

Breakdown of the \mathbf{k} -Conservation Rule in Si Nanocrystals

D. Kovalev,¹ H. Heckler,¹ M. Ben-Chorin,^{1,2} G. Polisski,¹ M. Schwartzkopff,¹ and F. Koch¹

¹*Physik-Department E16, Technische Universität München, D-85747 Garching, Germany*

²*Department of Chemical Physics, Weizmann Institute of Science, Rehovot 76100, Israel*

(Received 20 July 1998)

We show that light emission from different systems of silicon nanocrystals does behave as expected for indirect-band-gap quantum dots. Photoluminescence excited on the low energy part of the distribution of Si nanocrystals exhibits a set of narrow peaks associated with Si TA and TO momentum-conserving phonon-assisted optical transitions. These spectra allow us to determine the ratio of no-phonon transitions to TA and TO phonon-assisted processes over a wide range of confinement energies. The ratio between these recombination channels changes by 2 orders of magnitude with increasing confinement energy. For confinement energies above 0.7 eV the radiative transitions are governed by no-phonon quasidirect processes. [S0031-9007(98)07199-3]

PACS numbers: 78.55.Ap, 78.66.Li

The influence of quantum confinement on the optical properties of semiconductor nanocrystals has been intensively investigated in recent years. Spectroscopic studies have revealed an increase of the band gap and the oscillator strength with decreasing size. The direct electronic band structure of II-VI semiconductor quantum dots and the advances in their synthesis and size selection have made them a perfect model system for spectroscopic studies of confinement effects. In order to overcome the inhomogeneous broadening of the emission band and to study single dot properties, several methods, including fluorescence line narrowing [1], photoluminescence excitation (PLE), and single quantum dot optical spectroscopy [2] have been applied.

One field of research that cannot be fully studied in these direct band-gap nanocrystals is the breakdown of the \mathbf{k} -conservation rule. In indirect band-gap semiconductors the optical transitions are allowed only if phonons are absorbed or emitted to conserve the crystal momentum. The spatial confinement of electrons and holes inside a nanocrystal increases the uncertainty of their crystal momentum, thus allowing optical transitions in which phonons are not involved. One of the general predictions of the theory is that in smaller Si nanocrystals the probability of no-phonon (NP) transitions should increase with respect to phonon-assisted (PA) processes [3]. Therefore, optical properties of Si nanocrystals have to be considered on the basis of a competition between indirect and quasidirect recombination channels.

Although much theoretical work has been done toward understanding this property of indirect-band-gap nanocrystals [3–6], experimental work lags behind. It is now generally accepted that quantum confinement is responsible for the efficient light emission from Si nanostructures [7]. A correlation between the Si nanocrystal size and the blueshift of optical transitions has been reported [8]. Thus, Si-based nanocrystal systems are good candidates for the study of the \mathbf{k} -conservation law breakdown in indirect band-gap semiconductor nanocrystals.

Porous silicon (PSi) and Si nanocrystals precipitated in SiO₂ matrix are two examples of nanoscaled Si-based systems. Structural investigations show that they consist of Si nanocrystals of different size and shape, which retain the diamond lattice structure of bulk Si [9]. Although Si nanocrystals have high photoluminescence (PL) yield they behave as indirect semiconductors. The PL observed under resonant excitation shows onsets related to momentum-conserving TO and TA phonons of bulk crystalline Si [10–12]. Since only two onsets are observed (for each phonon) the only possible processes in the absorption-emission cycle involve zero, one, or two momentum-conserving phonons. These processes correspond to no-phonon transitions in both emission and absorption, to one phonon-assisted process in either the absorption or the emission, and to phonon-assisted transitions in both emission and absorption. PL hole burning experiments demonstrated that all the light emission from PSi is due to radiative recombination of confined indirect excitons [13].

In this Letter we describe extremely energy-selective optical spectroscopy and show that light emission from Si nanocrystals does behave as expected from a system of indirect band-gap Si quantum dots. Resonant PL spectra excited at the edge of the luminescence band show distinctive emission peaks from quantum confined exciton states recombining via NP, TA, and TO phonon-assisted processes. From the amplitudes of the different transitions we find the relative strengths of the no-phonon transitions and the various momentum conserving phonon-assisted processes. The dependence of these ratios on the confinement energy appears to be in good agreement with the theoretical predictions [3].

In order to perform resonant PL experiments over a wide spectral range, while monitoring only a very small fraction of nanocrystals at the low energy side of the particles distribution, a set of hydrogen-passivated or naturally oxidized PSi samples is prepared. These samples have nonresonant PL maxima in the range 1.3–2.2 eV. Heavily oxidized

Si nanocrystals are prepared by either oxidation of mesoporous Si (containing initially crystallites with a typical size of 10–20 nm) [9] at $T = 1000^\circ\text{C}$ for 40 min or by Si ion implantation in a SiO_2 layer ($N_{\text{Si}} = 5 \times 10^{16} \text{ cm}^{-2}$ 50 keV) with subsequent annealing at $T = 1100^\circ\text{C}$ for 15 min. A dye or a Ti-sapphire laser is used to excite resonantly the PL, and a Si charge-coupled device array is employed for detection. To suppress stray light from the exciting laser the entrance slit of the monochromator is blocked when the laser beam illuminates the sample. The experiments are performed at $T = 4.2 \text{ K}$. All PL spectra are normalized to correct for the sensitivity of the optical system.

A typical resonant PL excited at the low energy side of the emission band is shown in Fig. 1a. It consists of a set of peaks with a full width at half maximum of $\sim 10 \text{ meV}$. From the energy separation between the peaks, we assigned them to transitions involving NP, 1TA, 2TA, 1TO, TO + TA, and 2TO momentum-conserving phonons in the absorption-emission cycle, respectively. No other strong features are seen in the PL spectrum. The same combination of peaks is found in the resonant PL spectrum of Si nanoparticles covered by a SiO_2 shell (Fig. 1b). However, in the oxidized samples the no-phonon processes seem to be stronger than in the hydrogen-passivated samples. From the number of emitted photons, knowing the maximum emission rate in the PL saturation limit (one photon per dot per e - h pair lifetime) we estimated the number of the excited Si nanocrystals to be of the order of 100.

The observation of peak structure in the resonant spectrum of an inhomogeneously broadened system of nanocrystals deserves further explanation. The probability of photon absorption in crystallites with a gap E_{gap} is a product of the density of such crystallites in the size distribution and the probability of absorbing a photon in one such crys-

tallite. In the tail of the distribution the density of crystallites is increasing with E_{gap} . The absorption of resonant light is, on the other hand, stronger for lower gap crystallites. The product of these two factors will give a peak at the “most favorable” gap. Since both NP and PA processes are possible (in both emission and absorption) this peak will be replicated at one and two phonon energies below the NP peak.

It is rather complicated to find accurately the ratio of NP:PA transitions because the exact shape of the size distribution and the energy dependence of the absorption in a crystallite are not known. We therefore assume that the absorption is an on/off process, namely, that all crystallites with E_{gap} below the excitation energy absorb with the same probability (i.e., the real absorption spectrum is replaced by a step function). Under this assumption the observed peak structure is just a product of the density of nanocrystals with step functions positioned one or two phonon energies below the excitation, with amplitudes determined by the relevant ratios of NP to PA transitions. To eliminate the effect of the size distribution we divide the resonant PL spectrum by the nonresonant one ($\hbar\omega_{\text{ex.}} = 2.8 \text{ eV}$), assuming that the nonresonant PL spectrum reflects the size distribution, since all crystallites absorb similarly at high excitation energy. The resulting spectra show a nearly rectangular sequence of steps (Fig. 2). The energy spread of the rising part of the steps is of the order of 4 meV and is most probably governed by the energy dispersion of the phonon branches and spread of the singlet-triplet splitting [10]. Each step represents another combination of phonon-assisted processes in the absorption-emission cycle. The relative amplitude of these steps is strongly spectrally dependent: with increase of the excitation energy there is a progressive growth of steps associated with no-phonon processes.

Although our assumption on the absorption behavior of a nanocrystal is rather crude (i.e., that it can be approximated by a step behavior), it probably does not affect our analysis very much. We find that in the tail region both the nonresonant and the resonant PL spectra decay exponentially with energy and with the same slope. This suggests that the change of the absorption with energy is rather weak with respect to the size distribution. Furthermore, resonant PL excitation measurements at the high energy tail of the distribution show that the PLE signal (which reflects the absorption) increases as $\sqrt{E - E_{\text{gap}}}$ which is quite similar in behavior to a step function.

At a certain detection energy, light is emitted from crystallites with $E_{\text{gap}} = E_{\text{det}}$, $E_{\text{det}} + E_{\text{TA}}$, and $E_{\text{det}} + E_{\text{TO}}$ (as long as $E_{\text{gap}} < E_{\text{exc}}$). The absorption in these crystallites is coming from NP or PA processes. If only one phonon is involved in the absorption-emission process, there are two possibilities: the phonon might be emitted during absorption at $E_{\text{gap}} = E_{\text{det}}$, or it is emitted during radiative recombination from nanocrystals with $E_{\text{gap}} = E_{\text{det}} + E_{\text{phonon}}$. Therefore two groups of nanocrystals

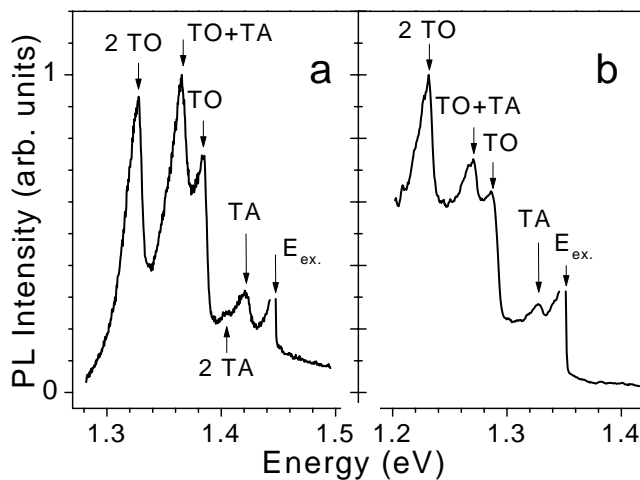


FIG. 1. The resonant PL spectra of naturally (a) and heavily oxidized (b) PSi. The arrows show the energy position of Si TA and TO momentum-conserving phonons with respect to the triplet exciton ground state.

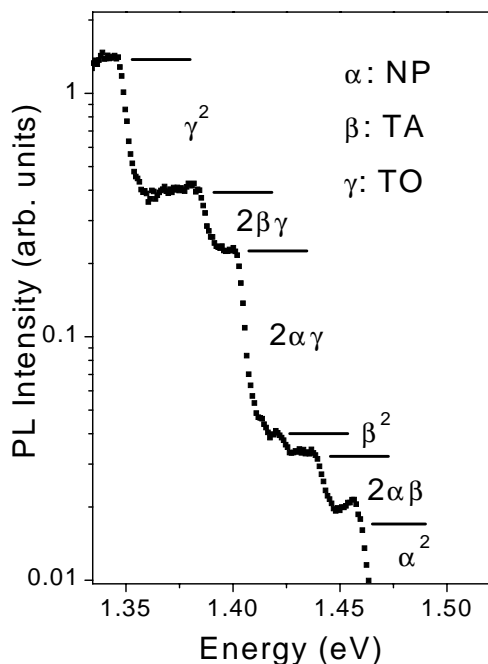


FIG. 2. "Density of states" spectrum of the system of resonantly excited Si nanocrystals. The solid horizontal lines show the amplitude of steps related to the different recombination channels. α , β , and γ denote the relative probabilities of NP, TA, and TO phonon-assisted processes, respectively. The weighted probability for each step is indicated on the graph.

contribute to emission at the same detection energy. The same is true for TA + TO phonon emission. On the other hand, for NP transitions and for two identical phonon combinations only one group of nanocrystals contributes. Therefore, the relative number of crystallites emitting at a certain energy is taken as one for NP, 2TA, and 2TO transitions and two for TA, TO, and TA + TO transitions. We further assume that the ratio of NP to TA and TO assisted processes is NP:TA:TO = α : β : γ . The absolute oscillator strength for the TO phonon-assisted process is not experimentally explored up to now; therefore in the further analysis its value is always taken as 1. The resulting weighting factors are indicated in Fig. 2. The solid lines in Fig. 2 represent the predicted height of steps based on the ratios α : β : γ = 0.093:0.085:1. The small discrepancy is most probably due to the fact that one and two TO (TA) phonon peaks result from crystallites having difference in quantization energies of the order of 56 meV (18 meV) [energy of Si TO (TA) phonon]. Therefore the ratio we obtain is an average value for a spectral window of the order of 56 meV. This is an inherent limitation of our evaluation procedure [14], and the real probabilities might slightly differ from those we calculate. We believe that the reasonably good fit we obtain for six spectral features using only two parameters asserts that the systematic error is small.

In Fig. 3 we plot the relative probabilities of NP to TA and TO phonon-assisted transitions, calculated according

to the procedure described above, as a function of confinement energy [15] in the spectral range of 1.3–1.9 eV. For higher excitation energies the peak structure in the resonant spectrum smears into steplike structures, even for samples having a nonresonant PL maximum at 2.2 eV. Our approach is in general valid when a peaklike spectrum ensures the absence of any nonresonant PL background. Therefore evaluation has been done only in limited spectral range.

One can see that in the vicinity of the crystalline Si band gap, in the weak confinement regime, TO phonon-assisted processes dominate. At ~ 1.8 eV no-phonon processes begin to take over. The ratio between TO and TA assisted-processes is of the order of 10 and appears to be independent of the confinement energy within the experimental accuracy. A similar ratio between TO and TA lines intensities is reported for free and bound exciton emission in bulk Si [16]. Si crystallites having SiO₂ shells behave in general in a similar way. However, the strength of no-phonon processes is significantly enhanced at the same emission energies.

The geometrical confinement of the exciton results in a blueshift of the optical transitions and a modification of the oscillator strengths of no-phonon and phonon-assisted processes. The major scaling parameter in all these effects is the size of the nanocrystal L . Theoretical predictions suggest that the confinement energy scales as $E_C \sim (1/L)^X$ ($1.2 \leq X \leq 2$ depending on the theoretical

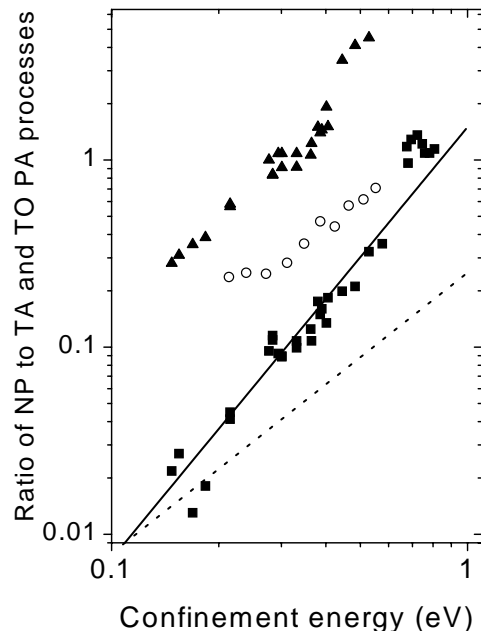


FIG. 3. The probability ratio of the no-phonon to TA phonon-assisted (solid triangles) and TO phonon-assisted process (solid squares) versus confinement energy for naturally oxidized Si nanocrystals. Open circles show the NP to TO ratio for Si crystallites embedded in the SiO₂ matrix. The dotted line shows a theoretical fit according to the effective mass theory prediction. The solid line is a theoretical fit assuming $X = 1.3$.

approach used [3–6]). The oscillator strength of the phonon-assisted transitions is expected to be inversely proportional to the volume of the nanocrystal and scales as $(1/L)^3$. The probability of the no-phonon transitions depends on the \mathbf{k} -space overlap of the electron and hole envelope functions, and it scales as $(1/L)^6$ [3]. Therefore, the ratio NP:PA scales as $(1/L)^3 \sim (E_C)^{3/X}$. The dotted line in Fig. 3 is the infinite barrier effective mass prediction ($X = 2$) and the solid line is for a more realistic value of $X = 1.3$ [4,6]. The effective mass approximation certainly does not describe the experimental behavior. We found that values of X between 1.2 and 1.4 give a best fit to our data. Good agreement is found not only in the overall energy dependence, but also for the numerical values. We find an NP:TO phonon transition ratio of 1:50 at weak confinement energies (≈ 200 meV). No-phonon transitions begin to dominate at confinement energies of the order of 0.65–0.7 eV. Both these numbers are in good agreement with estimates done for the wirelike Si crystallites [3].

We have already mentioned that for the same confinement energy NP transitions are about 3 times stronger in Si nanocrystals having a SiO_2 shell. Two effects of opposite nature can account for the observed tendency depending on the quality of the Si-SiO₂ interface. First, carrier scattering at the heterointerface, responsible for the breakdown of the \mathbf{k} -conservation rule, is known to be strongly dependent on the interface abruptness [17]. Therefore one might expect an enhancement of NP processes in nanocrystals having a good quality Si-SiO₂ interface. Second, the confining potential (and the confinement energy for a fixed size) is lower for a Si nanocrystal surrounded by SiO_x compound [18]. To achieve the same confinement energy, smaller size nanocrystals are required, giving rise to a relative increase of NP transitions.

To conclude, we have measured the ratio of probabilities of NP processes to TA and TO phonon-assisted transitions over a wide range of confinement energies for different systems of indirect Si nanocrystals. The crossover between these two recombination channels is found to occur at emission energies around 1.8–1.9 eV. A comparison of the experimental results with theoretical predictions may open the way for an accurate cor-

relation of the confinement energies with the size of nanocrystals.

-
- [1] D. J. Norris, Al. L. Efros, M. Rosen, and M. G. Bawendi, *Phys. Rev. B* **53**, 16 347 (1996).
 - [2] S. A. Empedocles, D. J. Norris, and M. G. Bawendi, *Phys. Rev. Lett.* **77**, 3873 (1996).
 - [3] M. S. Hybertsen, *Phys. Rev. Lett.* **72**, 1514 (1994); M. S. Hybertsen, in *Porous Silicon Science and Technology*, edited by J.-C. Vial and J. Derrien (Springer-Verlag, Les Editions, Berlin, New York, Les Ulis, 1995), p. 67.
 - [4] C. Delerue, G. Allan, and M. Lannoo, *Phys. Rev. B* **48**, 11 024 (1993).
 - [5] R. J. Needs, S. Bhattacharjee, K. J. Nash, A. Qteish, A. J. Read, and L. T. Canham, *Phys. Rev. B* **50**, 14 223 (1994).
 - [6] N. A. Hill and K. B. Whaley, *Phys. Rev. Lett.* **75**, 1130 (1995).
 - [7] L. T. Canham, *Appl. Phys. Lett.* **57**, 1046 (1990).
 - [8] A. G. Cullis, L. T. Canham, and P. D. J. Calcott, *J. Appl. Phys.* **82**, 909 (1997).
 - [9] A. G. Cullis and L. T. Canham, *Nature (London)* **353**, 335 (1991).
 - [10] P. D. J. Calcott, K. J. Nash, L. T. Canham, M. J. Kane, and D. Brumhead, *J. Phys. Condens. Matter* **5**, L91 (1993).
 - [11] T. Suemoto, K. Tanaka, A. Nakajima, and T. Itakura, *Phys. Rev. Lett.* **70**, 3659 (1993).
 - [12] L. E. Brus, P. F. Szajowski, W. L. Wilson, T. D. Harris, S. Schuppler and P. H. Citrin, *J. Am. Chem. Soc.* **117**, 2915 (1995).
 - [13] D. Kovalev, H. Heckler, B. Averboukh, M. Ben-Chorin, M. Schwartzkopff, and F. Koch, *Phys. Rev. B* **57**, 3741 (1998).
 - [14] P. D. J. Calcott, K. J. Nash, L. T. Canham, M. J. Kane, and D. Brumhead, *J. Lumin.* **57**, 257 (1993).
 - [15] The confinement energy is calculated with respect to the band gap of crystalline Si at $T = 4$ K (1.17 eV) assuming that zero phonon absorption takes place in the lowest optically active state of the exciton [10].
 - [16] D. J. Dean, J. R. Haynes, and W. F. Flood, *Phys. Rev.* **161**, 711 (1967).
 - [17] V. A. Kharchenko and M. Rosen, *J. Lumin.* **70**, 158 (1996).
 - [18] Y. Kanemitsu, T. Ogawa, K. Shiraishi, and K. Takeda, *Phys. Rev. B* **48**, 4883 (1993).