillator strength and the energy gap.

To compute a general expression for the PL spectrum, we assume a Gaussian size distribution for the nanocrystallites,

$$P(d) \propto \exp\left[-\frac{(d-d_0)^2}{2\sigma^2}\right], \quad (3)$$

where d_0 is the mean crystallite diameter and σ the variance of the crystallite size distribution. The number of atoms participating in the radiative process is proportional to the vol-

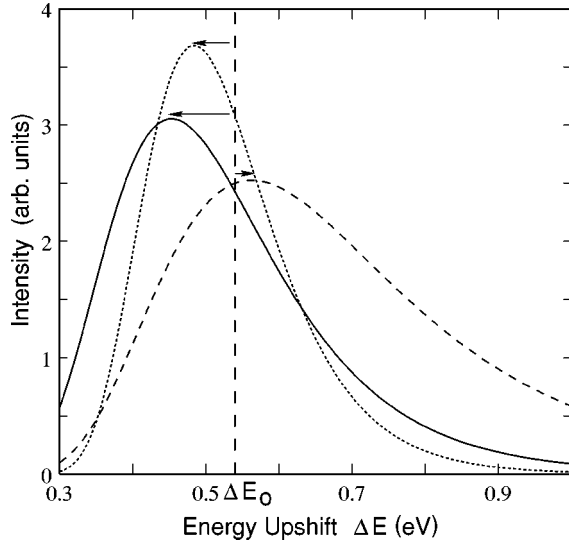


FIG. 1. Theoretical PL spectra based on Eq. (5). The solid line depicts the case when $k=5$ (i.e., $m=2$, $x=2$, and $\beta=0$). The broken line is plotted with $m=2$, $x=2$, and $\beta=6$ ($k=-1$), and shows a blueshift. The dotted line corresponds to $m=2$, $x=1.4$, and $\beta=0$. The plots are normalized, with $c=485.816$ eV/Å².

ume of the crystallite. Hence we can write the probability of emission from a nanocrystallite of diameter d as

$$P_r(d) = K V(d) f_{osc}(d) P(d) = K d^m \frac{1}{d^\beta} \exp\left[-\frac{(d-d_0)^2}{2\sigma^2}\right], \quad (4)$$

where K is an appropriate normalization constant, and $m=2$ for columnar crystallites and $m=3$ for nearly spherical crystallites. Transforming the above expression to the energy axis,⁵ we obtain

$$\begin{aligned} P(\Delta E) &= K \int_0^\infty \delta\left(\Delta E - \frac{c}{d^x}\right) d^m \frac{1}{d^\beta} \exp\left[-\frac{(d-d_0)^2}{2\sigma^2}\right] d(d) \\ &= N \Delta E^{-k/x} \exp\left[-\frac{\alpha^2}{2} \left\{\left(\frac{\Delta E_0}{\Delta E}\right)^{1/x} - 1\right\}^2\right], \end{aligned} \quad (5)$$

where N is a normalization constant, and we have defined

$$\begin{aligned} \Delta E_0 &= \frac{c}{d_0^x}, \\ k &= m - \beta + x + 1, \\ \alpha &= \frac{d_0}{\sigma}. \end{aligned} \quad (6)$$

In Fig. 1, we depict theoretical spectra based on Eq. (5). The values assigned to various parameters correspond to those found in the literature for silicon nanocrystallites. c was chosen to be 485.816 eV/Å² based on the work of Read *et al.*¹⁷ Most of the experiments on porous silicon report the crystallite sizes to be in the range 20–40 Å. We have chosen our mean crystallite size to be 30 Å, and assumed $\sigma=3$ Å. The solid line ($m=2, x=2$) and the dotted line ($m=2, x=1.4$) are for the case $\beta=0$. The broken line depicts the

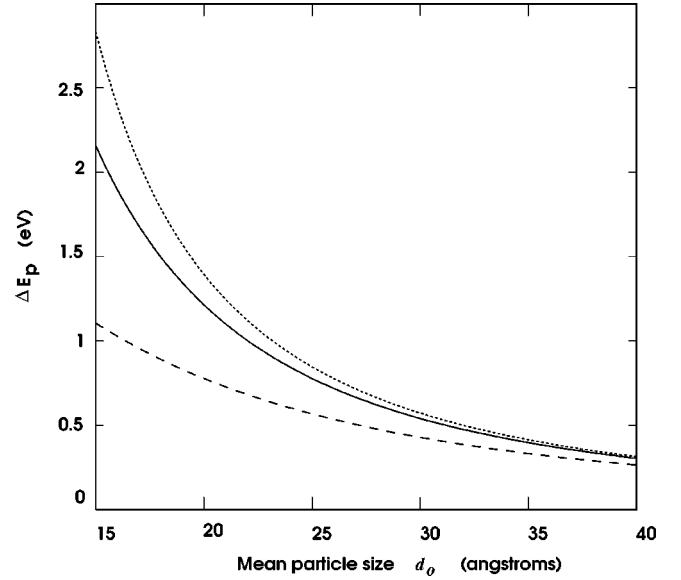


FIG. 2. The dependence of the peak position ΔE_p on the mean crystallite size, assuming a normal distribution of dots with $\sigma=5$ Å and $x=2$. The broken line at the bottom ($m=3, \beta=0$) shows an extremely weak variation in energy with size. The dotted line at the top ($m=3, \beta=6$) shows a strong dependence which is supraquadratic. The distribution in crystallite sizes results in a considerable deviation from a simple c/d^x variation, which is depicted by the solid line.

case when $m=2$, $x=2$, and $\beta=6$. We see that the peak positions in both cases are substantially different. This raises questions about the assignment of the exciton binding energy, which was discussed in an earlier work.⁵ We shall discuss this issue later in this paper.

Most experiments report a variation of the luminescence peak with experimental parameters. The PL peak position ΔE_p is given by the maxima in Eq. (5),

$$\Delta E_p = \Delta E_0 \left(\frac{\alpha^2}{2k}\right)^x \left[-1 + \sqrt{1 + \frac{4k}{\alpha^2}}\right]^x. \quad (7)$$

For typical values⁵ $d_0=30$ Å, $\sigma=3$ Å, $x \in [1.4, 2]$, and $k/\alpha^2 \rightarrow 0$; hence

$$\Delta E_p \approx \Delta E_0 \left[1 - \frac{k}{\alpha^2}\right]^x. \quad (8)$$

This can be written as

$$\Delta E_p \approx \Delta E_0 \left[1 - x \frac{k}{\alpha^2}\right]. \quad (9)$$

Equation (7) implicitly contains the dependence of the peak ΔE_p on the mean crystallite size d_0 . This dependence may be different from the one suggested by Eq. (2) ($\Delta E = c/d^x$). This is shown in Fig. 2. The solid line depicts the canonical (EMT) behavior given by Eq. (2) with $x=2$. We plot the variation of the peak energy ΔE_p with mean diameter d_0 for a collection of spherical nanocrystallites ($m=3$) with varying sizes. The variance in diameter σ is assumed to be 5 Å. The dotted line represents the case when the oscillator strength is strongly dependent on the crystallite size (β

TABLE I. Table of effective exponents. The variance σ is in Å, and constant c' is in appropriate units. Note the variation in γ_{eff} with disorder σ for the same k and its deviation from the assumed value of $x=2$.

k	σ	c'	γ_{eff}
5	3	213.279	1.786
	5	80.307	1.541
4	3	245.967	1.823
	5	104.260	1.606
3	3	286.396	1.862
	5	140.305	1.680
2	3	337.114	1.904
	5	197.772	1.767
1	3	401.785	1.950
	5	296.668	1.871
-1	3	597.404	2.054
	5	908.810	2.166
-2	3	749.461	2.114
	5	2133.310	2.397

=6), and the broken line depicts the opposite case, where the oscillator strength is size independent ($\beta=0$). If we assume a variation of the form

$$\Delta E_P = \frac{c'}{d_0^{\gamma_{eff}}}, \quad (10)$$

with γ_{eff} as an effective exponent, we can see that in the first case $\gamma_{eff} > 2$, whereas for the latter $\gamma_{eff} < 2$. Note that the size dependence of the PL peak in the broken curve is extremely weak in the region 20–40 Å, the range considered in most experiments. A similar behavior was reported by several workers who failed to observe a significant upshift in emission energy with a reduction in crystallite size.^{9,10}

We have fitted several such curves to the functional form of Eq. (10). In Table I, we depict the effective exponent γ_{eff} for a range of values of the parameter k [Eq. (6)] for a distribution of columnar crystallites. A value of k around 5 implies a weak oscillator strength dependence on size, while a value of k around 0 implies a strong dependence. The physical conditions determining the oscillator strength on size were described by various workers.¹⁸ The exponent γ_{eff} is obtained using the Levenburg-Marquardt nonlinear least-squares fitting method. Note that we would obtain an effective exponent γ_{eff} distinct from x irrespective of whether the latter is obtained by EMT or tight-binding calculations.

We now proceed to obtain an analytic expression for the exponent γ_{eff} by a method employed in the modern theory of critical phenomena.¹⁹ First we take the logarithm of ΔE_P in Eq. (8) to obtain

$$\ln \Delta E_P = \ln c - x \ln d_0 + x \ln \left(1 - \frac{k}{\alpha^2} \right). \quad (11)$$

From Eq. (10), we have

$$\ln \Delta E_P = \ln c' - \gamma_{eff} \ln d_0. \quad (12)$$

We differentiate Eq. (11) with respect to $\ln d_0$ to obtain

$$\frac{\partial \ln \Delta E_P}{\partial \ln d_0} = -x \left[1 - \frac{2k}{(d_0/\sigma)^2 - k} \right], \quad (13)$$

where we recall that (d_0/σ) is α . Differentiating Eq. (12) with respect to $\ln d_0$ yields

$$\frac{\partial \ln \Delta E_P}{\partial \ln d_0} = -\gamma_{eff}. \quad (14)$$

Equating Eqs. (13) and (14), we obtain the effective exponent γ_{eff} as

$$\gamma_{eff} = x \left[1 - \frac{2k}{(d_0/\sigma)^2 - k} \right]. \quad (15)$$

Equation (15) has a number of physical implications.

(1) γ_{eff} is distinct from x as long as $k \neq 0$. Thus the quantum confinement that one observes (γ_{eff}) may be different from the calculated one (x) irrespective of the method of calculation, whether EMT or tight binding (TB).

(2) The exponent γ_{eff} is *universal* in the sense that it depends on the ratio d_0/σ and not separately on the mean size d_0 and the variance σ . In other words, ensembles of equivalent disorder will have the same exponent γ_{eff} .

(3) Note that k is usually small and in the range $[-2:6]$. Hence the denominator in Eq. (15) will be positive. Thus γ_{eff} can be greater or less than x depending on the sign of k .

(4) If k is negative, the peak is blueshifted [Eq. (8)], and the size dependence is more pronounced, e.g., $\gamma_{eff} > x$ [Eq. (15)]. On the other hand, redshifted peaks will exhibit a weaker size dependence.

(5) As expected, in the limit of small disorder $\sigma \rightarrow 0$, Eq. (15) yields $\gamma_{eff}|_{\sigma \rightarrow 0} = x$.

Almost all electronic structure calculations reported so far have been done on single nanocrystals with size d as a parameter, and these yield an upshift of the gap as given in Eq. (2). These calculations have been done at various levels of sophistication. EMT yields $x=2$. Tight-binding calculations by Delerue, Allan, and Lannoo¹⁶ and more recently by us²⁰ yielded $x \in [1.4:1.6]$. Earlier tight-binding calculations by Lippens and Lannoo²¹ and by Wang and Herron¹⁸ on II–VI nanocrystals also yielded $x < 2$. Several experiments are used to probe the blueshift due to quantum confinement. Typically these are optical studies of the absorption edge and the peak energy of PL emission as well as PL excitation studies. There were also reports of nonoptical observations such as valence band photoemission.²² These studies are *invariably* for an ensemble of nanocrystallites. Our analysis above indicates that for these systems, the peak energy size dependence follows Eq. (10) where $\gamma_{eff} \neq x$.

Further several attempts to estimate the size of a nanocrystallite using Eq. (2) have been made in the past. Lippens and Lannoo²¹ correlated the positions of the exciton peaks to size, and compared it favorably with their TB calculations. Colvin, Alivasatos, and Tobin²² used TB results on small CdS particles to extract the sizes of CdS cluster. Wang and Herron¹⁸ studied the dependence of the optical band gaps of CdS and PbS on the cluster size. They claimed that TB calculations would provide a better description of size dependence than the EMT. Nomura and Kobayashi²³ claimed that the size-dependent results are in good agreement with experi-

ments on CdSe and CdS_xSe_{1-x} microcrystallites once the nonparabolicity of the conduction band is taken into account. Marzin *et al.*²⁴ correlated the PL peak energy of InAs quantum dots to the cluster size using a modified EMT approach. A similar EMT approach was employed by Farfad *et al.*²⁵ to correlate PL excitation spectra to InGaAs. Roy and Sood²⁶ employed the TB calculations of Ramaniah and Nair²⁷ to correlate the optical absorption edge of CdS_xSe_{1-x} nanoparticles to size. These attempts may be flawed principally because our analysis shows that disorder modifies the exponent.

First-principles calculations on silicon clusters have predicted large upshifts in energy, and consequently needed to postulate high exciton binding energies to explain experimentally observed emission frequencies.¹⁷ Our work shows that the presence of disorder can shift the luminescence peak position. In the absence of a strong size dependence of the oscillator strength, the peak is redshifted, as shown in Fig. 1. This allows one to assume reasonable values for the excitonic energy (~ 50 meV).⁵ However, if the oscillator

strength is strongly dependent on size, the peak blueshifts, as shown by the broken line in Fig. 1, and large excitonic energies are needed to explain the disparity. This may indicate that the size dependence of the oscillator strength does not follow the simple EMT prediction, but has a much weaker dependence, or a nonmonotonic variation with size, as predicted by several electronic structure calculations.^{14,15}

Attempts to understand experimental data on the basis of calculations on single nanocrystals can be misleading. The simple model presented here outlines the pitfalls of carrying out such an exercise. Properties besides the PL broadening and band shift examined herein, such as dielectric absorption, radiative lifetime, etc., also need to be more carefully studied in the light of our observations.

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