Influence of Quantum Confinement on the Critical Points of the Band Structure of Si

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The photoluminescence excitation technique is used to monitor the absorption characteristics of Si nanocrystals. Contributions from different critical points are identified, and their shift with reduced size is deduced. The enhancement of the oscillator strength of the indirect optical transitions due to the confinement is estimated. [S0031-9007(96)00665-5]

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In recent years there has been an increasing interest in quantum confined systems based on indirect semiconductors. Si-Ge superlattices, Si and Ge nanoparticles, and porous Si (PS) are some examples. Quantum confinement (QC) effects have been widely investigated in nanocrystals made from II-VI and other direct band-gap compounds. In direct band semiconductors both absorption and emission are governed by the fundamental direct gap. Therefore, most properties of the II-VI nanocrystals, as well as GaAs/GaAlAs quantum wells, can be predicted by relatively simple effective-mass calculations based on the known parameters of the band edge states. In Si the situation is different. Optical transitions related to the fundamental gap are weak, due to its indirect nature, and QC further reduces the density of states near the fundamental band edge. In the bulk material, the contribution of higher energy bands to the absorption is much stronger than that of states near the fundamental gap. Therefore, a study on the influence of QC on higher critical points is essential. In particular, since effective mass theories assume that the lowest electronic levels have the same nature as states at the fundamental gap edge, it is important to assure that in the relevant range they do not mix with higher critical points.

The maximum of the valence band in Si is at the center of the Brillouin zone, at the $\Gamma_{25',V}$ point. The conduction band has 6 minima at the equivalent (100) directions, centered at $\Delta_{1,C} = (0.86, 0, 0)$ points [1]. The fundamental gap is the energy difference between the $\Gamma_{25',V}$ and $\Delta_{1,C}$ points. Above this transition the absorption coefficient, α, follows a $\sqrt{\alpha \hbar\omega} \sim \hbar\omega - E_{\Gamma-\Delta}$ law [2]. At $\sim$1.6 eV deviation from this relation has been observed, which is attributed to transition from the $\Gamma_{25',V}$ point to 8 equivalent minima in the conduction band centered at the $L_{1,C} = (1, 1, 1)$ points [3]. The $\Gamma_{25',V}$-$L_{1,C}$ gap is indirect, and its value is $\sim$1.6 eV [3]. The ratio between the oscillator strength of the $\Gamma_{25',V}$-$L_{1,C}$ and $\Gamma_{25',V}$-$\Delta_{1,C}$ transitions is about 5 [4]. Taking into account these two gaps, the measured spectral dependence of the absorption coefficient of *c*-Si is described up to $\sim$3 eV. Above that a strong increase of the absorption is seen, due to the onset of the direct transitions $\Gamma_{25',V}$-$\Gamma_{15,C}$ at 3.4 eV (E_0') and $\Gamma_{25',V}$-$\Gamma_{2',C}$ at $\sim$4.2 eV (E_0) [5].

Ellipsometry and absorption studies are used to identify critical points in bulk semiconductors. However, in nanocrystals inhomogeneous broadening due to size distribution smears the transitions. In PS, no trace of the indirect gaps at the $\Gamma_{25',V}$-$\Delta_{1,C}$ and $\Gamma_{25',V}$-$L_{1,C}$ is observed. Instead, the absorption increases exponentially with energy [6]. No features that can be identified as related to QC states and no definite absorption edge are resolved. The E_0' and E_0 critical points are seen, but they are smeared with respect to the bulk [7].

Photoluminescence excitation (PLE) is employed to monitor selectively the absorption in inhomogeneously broadened emission bands. Detecting the emitted light within a narrow spectral window measures only a subset of the wide distribution of emission energies. In a granularlike system, in which the motion of excited carriers is restricted, the excited pair is only able to relax in energy and recombine. The number of emitted photons at the recombination energy depends linearly on that absorbed in the particle. Therefore, the PLE signal is proportional to the absorption in the limit of an optically thin sample, if the quantum efficiency is independent of the exciting photon energy [8]. The method has been applied successfully for GaAs-GaAlAs quantum wells [9] and II-VI nanocrystals [10]. Si nanostructures, like PS [11,12] and Si nanocrystals suspensions [13], have also been investigated using PLE.

In this paper we use PLE measurements on extremely thin layers of PS to study the behavior of the higher energy gaps. We show that the $\Gamma_{25',V}$-$\Delta_{1,C}$, $\Gamma_{25',V}$-$L_{1,C}$, and $\Gamma_{25',V}$-$\Gamma_{15,C}$ transitions are all blueshifted. We obtain the shifts as a function of QC, and measure the enhancement of the oscillator strength.

The samples are prepared from (100) *p*-type substrates, B doped to 5 Ω cm. The anodization solution is a 1:1 by volume mixture of 50% HF (in water) and ethanol. Current densities used are in the 50 mA/cm^2 range and the anodization times are tuned from seconds to less than a minute to obtain the desired thickness. The thickness is measured by SEM and ranges from 35 nm to 1 μm. The very thin samples are prepared in order to obtain a PLE spectra at high excitation energies. All PLE spectra shown here are in the limit of optically thin samples.

The measurements are carried out at low temperatures (7 K) inside a helium flow cryostat with quartz windows. The light of a Xe-arc lamp is dispersed by a 22 cm SPEX single monochromator, and focused onto the sample. The luminescence light is collected by lens optics, and spectrally resolved with a second 22 cm SPEX monochromator. In order to achieve better stray light rejection, the emitted light is detected while the exciting light is switched off. This can be done due to the long lifetime of the luminescence at low temperatures. The excitation light is chopped and the out-of-phase component of the emitted light signal is detected in a standard lock-in technique. To account for the spectral variation of the excitation power, a normalization spectrum is recorded simultaneously with the PLE data using a quartz beam splitter and a pyrodetector. The normalization is possible due to the linearity of the PL intensity on the incident light power [8].

The dependence of the PLE signal, detected at 1.7 eV (near the luminescence peak), as a function of excitation energy is shown in Fig. 1. For low excitation energies $\hbar\omega < 2.5$ eV the PLE signal follows the behavior of an indirect semiconductor, namely, $\sqrt{\alpha_{\mathrm{PLE}}\hbar\omega} = A_1(\hbar\omega - E_{g1})$ [see Fig. 1(a)] [8]. The gap, E_{g1}, extrapolated from this dependence is about 1.9 eV. E_{g1} lies about 0.2 eV above the detection energy. Note that the extrapolation is taken from a region of energies well above E_{g1} (and the detection energy), where the joint density of states is quasicontinuous and the relation for bulk indirect semiconductor would therefore hold.

Above 2.3 eV a deviation from $\sqrt{\alpha_{\mathrm{PLE}}\hbar\omega} = A_1 \times (\hbar\omega - E_{g1})$ is observed. The extra absorption in the intermediate regime follows a similar behavior, $\sqrt{\alpha_{\mathrm{PLE}}\hbar\omega} = A_2(\hbar\omega - E_{g2})$, but with a different gap, $E_{g2} = 2.5$ eV. The prefactor A_2 is 4.4 times larger than A_1. For $\hbar\omega > 3.2$ eV the influence of the direct transition is seen in a fast increase of the PLE signal [see Fig. 1(c)]. Here $(\alpha_{\mathrm{PLE}}\hbar\omega)^2 = A_3(\hbar\omega - E_{g3})$, the dependence expected for an allowed direct transition. E_{g3} is $\sim$3.5 eV close to the first direct gap in *c*-Si. The observed spectral behavior is similar to that of bulk Si, suggesting that the absorption in PS take place within the Si crystallites. This is supported by the recent observation of phonon steps in PLE spectra taken under resonant excitation [14].

Figure 2 shows the change of these three different band gaps with the detection energy, E_d. The narrow energy range from which the E_g's are extrapolated limits the accuracy of their determination, especially for E_{g2}. Nevertheless, a clear tendency is seen: all E_g's increase with the detection energy, and this increase is stronger the lower the energy of the gap is. With increasing detection energy we probe a subsystem of the distribution of crystallites, for which the average QC energy is higher. Therefore, the results in Fig. 2 suggest that all three gaps are blueshifted with reduced particle size.

Although a qualitative picture of the effect of QC on the different transitions can be deduced from Fig. 2, a quantitative result is not straightforward. To illustrate this let us examine the behavior of the lowest gap E_{g1}. Higher lying critical points contribute strongly to the absorption, but the emission would always occur at the vicinity of E_{g1}, since energy relaxation processes in Si are much faster than the radiative recombination rate. Therefore, the gap E_{g1} and the emission energy E_d are related. In this respect we point out that the slope $dE_{g1}/dE_d < 1$. In a simple model in which the crystallites emit from the band edge, and there is no broadening (namely, all

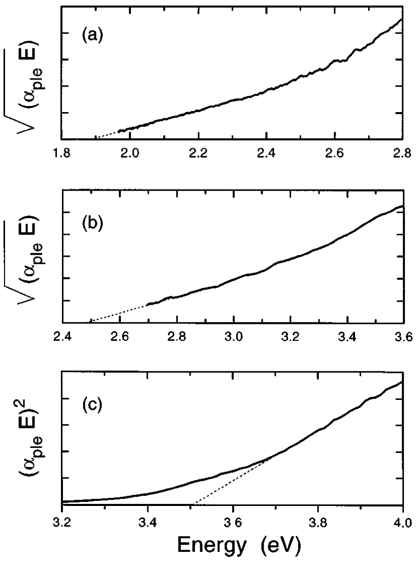

FIG. 1. The dependence of the PLE signal on the excitation photon energy in (a) the low energy regime, (b) the intermediate regime, and (c) the first direct band-gap regime.

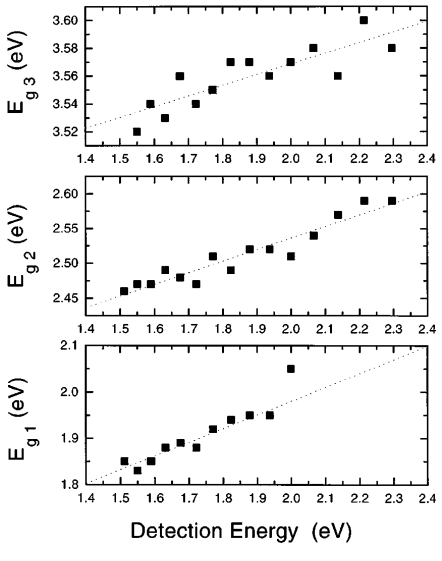

FIG. 2. The dependence of the three different gaps extrapolated from the PLE signal on the detection energy. The dotted lines are the fits described in Eq. (1).

crystallites with the same E_{g1} emit at the same energy), light detected at E_d is emitted only from crystallites with $E_{g1} = E_d$, and dE_{g1}/dE_d should be 1. If we allow for further relaxation, from the band edges to an emitting state, so that $E_d = E_{g1} - \delta$, and δ is uniquely defined by E_{g1} (e.g., δ being the exciton binding energy), then the slope has to be larger than 1 since δ increases monotonically with E_{g1}.

The fact that the slope is smaller than 1 implies that crystallites with the same gap do not emit at a well defined energy [12]. Therefore, the influence of broadening should be considered. The luminescence detected at E_d is emitted not only from crystallites with a unique gap, but also from other crystallites with higher or lower E_{g1}'s. The distribution of E_{g1}'s has a peak at a certain energy, E_{g1}^0. If $E_d < E_{g1}^0$ the number of crystallites with gap larger than E_d will be higher and the average gap detected at E_d will be above E_d. A similar argument shows that the average gap for $E_d > E_{g1}^0$ will be smaller than E_d. Thus, the slope dE_{g1}/dE_d will always be smaller than 1, as observed in the experiment.

In spite of the interfering effect of the broadening, a quantitative estimation of the magnitude of the blueshift of the different gaps with QC can be done. From Fig. 2 it seems that all gaps depend *linearly* on E_d. In Ref. [12] a simple model for the dependence of E_{g1} on E_d, taking into account the effect of broadening, has been developed. It predicts that E_{g1} should increase *linearly* with E_d. A simple extension of this model suggests a similar dependence for the higher energy gaps. Therefore, we fit the results of Fig. 2 using linear regression to obtain

$$\begin{aligned} E_{g1}(E_d) &= (0.32 \pm 0.03)E_d + (1.35 \pm 0.05), \\ E_{g2}(E_d) &= (0.14 \pm 0.02)E_d + (2.25 \pm 0.03), \\ E_{g3}(E_d) &= (0.08 \pm 0.01)E_d + (3.45 \pm 0.05). \end{aligned} \tag{1}$$

Inserting the first relation into the last two we find

$$\begin{aligned} E_{g2}(E_d) &= (0.44 \pm 0.10)E_{g1}(E_d) + (1.65 \pm 0.16), \\ E_{g3}(E_d) &= (0.25 \pm 0.05)E_{g1}(E_d) + (3.11 \pm 0.13). \end{aligned} \tag{2}$$

In these last relations between the different gaps, E_d is only a parameter and does not appear explicitly. One can speculate that these relations should hold within each of the crystallites, regardless of their emission energy. To examine this idea we look at the limit of bulk Si. For c-Si $E_{g1} = 1.17$ eV at low temperatures, and we find using Eq. (2), $E_{g2} = 2.16 \pm 0.28$ eV and $E_{g3} = 3.40 \pm 0.19$ eV. These values are close to the $\Gamma_{25',V}$-$L_{1,C}$ and the $\Gamma_{25',V}$-$\Gamma_{15,C}$ transitions, suggesting they should be identified with E_{g2} and E_{g3}, respectively. Note also that in the range of investigation we could resolve only three critical points, which correspond to those known for c-Si.

Equation (2) predicts the value of the higher lying transitions as a function of the energy of the "fundamental" transition in the crystallite, E_{g1}. Rama Krishna and Friesner [15] have calculated the band structure of Si quantum dots as a function of their size. Their results and the predictions of Eq. (2) are shown in Fig. 3. There is a good agreement for the $\Gamma_{25',V}$-$L_{1,C}$ transitions, but for $\Gamma_{25',V}$-$\Gamma_{15,C}$ the agreement is only reasonable for low confinement energies. At higher confinement energies the experiments suggest blueshift of the $\Gamma_{25',V}$-$\Gamma_{15,C}$ gap, while the theory predicts redshift [15].

The identification of E_{g1} and E_{g2} with the two indirect transitions is also supported by the relative strength between them. As we have stated before, below the second indirect gap $\sqrt{\alpha_{\mathrm{PLE}}\hbar\omega} = A_1(\hbar\omega - E_{g1})$, while above it $\sqrt{\alpha_{\mathrm{PLE}}\hbar\omega} = A_2(\hbar\omega - E_{g2})$, and $A_2/A_1 \simeq 4$. The absorption of c-Si follows similar relations, and the ratio of the prefactors is ~5. Therefore, E_{g1} and E_{g2} reflect the $\Gamma_{25',V}$-$\Delta_{1,C}$ and $\Gamma_{25',V}$-$L_{1,C}$ transitions.

The situation for the $\Gamma_{25',V}$-$\Gamma_{15,C}$ transition is more complicated. The ratio between the strength of this direct transition and the indirect transitions, as estimated from the PLE data, is $A_3/A_2 \cong 10^7$ (eV/cm)$^{3/2}$. For bulk c-Si $A_3/A_2 \cong 10^{11}$ (eV/cm)$^{3/2}$. This discrepancy might be explained if the quantum efficiency decreases for higher excitation energies. However, examination of the PLE signal of a thick sample in the saturation regime allows us to conclude that the quantum efficiency is constant within 10% for excitation in the range 2.8–4.5 eV. Therefore, the observed reduction in the ratio A_3/A_2 is due to a change in the absorption characteristics.

The absorption of PS (as measured from transmission) above the first direct gap ($\hbar\omega \geq 3.3$ eV) is similar, both in spectral dependence and magnitude, to that evaluated from Bruggeman effective medium approximation for Si spheres embedded in vacuum [16]. Thus, the absorption

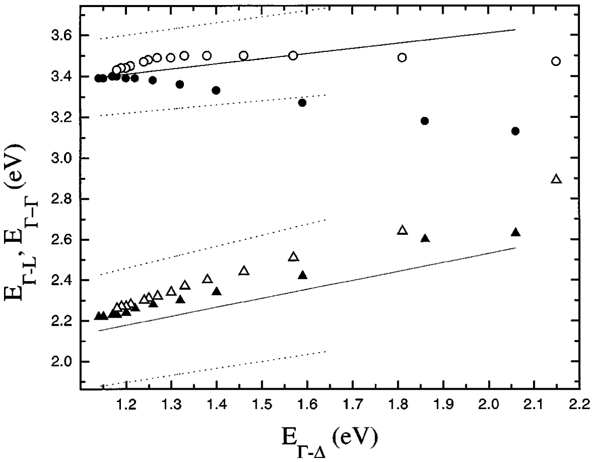

FIG. 3. The Γ-L and the Γ-Γ transitions as a function of the Γ-Δ gap. The triangles and the circles are the theoretical predictions of Ref. [15] to the Γ-L and the Γ-Γ transitions, respectively. The full signs stand for the excitonic energies and the open ones for the gaps. The continuous lines are the experimental estimates [Eq. (2)]. The dotted ones are the upper and lower limits.

in this high energy regime reflects the total amount of Si-Si bonds, and is not affected by QC. If the strength of the $\Gamma_{25',V}$-$\Gamma_{15,C}$ transition is the same as in the bulk, the reduction of the ratio between the strengths of the direct and the indirect transitions results from an increase of the oscillator strength of the indirect transitions, due to the relaxation of the $\vec{k}$ selection rules via QC. The enhancement of the oscillator strength of the indirect transitions is estimated from the PLE data to be of the order of $10^{11}/10^7 = 10^4$.

Finally, we would like to use the relations between the different gaps given in Eq. (2) to study the shifts of different points in the band structure. The relative shifts of the valence (the $\Gamma_{25',V}$ point) and the conduction band (the $\Delta_{1,C}$ point) are $\Delta E_{\Delta,C}/\Delta E_{\Gamma,V} = 1/2$ [17]. Therefore,

$$\begin{aligned} \Delta E_{g1} &= \Delta E_{\Gamma,V} + \Delta E_{\Delta,C} = \tfrac{3}{2}\Delta E_{\Gamma,V}\,, \\ \Delta E_{g2} &= \Delta E_{\Gamma,V} + \Delta E_{L,C}\,, \\ \Delta E_{g3} &= \Delta E_{\Gamma,V} + \Delta E_{\Gamma,C}\,, \end{aligned} \tag{3}$$

using Eqs. (3) and (2) we find

$$\begin{aligned} \Delta E_{\Delta,C} &= \tfrac{1}{2}\Delta E_{\Gamma,V}\,, \\ \Delta E_{L,C} &= -0.33\Delta E_{\Gamma,V}\,, \\ \Delta E_{\Gamma,C} &= -0.62\Delta E_{\Gamma,V}\,. \end{aligned} \tag{4}$$

This implies that while QC shifts the $\Delta_{1,C}$ point to higher energies, the $L_{1,C}$ and the $\Gamma_{15,C}$ points move towards lower energies. An examination of the band structure of *c*-Si tends to support this suggestion. The curvature of the dispersion relation $E(\vec{k})$ at the vicinity of the $\Gamma_{15,C}$ point is opposite to that in the $\Delta_{1,C}$ point, suggesting that they would move in opposite directions with QC. For the $L_{1,C}$ point the situation is not so clear, but it is obvious that the curvature of the $E(\vec{k})$ relation is much smaller than in the vicinity of the $\Delta_{1,C}$ point. Therefore, the shift of the $L_{1,C}$ point with QC is expected to be weaker than that of the $\Delta_{1,C}$ point.

We now examine the conditions under which the different gaps will start to mix. By setting $E_{g1} = E_{g2}$ we find that at ~3 eV these two gaps start to mix. Above that the approach taken here is not meaningful. Nevertheless, even at this energy the direct $\Gamma_{25',V}$-$\Gamma_{15,C}$ gap is still much higher. Mixing with the direct gap would occur only for $E_{g2} \approx 5$ eV.

To summarize, the analysis of PLE data shows that the absorption of Si nanocrystals has a similar spectral dependence to that of bulk Si. QC blueshifts all the critical points by different amounts, the higher the transition is, the weaker the shift is. QC enhances the oscillator strength of the indirect transitions by a factor of 10^4, making their contribution to the absorption relatively more important with respect to that of the direct transition. These data enable prediction of the absorption characteristics of Si nanocrystals with different confinement energies.

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