

Absorption and Emission of Light in Nanoscale Silicon Structures

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A unified model of phonon-assisted and zero-phonon radiative transitions in nanoscale silicon structures is presented. For characteristic size above 15–20 Å, phonon-assisted transitions dominate, while zero-phonon transitions, allowed due to the finite-size effect, are more important for smaller length scales. Light emission from porous silicon is analyzed on the basis of these results showing that phonon-assisted transitions should dominate the emission in the observed red band.

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Recent reports [1] of bright luminescence from porous Si samples have stimulated considerable experimental effort to understand and optimize the conditions for this novel light emission from Si [2]. Normally, band edge luminescence in bulk Si is very weak due to the indirect band gap. The substantial blueshift of the luminescence band in porous Si relative to bulk Si as well as the frequently observed nanometer scale sample morphology [3] have prompted discussion of this phenomenon in terms of quantum confined states in reduced dimensionality structures, e.g., small “boxes” or “wires.” In parallel with this development, synthetic techniques have been applied to produce samples consisting of passivated Si crystallites with diameters in the 20–60 Å range which show very similar optical properties [4]. The crystallite model remains controversial and an adequate theoretical framework for analyzing the optical properties of nanoscale Si structures has been lacking. In this paper, radiative transitions in Si crystallites are analyzed in general terms using an effective mass approach, incorporating both the finite-size effects as well as the coupling to the phonons. Using this new model, the predictions of the crystallite model are compared to data for porous Si.

The samples are assumed to consist of an ensemble of crystallites with passivated surfaces. States in the body of the crystallite are confined by the finite size and the lowest transitions are blueshifted. The electron and hole wave functions are spread in k space, breaking the usual crystal momentum selection rules so that it is no longer meaningful to debate whether the gap is “direct” or “indirect.” In the bulk, absorption of a photon proceeds by second order processes involving an electron- or hole-phonon scattering event [Fig. 1(a)]. Each phonon mode gives a distinct channel for absorption or emission of light with the transverse optic (TO) modes dominant and smaller contributions from the longitudinal optic (LO) and transverse acoustic (TA) modes [5]. In a crystallite, the extent to which the crystal momentum conservation is broken depends on size, represented by the spread of the electron and hole wave functions in reciprocal space [Fig. 1(b)]. Zero-phonon transitions become allowed because of the small weight for each vertical transition according to the overlap of the wave functions. Physically, the needed momentum derives from scattering from the crys-

tallite surface. The resulting amplitude for zero-phonon transitions is strongly size dependent. Finite size also modifies the phonon-assisted transitions: Part of the momentum comes from the surface scattering, and part from the phonon. A range of phonons contribute. This carries a weaker, but important, size dependence. In this work, the phonon-assisted transitions are found to dominate for size scales greater than about 15–20 Å. This corresponds to the red emission band observed commonly in porous Si samples. The present model is consistent with the observed absorption and emission of light by porous Si including the fine structure in emission related to the phonons [6,7].

The qualitative picture from Fig. 1 can be analyzed more quantitatively using an envelope function approach. The electron state in the crystallite is expanded in crystal basis states which include the effect of electron-phonon coupling,

$$\phi_e(\mathbf{r}) = \int d\mathbf{k} \psi_e(\mathbf{k} - \mathbf{k}_0) \phi'_{c\mathbf{k}}(\mathbf{r}), \quad (1)$$

where the Fourier transform of the envelope function ψ_e is developed around the band edge position \mathbf{k}_0 . The crystal basis function $\phi'_{c\mathbf{k}}$ is given by the usual Bloch function

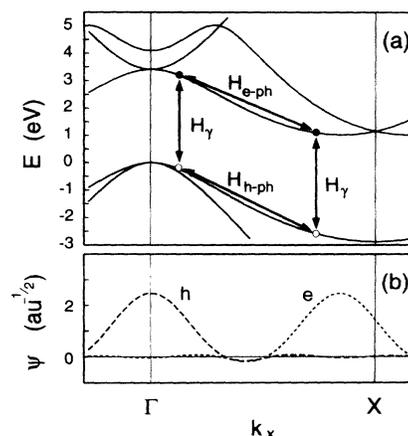


FIG. 1. (a) The Si band structure near the gap region along the (100) direction. The processes for phonon-assisted optical transitions are illustrated. (b) The k_x dependence of the envelope function for an electron and a hole confined to $L_x = 25$ Å.

plus those coupled in through the electron-phonon interaction,

$$\phi'_{c\mathbf{k}} = \phi_{c\mathbf{k}} + \sum_{\lambda\mathbf{q}} \frac{\phi_{c\mathbf{k}-\mathbf{q}} \langle c\mathbf{k}-\mathbf{q} | H_{e-ph}^\lambda | c\mathbf{k} \rangle (1+n_{\lambda\mathbf{q}})^{1/2}}{E_{c\mathbf{k}} - E_{c\mathbf{k}-\mathbf{q}} - \hbar\omega_{\lambda\mathbf{q}}} + (\text{phonon absorption}). \quad (2)$$

The phonon degrees of freedom are described by polarization λ , wave vector \mathbf{q} , occupation number $n_{\lambda\mathbf{q}}$, and energy $\hbar\omega_{\lambda\mathbf{q}}$. The influence of confinement on the phonon modes is not explicitly considered, but would not alter the main conclusions. Using a similar form for the hole wave function, it is straightforward to calculate the matrix element $\langle \hbar | \hat{\mathbf{e}} \cdot \mathbf{p} | e \rangle$ for interaction with the light field. The result for the imaginary part of the dielectric function of an array of N_c crystallites per unit volume is

$$\varepsilon''(\omega) = \frac{8\pi^2 e^2}{\omega^2 m_0^2} N_c \left[\sum_{eh} |p_{eh}^{(1)}|^2 \delta(E_g + E_e + E_h - \hbar\omega) + \sum_{eh,\lambda\mathbf{q}} |p_{eh,\lambda\mathbf{q}}^{(2a)}|^2 n_{\lambda\mathbf{q}} \delta(E_g + E_e + E_h - \hbar\omega_{\lambda\mathbf{q}} - \hbar\omega) + \sum_{eh,\lambda\mathbf{q}} |p_{eh,\lambda\mathbf{q}}^{(2e)}|^2 (1+n_{\lambda\mathbf{q}}) \delta(E_g + E_e + E_h + \hbar\omega_{\lambda\mathbf{q}} - \hbar\omega) \right], \quad (3)$$

where the quantized electron and hole energies $E_{e,h}$ enter together with the bulk band gap E_g . The terms correspond to the zero-phonon, phonon-absorption, and phonon-emission-assisted transitions, respectively. The detailed expressions for the matrix elements reduce to the usual form [5] in the bulk limit with $p_{eh}^{(1)} \rightarrow 0$.

The dipole matrix elements $p_{cv} = \langle v\mathbf{k} | \hat{\mathbf{e}} \cdot \mathbf{p} | c\mathbf{k} \rangle$ are assumed to be independent of \mathbf{k} . The electron-phonon matrix elements and the energy denominators are assumed to be independent of both \mathbf{k} and \mathbf{q} . The severity of this approximation depends on the spread in momentum induced by the finite size and will tend to break down as the length scale drops below a few unit cells. Then

$$p_{eh}^{(1)} \approx p_{cv} M_{eh}(\mathbf{k}_0), \quad (4a)$$

$$p_{eh,\lambda\mathbf{q}}^{(2e)} \approx p_{eh,\lambda\mathbf{q}}^{(2a)} \approx p_{cv} R_\lambda M_{eh}(\mathbf{q} - \mathbf{k}_0) / N_a^{1/2}, \quad (4b)$$

$$M_{eh}(\mathbf{q}) = \int d\mathbf{r} \psi_e^*(\mathbf{r}) \psi_h(\mathbf{r}) e^{-i\mathbf{q} \cdot \mathbf{r}}. \quad (4c)$$

The number of atoms per crystallite N_a enters explicitly and the electron- and hole-phonon matrix elements are combined with the energy denominator into the net ratio R_λ for each phonon branch. The important dependence on crystallite geometry is carried by the Fourier transformed overlap factor $M_{eh}(\mathbf{q})$. Since the important \mathbf{q} are from a restricted region, the phonon frequencies can be taken to be approximately constant and the sum on \mathbf{q} in Eq. (3) can be done explicitly:

$$\sum_{\mathbf{q}} |M_{eh}(\mathbf{q})|^2 = \frac{\Omega}{(2\pi)^3} \int d\mathbf{r} |\psi_e(\mathbf{r})|^2 |\psi_h(\mathbf{r})|^2, \quad (5)$$

with Ω the crystallite volume. Equations (3)–(5) give a unified model for the optical absorption in nanoscale Si structures within the envelope function approximation.

The case of Si is to be contrasted with that of semiconductors with direct band gaps. For example, in a GaAs quantum dot, the electron-phonon coupling leads to a classic Huang-Rhys ladder of phonon sidebands to the strongly dipole allowed excitons [8]. In Si, the electron-phonon coupling must be considered at the outset to determine the dipole allowed radiative channels. In ei-

ther case, the effective coupling strength varies inversely with the volume [8], as seen from Eqs. (4b) and (5).

To illustrate these ideas, a model calculation is used to give the trends and magnitudes. Details of the calculations appear elsewhere [9,10], but the main points follow. Silicon crystallites with (100) symmetry planes at the surface are considered. Then the envelope functions have a simple product form. The quantum numbers describing the electron and hole states are three integers (n_x, n_y, n_z) , plus a valley index for the conduction bands. Finite barriers of 3 eV and unit band mass are employed, modeling an oxide surface coating. A degenerate, spherical valence band ($m_h = 0.54m_0$) and ellipsoidal conduction band valleys ($m_t = 0.19m_0$, $m_l = 0.92m_0$) are assumed. Nonparabolicity is included by a multiplicative enhancement of the mass: $1 + aE$. The calculated blueshift of the crystallite band gap scales with length approximately as $1/L^a$ with a in the range 1.2–1.8, similar to the results of recent tight binding calculations [11(b)]. However, the present value of the blueshift is about 20% smaller. The selection rules for zero-phonon transitions implied by Eq. (4a) require, e.g., for the valley along k_x , $n_{y,e} = n_{y,h}$ and $n_{z,e} = n_{z,h}$, but with $n_{x,e} \neq n_{x,h}$ generally allowed. All phonon-assisted transitions are allowed in Eq. (5). The bulk value $|p_{cv}|^2/2m_0 = 4$ eV is used. The effective electron-phonon coupling parameter is fit to the experimental absorption data in bulk Si [10], maintaining the relative oscillator strength of the TO, LO, and TA assisted transitions from the bulk [5]. Finally, for nanoscale crystallites, excitonic correlations only weakly influence oscillator strengths [8], but shift the energy scale. The electron-hole interaction energy is estimated (first order) to be $E_{eh} \approx -3e^2/\epsilon_0 L$ for a cube and is used to adjust the energy scale.

The calculated ε'' is shown in Fig. 2 for an ensemble of crystallites of average size near 20 Å, including fluctuations in shape and size of 1–2 Å. The inset shows the first set of allowed transitions for a single, asymmetric crystallite. The x , y , and z oriented conduction valleys are not equivalent, and split into the triplets seen. The

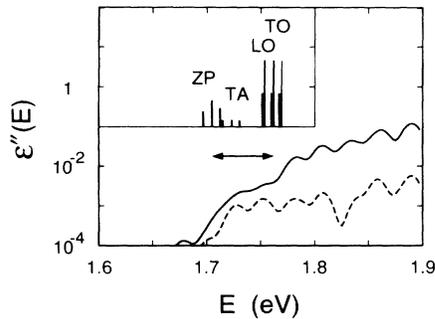


FIG. 2. Imaginary part of the dielectric constant (log scale) calculated for ensembles of Si crystallites. The zero-phonon contribution is shown separately (dashed line) from the total (solid line) for average size near 20 Å. Gaussian broadening of 0.015 eV, FWHM, is included. Inset: near threshold transitions for a 19 Å×20 Å×21 Å crystallite labeled by phonon channel.

lowest transition has zero-phonon character but the oscillator strength is not equal among the valleys. This is due to the sensitive dependence of $M_{eh}(\mathbf{k}_0)$ on the size of the crystallite parallel to \mathbf{k}_0 [9]. The TO modes dominate among the phonon-assisted channels. The combination of the valley splitting and the various phonon contributions gives a considerable spread of transitions near threshold, which is averaged for an ensemble. However, a steplike structure remains which is characteristic of the dominant TO phonon mode energy (arrow in Fig. 2). This energy range corresponds to the red emission band observed in porous Si. The phonon-assisted transitions have 3 to 10 times more oscillator strength. This ratio is in rough agreement with the relative sizes of the phonon-related features observed in selective photoluminescence [6].

To analyze absorption, the microscopic response ϵ'' must be related to the macroscopic response. This involves an important local field correction. Then the present model accounts for the observed magnitude of absorption in porous Si [10]. Radiative recombination of an electron-hole pair in their lowest states in the crystallite can proceed with or without a phonon. Accounting for the local field correction, the oscillator strengths in Eqs. (4) yield the spontaneous emission rates for each channel. This is a key signature for comparison to experiment.

The radiative emission times are summarized in Fig. 3. For each linear dimension L , in monolayer increments, a series of crystallites is considered with transverse dimensions varying from L by up to $\pm 20\%$. The zero-phonon radiative time is calculated and plotted as a separate point, for each case, versus *blueshift*. The strong dependence of the oscillator strength on size and shape yields the larger scatter, but a strong overall trend. This is also found in more detailed calculations [11,12]. The TO phonon-assisted emission has much smoother size dependence (line in Fig. 3) but systematically gets faster for smaller crystallites. For roughly symmetric crystallites, phonon-assisted transitions dominate across the entire

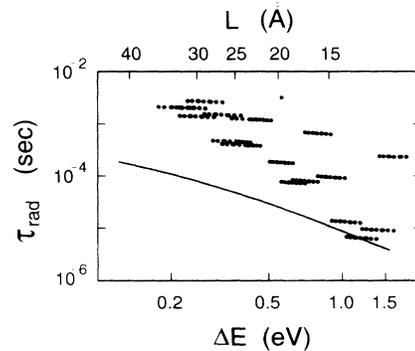


FIG. 3. Radiative recombination time as a function of the blueshift of the photon energy from the bulk Si band edge: zero-phonon transitions (dots); TO phonon-assisted transitions (line). This scatter plot shows the radiative time for each member of an ensemble uniformly distributed around a cubic geometry. The top scale indicates the equivalent cube size.

spectral range of the red emission. The zero-phonon transitions only become comparable for a blueshift near 1 eV (emission near 2.1 eV). The energy for this crossover is shape dependent; e.g., for elongated crystallites, the crossover shifts to the red. The previous calculations [9,11-13], which attribute the light emission solely to zero-phonon ("pseudodirect") transitions, can only be applicable for larger emission energy.

The predicted *radiative* time scale for 70% porosity ranges from a few microseconds in the blue spectral region to of order 100 μs at the bottom of the red region. Extracting *radiative* times from experimentally measured luminescence *decay* times for porous Si is nontrivial [6,10,14,15]. Many samples show an anomalous lengthening of the decay times at low temperatures, attributed to low energy (≈ 10 meV) splitting in the lowest exciton manifold [6]. This splitting is not explicitly included in Fig. 3 so the calculated results refer to the "fast" levels in such a scheme. The measured decay times show strong energy dependence, as suggested by the calculations. This "spectral diffusion" is an intrinsic feature of the crystallite model. It would be quite interesting if the predicted crossover in the energy dependence could be observed. The trend in Fig. 3 is confirmed by the relative strengths of the phonon replicas observed [6,7], with the phonon-assisted transitions being relatively weaker for larger blueshift.

The measured room temperature decay times bracket the theory. For example, for emission near 2.0 eV (i.e., a blueshift near 1 eV), measured times fall in the range 4 μs [6,14] to 20 μs [10,15], as compared to about 10 μs predicted in Fig. 3. However, the experimental radiative times must be slower, and a lower bound in the range 50-100 μs is reasonable. Therefore the radiative component is typically *slower* than calculated. This is extremely interesting. It implies that the excitons which luminesce have even weaker oscillator strength than predicted for recombination of confined states in nanocrystals.

tallites. This might reflect the low energy splitting mentioned above. Alternatively, there may be some degree of trapping or electron-hole separation in real space. This was a central point in understanding the luminescence of CdSe nanocrystallites [16], and has also been discussed for the case of porous Si [17]. In the present theory, this enters naturally through Eqs. (4c) and (5) where electron-hole separation would reduce the oscillator strength.

Quantitative comparison of the relative oscillator strength for zero-phonon and phonon-assisted transitions to the low temperature luminescence experiments depends on details of the luminescence mechanism. However, some general observations can be made. Even if a low energy splitting of the exciton manifold is important at low temperature, the *ratio* of zero-phonon to phonon-assisted oscillator strength should still be preserved, at least for low symmetry crystallites. Also, if shallow trap states are involved, then the zero-phonon and phonon-assisted oscillator strengths should be altered in roughly the same way. However, for deep surface traps, where the state is localized in a region which is distinct from bulk coordinated Si atoms, an atomic scale model is required to assess the relative intensities. Also, the phonon energies in that case could differ from those relevant for bulk Si.

The present model shows that phonon-assisted transitions dominate radiative recombination of excitons in Si nanocrystallites in the region of red emission. This agrees with the observation of Si phonon replicas. Important unresolved questions surround the implied role of traps in the observed luminescence.

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