Theory of the photoluminescence spectra of porous silicon

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Porous silicon (PS) with its distribution of crystallite sizes is a highly disordered material. We present a theoretical formulation to explain the photoluminescence (PL) spectra of porous silicon. We base our formalism on the quantum confinement model using methods similar to those of Kane and Lifshitz. A minimal set of parameters is employed whose numerical values are obtained from independent experiments and/or microscopic theories. Our work demonstrates (i) a downshift in the PL peak due to the size distribution, thus facilitating the use of smaller and physically reasonable exciton binding energy; (ii) a PL spectrum with a line-shape asymmetry on the energy scale, having a full width at half maximum of $\simeq 350$ eV, in consonance with experiments; (iii) the presence of both columns and dots in PS; (iv) the presence of local inhomogeneities. Modifications of our model and extensions to related experimental phenomena are also discussed.

I. INTRODUCTION

The discovery of visible photoluminescence (PL) in porous silicon (PS) has attracted a lot of attention in the past few years.[1,2] Almost all recent works on PS report at least one PL spectrum with a peak in the visible region.[1,3] Indeed, PL has acquired the role of a central characterizing tool in this field. The objective of this work is to report a simple theoretical framework with a minimal set of plausible parameters to explain the PL spectra.

Primarily, porous silicon is a disordered system. It consists of an intricate network of crystallites with varying sizes and shapes. The large surface supports hydrogen and oxygen complexes. At the microscopic level there exists dangling bonds and voids. Constructing a theory for the PL spectrum which encompasses all levels of disorder is a difficult task. Further, it may not be a desirable goal as it would entail the use of a large set of parameters whose numerical values are not accessible either by microscopic calculations or by experimental observations. Hence, a modest approach to explain the overall features of the PL spectrum, which operates within a circumscribed and limited set of plausible parameters, is a desirable alternative.

Our work is based on the quantum confinement model.[1,2,4] Most workers employ a simple quantum confinement model where the PL peak alone is sought to be explained. We believe that *disorder plays a key role* and model it by a distribution of crystallite sizes. This work, described in Sec. II, is similar in spirit to the mean-field approach of Kane and the probabilistic arguments of Lifshitz to explain the Urbach tail in optical absorption.[5,6] A large body of theoretical work in the Urbach tail problem assume that the absorption edge $\alpha(E)$ is simply proportional to the electronic density of states and ignore the energy dependence of the transition matrix element and the electron-electron interaction.[7] There are several features which we choose to ignore in our formalism. Some of these are relaxation of carriers, gap states due to voids and defects, thermal disorder, and the distinction between hole and electron contributions to exciton energies. We wish to employ a small set of plausible parameters, and further, observe (Sec. III) that these explain several reported PL spectra. Our formalism can be extended to include the above-mentioned factors as well as important experimental parameters such as the frequency and intensity of the incident excitation. These are indicated later (Sec. IV). We note that there exists an alternate hypothesis for visible PL in PS, namely, the "siloxene model."[8] Theoretical work on this model has also been reported.[9–11]

In Sec. II, we describe our theoretical formalism. We derive expressions for PL spectra originating from both column and dot distributions. The presence of local inhomogeneities where either columns or dots might dominate requires a Lifshitz-like argument for modeling the edges of the PL spectrum. The PL spectra, which may appear Gaussian when plotted against the wavelength, has a distinct asymmetry on the energy scale. This is naturally obtained in our formalism. A further noteworthy feature is a shift in the PL peak due to the distribution of crystallite sizes (Fig. 1). This enables us to employ a small and physically reasonable exciton binding energy.

In Sec. III we outline how the numerical values of the parameters employed are obtained from experimental observations and microscopic calculations. Our calculations compare favorably with the PL spectra obtained by several workers.

In Sec. IV, we briefly discuss earlier works based on the quantum confinement model. We outline extensions of our formalism to include some of the features mentioned in the third paragraph of this section. We also indicate how some insight into related experimental observations such as photoluminescence excitation (PLE) can be attained based on our model.

II. THEORETICAL FRAMEWORK

Our aim is to explain the photoluminescence spectra employing a minimal set of broad and plausible assump-

tions. There exists in literature a variety of approaches to the Urbach tail in optical absorption. We propose to work along the lines of two sister approaches: the one due to Kane and the well-known Lifshitz argument.[5,6]

There exist two classes of explanation for the origin of visible PL in porous silicon: (i) the quantum confinement model in which luminescence is due to electronic confinement in the columnarlike (or dotlike) structure of porous silicon,[1,2,4] and (ii) the chemical model in which the large surface area presented by PS support luminescing siloxenes.[8] In the recent past evidence for the former model has been accumulating.[12–15] We work within the quantum confinement model but avoid the oversimplifying assumptions made by some of its proponents.

Columns of mean diameter d_0 in the nanometer range have been reported by several independent groups.[2,16,17] The growth of these columns is a stochastic process and it appears reasonable to assume columns of silicon with a Gaussian distribution of diameter d centered around a mean d_0,

$$P_d=\frac{1}{\sqrt{2\pi}\sigma}\exp\left[-\frac{(d-d_0)^2}{2\sigma^2}\right] \tag{2.1}$$

The number of electrons in a column of diameter d participating in the PL process is proportional to d^2. The heights of the columns depend only on the growth time and are approximately the same. Hence

$$N_e=N_e(d)=ad^2 , \tag{2.2}$$

where a is a constant.

For a PS sample consisting of varying column diameters the probability distribution of electrons participating in the PL process is given by a product of the above two expressions:

$$P_{ed}=\frac{1}{\sqrt{2\pi}\sigma}bd^2\exp\left[-\frac{(d-d_0)^2}{2\sigma^2}\right] , \tag{2.3}$$

where b is a suitable normalization constant.

In the quantum confinement model, the PL process is attributed to the energy upshift of the electrons and is proportional to $1/d^2$.

The PL energy $\hbar\omega$ is given by

$$\hbar\omega=E_g-E_b+\frac{c}{d^2} , \tag{2.4}$$

where E_g is the bulk silicon gap (1.17 eV), E_b the exciton binding energy, and c an appropriately dimensioned constant. The energy upshift due to confinement ΔE is

$$\Delta E=\hbar\omega-(E_g-E_b) , \tag{2.5a}$$

$$\Delta E_0=\frac{c}{d_0^2} , \tag{2.5b}$$

where we have also paused to define a mean upshift ΔE_0 related to the mean column diameter d_0.

The PL line shape is then determined by transforming Eq. (2.3) to the energy axis as is commonly done,

$$P(\Delta E)=\frac{1}{\sqrt{2\pi}\sigma}b\int_0^\infty\delta\left[\Delta E-\frac{c}{d^2}\right]\times d^2\exp\left[-\frac{(d-d_0)^2}{2\sigma^2}\right]\mathrm{d}(d) \tag{2.6}$$

The Dirac delta function facilitates a straightforward integration and yields

$$P(\Delta E)=\frac{1}{\sqrt{2\pi}\sigma}\frac{b}{2\Delta E}\left[\frac{c}{\Delta E}\right]^{3/2}\times\exp\left\{-\frac{1}{2}\left[\frac{d_0}{\sigma}\right]^2\left[\left[\frac{\Delta E_0}{\Delta E}\right]^{1/2}-1\right]^2\right\} . \tag{2.7}$$

The PL line shape is approximately Gaussian if σ is small. For finite σ the $\sqrt{1/\Delta E}$ factor in the exponential outweighs the polynomial dependence in the prefactor, resulting in an asymmetric curve with the shoulder on the high-energy side (see Fig. 1).

Another aspect we need to note is that the mean energy of the upshift ΔE_0 [Eq. (2.5b)] and the location of the PL peak ΔE_p [$=\hbar\omega_p-(E_g-E_b)$] are not identical. To see this, we differentiate and set to zero the above expression (2.7). This yields

$$\Delta E_p=\Delta E_0\left[\frac{1}{10}\left[\frac{d_0}{\sigma}\right]\left\{-\left[\frac{d_0}{\sigma}\right]+\left[\left[\frac{d_0}{\sigma}\right]^2+20\right]^{1/2}\right\}\right]^2 . \tag{2.8}$$

For $\sigma/d_0\to 0$, $\Delta E_p=\Delta E_0$, as expected. However, for reasonable σ the above expression can be Taylor expanded to yield

$$\Delta E_p=\Delta E_0\left[1-10\left[\frac{\sigma}{d_0}\right]^2\right] .$$

From the values reported by Read *et al.*,[18] $d_0=30$ Å, $\sigma\simeq 3$ Å, $\sigma/d_0\simeq 0.1$, and $\Delta E_p=0.9\Delta E_0$.

Thus, there is a downshift. This is depicted by a horizontal bar in Fig. 1. It is important to realize the physical significance of this. As will be explained in the next section, the downshift dispenses with the need to invoke large and physically unreasonable exciton binding energies.

The peak in PL intensity is $P(\Delta E_p)$. We can obtain an approximate expression for the full width at half maximum (FWHM) (ΔE_{FWHM}) of the PL spectrum if the prefactor energy dependence $\Delta E^{-5/2}$ is ignored. This is

$$\Delta E_{\mathrm{FWHM}}=\Delta E_0\left\{\left[1-\left[\frac{\sigma}{d_0}\right]\right]^{-2}-\left[1+\left[\frac{\sigma}{d_0}\right]\right]^{-2}\right\}$$

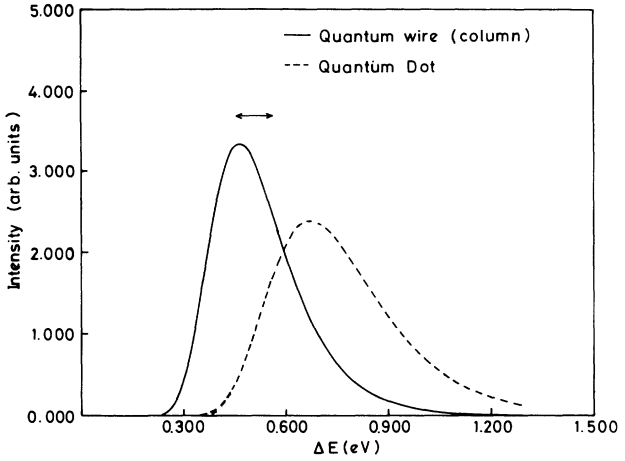

FIG. 1. Theoretical PL spectra. The solid line is due to columns (peak at $\Delta E_p = 0.46$ eV) and the dashed line is due to dots (peak at $\Delta E_p = 0.67$ eV). The mean diameter is $d_0 = 30$ Å and variance $\sigma = 4$ Å for both spectra. The quantum confinement constant c (in c/d^2) $= 485.816$ eV Å^2 [the same as calculated by Read *et al.* (Ref. 18)] and the binding energy $E_b \simeq 0.14$ eV. The horizontal bar at the peak of the column spectrum indicates a downshift ($\simeq 0.1$ eV) from $\hbar\omega_0 = c/d_0^2$ on account of the statistical distribution of the column sizes. (See text in Sec. II for further discussion.) Both spectra are normalized to unity.

For small (σ/d_0),

$$\Delta E_{\text{FWHM}} \simeq \frac{4\Delta E_0 (d_0/\sigma)}{(d_0/\sigma)^2 - 2} . \tag{2.9a}$$

A similar result can be obtained using a simple quantum confinement model. Noting that $\Delta E = c/d^2$ [Eq. (2.5b)]

$$\begin{aligned} \Delta E_{\text{FWHM}} &= 2|\delta(\Delta E)||_{d=d_0} \\ &= \frac{4c\,\delta d}{d_0^3} \\ &= \frac{4\Delta E_0 \sigma}{d_0} . \end{aligned} \tag{2.9b}$$

The above expressions are identical for small (d_0/σ). Using $c = 485.816$ eV Å^2, $\delta d = \sigma = 3$ Å, and $d_0 = 30$ Å (see the next section, Sec. III for a discussion of the numerical values), we obtain from Eq. (2.9b), $\Delta E_{\text{FWHM}} \simeq 200$ meV. A larger and experimentally reported ΔE_{FWHM} is obtained if the full expression [Eq. (2.7)] is employed.

Some workers have hypothesized the existence of dots instead of columns of silicon.[19,20] An analysis similar to the above can be carried out for dots. Employing $N_c \propto d^3$ in Eq. (2.2) and carrying out the integration, the line shape for the dot is

$$P_D(\Delta E) = \mathcal{N} \frac{1}{\Delta E^3} \exp\left\{ -\tfrac{1}{2} \left[\frac{d_0}{\sigma} \right]^2 \left[\left[\frac{\Delta E_0}{\Delta E} \right]^{1/2} - 1 \right]^2 \right\} , \tag{2.10}$$

where $\mathcal{N}$ is a normalization constant. It is conceivable that both columns and dots are present in porous silicon. The experimental PL spectrum is a weighted sum of the column and dot spectra. Statistically speaking, there would be inhomogeneities resulting in a region (say of volume V) having an overwhelming column concentration c ($\gg c_0$ the mean column concentration). One can then invoke a methodology along the lines of the Lifshitz argument.[6] The probability is given by

$$P(C) = K \exp\left[-N_e c \ln\left[\frac{c}{c_0} \right] \right] , \tag{2.11}$$

where K is a normalization constant and N_e the total number of electrons participating in the PL process within volume V. If $\bar{v}_c$ is the mean volume of the column crystallite in this region, then

$$N_e \propto \frac{V}{\bar{v}_c} . \tag{2.12a}$$

The confinement energy for $\bar{v}_c$ is [from Eqs. (2.2) and (2.5)]

$$\Delta E \propto 1/\bar{v}_c . \tag{2.12b}$$

Using (2.12) in (2.11),

$$P(c) \simeq \exp[-K_1 \Delta E] , \tag{2.13}$$

where K_1 is a constant. Thus the low-energy (infrared) part of the PL spectrum has an exponential tail. The presence of this tail accounts for some discrepancy between the theoretical PL spectrum based on Eq. (2.7) and the experimentally reported ones.

III. RESULTS

We shall now present calculations based on our expressions in the previous section and compare them with experimentally reported PL spectra. There exists a plethora of experimental spectra including some that we have obtained. Almost all reports on porous silicon report at least one PL spectrum. Indeed, visible PL has acquired the role of a central characterization tool in this field. We have selected a representative set which highlights both the promises and problems associated with the natural theoretical framework outlined in the previous section. Variations in the proposed model and alternative explanations are outlined in the next section.

We note that the majority of the PL spectra reported have been recorded against the wavelength λ on the x axis. In our comparison, we have faithfully transformed λ to the energy $\hbar\omega$. Note that $\hbar\omega$ (in eV) $= 1.24/\lambda$ where λ is in μm. Recall that $\hbar\omega = \Delta E - (E_g - E_b)$ from Eq. (2.5a).

The numerical values of physically important variables in our calculations are as follows: The band gap of silicon E_g ranges from 1.14 to 1.17 eV depending on the temperature. The exciton binding energy ($E_b \simeq 0.15$ eV) is small and physically more reasonable (than, for example, 0.32 eV proposed by Read *et al.*[18]). This is possible because the existence of a distribution of column diame-

ters results in a downshift from the mean peak (see the horizontal bar in Fig. 1). Thus $E_g - E_b = 1.00$ eV. The constant c associated with the confinement energy ($=c/d^2$) is taken from the careful calculations of Read *et al.*[18] Its value is 485.816 eV Å^2.

Computer simulations indicate that the surface has a "fractal-like" character.[21] The slow PL decay may be attributed to the fractal structure of PS (Ref. 22) provided the model proposed by Klafter and Blumen[23] holds. A fractal structure would imply a large value for σ. We, however, rely on electron microscopy measurements which suggest the variations around d_0 to be $\simeq 10$ Å.[3,18] Thus the variance $\sigma \simeq \frac{10}{3} \simeq 3$–4 Å. Thus 99% of all columns or dots lie within 3σ. We take $d_0 \simeq 30$ Å, a number reported by several workers.[2,3,18,24] The specific values of $\{d_0, \sigma\}$ for a given spectrum are cited in the figure captions and these happens to lie close to the above quoted values. In all our calculations we take the mean diameter (d_0) of the column and/or dot to be the same. *A priori,* there is no reason for them to be different.

In Fig. 2 we compare the theoretical spectrum (solid line) with one experimentally obtained by Cullis and Canham (dashed line).[3] The experimental spectrum with a peak at $\hbar\omega_p = 1.48$ eV, a FWHM of 325 meV has also been theoretically studied by Read *et al.*[18] The theoretical spectrum is obtained with mean diameter $d_0 = 30$ Å and $\sigma = 4$ Å. These values are the same as the ones suggested by Read *et al.* and so no "fitting" or "adjustment" on our part has been carried out. The agreement is excellent ($\hbar\omega_p = 1.45$ eV, FWHM is equal to 300 meV) except at the low-energy end. The Lifshitz-like argument outlined at the end of the previous section provides a substantial improvement at the lower end with constant $K_1 = 0.13$ eV^{-1}. We do not wish to overemphasize its importance at this juncture except to indicate that it suggests inhomogeneities in porous silicon.

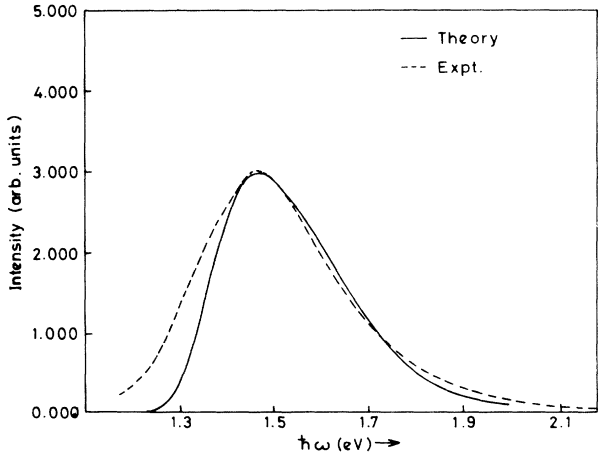

FIG. 2. Comparison of experimental (dashed line) and theoretical (solid line) PL spectra. The experimental curve, from Cullis and Canham (their Fig. 1, sample 3) (Ref. 3), has also been discussed by Read *et al.* (Ref. 18). The theoretical spectrum is obtained using a mean diameter $d_0 = 30$ Å and variance $\sigma = 4$ Å (see also, text in Sec. III) for both dots and columns. The dot and column concentrations are 10% and 90%, respectively.

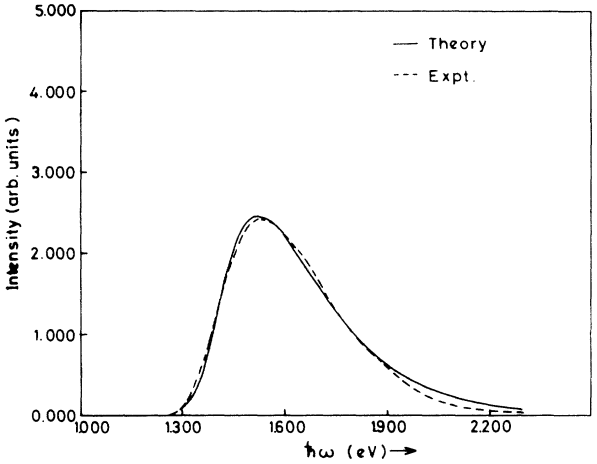

FIG. 3. Comparison of experimental (dashed line) and theoretical (solid line) PL spectra. The experimental curve is from Vial *et al.* (their Fig. 2, oxidation level $Q_0/4$) (Ref. 19). The theoretical curve was generated employing the presence of both dots (as conjectured by Vial *et al.*) and columns, each with mean diameter $d_0 = 28$ Å and variance $\sigma = 4$ Å. Dots and columns are present, the population being 15% and 85%, respectively.

In Fig. 3 the experimental PL spectra of Vial *et al.* (dashed curve) is compared with our theoretical calculations (solid line).[19] The experimental PL spectrum has a peak at $\hbar\omega_p = 1.54$ eV with a FWHM of 270 meV. It was obtained for an oxidation rate of $Q_0/4$ where Q_0 is a threshold exchanged charge and is proportional to the layer thickness. The theoretical PL spectrum was obtained for a mean diameter of $d_0 = 28$ Å whereas Vial *et al.* quote a theoretically calculated value of 30 Å. The variance $\sigma = 4$ Å (same as for Fig. 2). Vial *et al.* propose

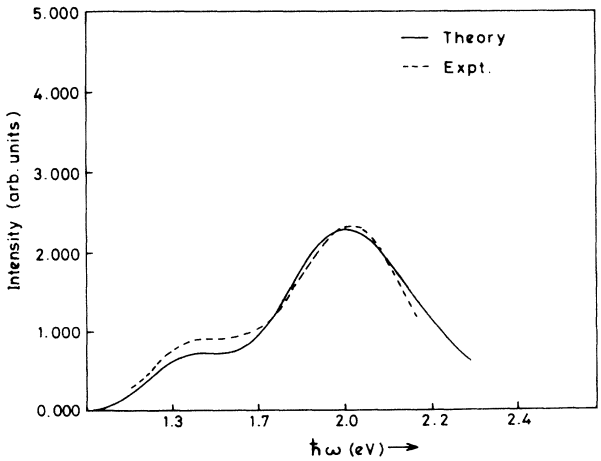

FIG. 4. Comparison of experimental (dashed line) and theoretical (solid line) PL spectra. The experimental spectrum is from Banerjee *et al.* (Fig. 2, curve *c*) (Ref. 25). The theoretical curve is obtained using mean diameter $d_0 = 28$ Å and variance $\sigma = 2$ Å. The dot and column concentration were 80% and 20%, respectively.

a purely quantum dot model. We need to invoke dot and column concentration of 15% and 85%, respectively, with both dots and columns having the same $\{d_0,\sigma\}$ as above mentioned. Our calculations are in excellent agreement with the experimental curve.

In Fig. 4 an experimental PL spectrum (dashed line), of Banerjee *et al.* is compared with our theoretical calculations (solid line).[25] The experimental room-temperature spectrum obtained after etching has a peak at 2.07 eV and a shoulder at 1.65 eV. Presumably the ambient oxidation and subsequent etching process creates dots, though this is not the contention of Banerjee *et al.* The theoretical spectrum is obtained on employing mean diameter $d_0=28$ Å, variance $\sigma=2$ Å, and concentration of dost and columns: 80% and 20%, respectively. The agreement with the experimental curve is good.

The above results have been demonstrated for representative experimental PL spectra. We have also performed a number of calculations for experimental spectra reported by several other workers in the field. These include the ones by Zhang *et al.* (Fig. 1, sample *g* and cited by Wang *et al.*),[12,15] Hummel and Chang after spark erosion (their Fig. 3),[26] Tsai *et al.* on Si:H passivation and immersion in HF (their Fig. 1),[27] and Jung *et al.* (Fig. 3).[28] The numerical values of the parameters used have not been adjusted and are the same as those outlined in the beginning of this section. The agreement in all cases is good.

IV. DISCUSSION

Most works on porous silicon report the photoluminescence spectra without any further theoretical analysis. There are notable exceptions and we briefly discuss some of them.

A series of works purport to explain the visible photoluminescence of porous silicon. Starting with the pioneering work of Canham, and Lehmann and Gosele, they posit the quantum confinement model as the source of visible PL.[1,2] Voos *et al.* consider the upshift (downshift) of electrons (holes), due to confinement and claim that the holes are primarily responsible for visible PL.[4] Read *et al.* perform a detailed first-principle calculation and attribute the electronic upshift to visible PL.[18] They report a peak at 1.48 eV in agreement with the experimental work of Cullis and Canham.[3] They, however, need to invoke a large exciton binding energy (E_b) of 0.32 eV. Buda, Kohanoff, and Parinello perform a first-principles calculation and report a peak at 1.84 eV for a 1.14-nm wire.[29] Ohno, Shiraishi, and Ogawa in another first-principles calculation report an upshift of 0.9 eV for a 1.53-nm wire.[30] Sanders and Chang carry out an empirical tight-binding calculation and report a peak at $\simeq 1.6$ eV for a 2.7-nm wire.[31] These calculations are focused solely on the peak position of the PL. Further, computational limitations prevent them from exploring the effects of larger diameters. A point to note is that several of these calculations report a direct gap at $k=0$.

There exists another first-principle calculation by Delley and Steigmeier.[32] This calculation goes beyond the local-density approximation and attempts to include self-energy corrections. The dependence of the band gap E_g on the cluster ("dot") diameter d is investigated. It is found that $E_g \propto d^{-1}$ and not d^{-2}. With this d^{-1} dependence, instead of Eq. (2.10), we obtain

$$P_D(\Delta E)=N\frac{1}{\Delta E^5}\exp\left[-\frac{1}{2}\left[\frac{d_0}{\sigma}\right]^2\left[\frac{\Delta E}{\Delta E_0}-1\right]^2\right], \tag{4.1}$$

where N is a normalization constant. The FWHM of the PL spectrum is found to be narrower in this case. The dependence of the band gap on the size needs further investigation.

There are attempts to model the effect of the size distribution on the PL spectrum. Behrensmeier *et al.* attempt to model the PL spectra as a superposition of distinct peaks due to discrete wire diameters.[13] Wang *et al.*, in a similar calculation, obtain pinning of peaks at certain discrete energies.[15] The growth process is however, stochastic, and wire diameters have a range as observed in transmission electron microscopy and scanning electron microscopy.[2,33] Hence our approach has, as its basis, a continuous distribution of sizes.

One approach is to fit the PL spectra to a single or series of peaks with a Gaussian convolution. Employing this, Narasimhan *et al.* have reported three peaks.[34] A sum over exponentials representation is nonunique.[35] Further, the physical origin of these peaks needs to be elucidated for such an endeavor to be meaningful. In the absence of this, one merely has a curve-fitting exercise. In contrast, our approach assumes a physical basis wherein not the spectra, but the underlying structure of crystallites has a Gaussian distribution.

The hypothesis that lattice vibrations are responsible for the broadened PL spectra is not plausible.[36] Lattice vibrations give a typical broadening ($\sim$ kT $\leq$25 meV) which is too small to explain the reported FWHM ($\sim$300–400 meV). An explanation of this broadening based on lattice vibrations would involve unphysical values of the Huang-Rhys factor. An anomalous temperature dependence of PL has been reported and needs to be understood further.[34,37]

We observe that in seeking an agreement with the reported PL spectra, we need to invoke both columns and dots. Further, as mentioned in Sec. III, a Lifshitz-like argument could ensure that the tail states are properly accounted for.[6] Thus, local inhomogeneities where columns predominate over dots (or vice versa) exist.

In an effort to employ a minimal set of plausible parameters, we have ignored several effects. These were mentioned in Sec. I. Recombination to defect states is a distinct possibility. Defect states, primarily those due to dangling bonds and voids, lie in the band gap.[24] These states may also be broadened due to the existing disorder in PS. Relaxation processes where the excited electron decays to an appropriate energy state and subsequently recombines is perhaps also present. The distribution of sizes in PS would exercise its influence over physical phenomena other than the PL spectrum. The dependence of

the oscillator strength[18,29,32] on the wire diameter would stand modified. Murayama, Miyazoki, and Hirose have reported an exponential Urbach tail in the PLE spectrum and this may be attributed to the above-mentioned distribution and inhomogeneities.[36] The effect of the surface contribution to the PL may be accounted for in our model by modifying the prefactor in the distribution [Eq. (2.3)] from bd^2 to $(b_1d^2-b_2d^\alpha)$ where b_1 and b_2 are volume- and surface-dependent constants, respectively. Since the surface has a "fractal"-like character, the exponent α may be different from unity. Further, Eq. (2.4) for the PL energy may be modified to

$$\hbar\omega=E_g-E_b+\frac{c}{d^2}+\mathcal{E}(I,\omega_I,\dots)\ .$$

Here, $\mathcal{E}$ accounts for nonlinear processes arising out of the influence of experimental parameters such as the intensity I and the frequency ω_I of the incident radiation. These extensions which are not included in our work may be relevant in explaining the PLE spectrum and an associated exponential Urbach tail. The decay of PL is a nonexponential process.[19,36] While there are several theoretical explanations for this decay, the distribution of energies leading to the Kohlraush type behavior is a possible explanation. We hope to extend our work to explain these and other experimental observations.

In conclusion, we emphasize that the attractive aspect of our model is the choice of a minimal set of parameters whose numerical values are dictated not by the exigencies of an individual PL spectrum, but by independent microscopic calculations and experiments.

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