

Optical absorption cross sections of Si nanocrystals

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Using the photoluminescence Auger saturation phenomenon, we deduce the values of the absorption cross section of silicon nanocrystals in a wide range of energies. The very large variation of their values versus energy of the absorbed light is attributed to the enhanced optical transition oscillator strength but reduced density of electronic states towards higher confinement energies. The overall spectral behavior of the absorption cross section reflects the indirect-gap nature of silicon nanocrystals.

The influence of quantum confinement on the optical properties of semiconductor nanocrystals has been intensively investigated in recent years (see the articles in Ref. 1). Spectroscopic studies have revealed an increase of the band gap and the oscillator strength of optical transitions with decreasing size of nanocrystals. Absorption and photoluminescence excitation experiments (PLE) have shown that the absorbing states of most of these systems have a discrete character in the vicinity of the ground luminescing state and merge to a quasicontinuum at higher energies.² However, despite the good qualitative understanding of the optical properties of nanocrystal assemblies, quantitative data are frequently lacking.

One of the most fundamental parameters describing the interaction of light with nanocrystals is their absorption cross section σ . It plays an essential role in modeling of the integral absorption or luminescence properties of nanocrystal assemblies. This value is a product of the density of electronic states and the oscillator strength of the optical transitions. Direct measurement of σ by absorption techniques is almost not possible because of the residual size distribution and unknown number of absorbing nanoparticles. The PLE technique, having the advantage of size (emission energy) selection, gives only qualitative information about the energy dependence of σ as well.

In this paper we report on a direct measurement of σ for silicon nanocrystals in a wide range of energies. We found an extremely large variation of their values versus both absorbed and emitted light energies. A comparison of these values with the spectral dependence of the bulk silicon absorption coefficient shows an indirect-band-gap nature of silicon nanocrystals and a reduction of the density of electronic states towards higher confinement energies.

The measurement technique is based on the Auger photoluminescence (PL) saturation phenomenon. Due to extremely long radiative lifetimes³ of excitons localized in Si nanocrystals at He temperatures (\sim milliseconds), an occupation of Si nanocrystals by two electron-hole ($e-h$) pairs can be achieved at very low excitation intensities. During a fast Auger recombination process^{4,5} one of the pairs recombines nonradiatively what leads to a reduction of the quantum yield of the PL. The key point of these experiments is that the power law of the PL (the dependence of the PL intensity on the optical excitation intensity) from optically thin samples is independent either of the number of nanocrystals luminescing

at a certain energy or of their size distribution. Since the generation rate of $e-h$ pairs is proportional to σ , a study of the PL saturation regime gives quantitative information about their values.

To ensure that the nanocrystal-containing layers are optically thin at all excitation energies used, a set of hydrogen-passivated or naturally oxidized porous silicon layers having a thickness from 0.05 to 20 μm has been prepared according to the conventional procedure described in Ref. 6. Different lines of cw Ar⁺, dye, and Ti:sapphire lasers have been used to cover the entire optical excitation and emission ranges of Si nanocrystals. To avoid persistent PL fatigue phenomena⁷ all PL power laws have been measured in a time domain of seconds using a single spectrometer combined with a Si charge-coupled device. The PL lifetime is measured with a fast photomultiplier and a storage oscilloscope. All experiments are performed at $T=4.2$ K.

Assuming that under optical excitation the only possible nanocrystal occupation states are N_0 (the number of unoccupied nanocrystals), N_1 (containing one $e-h$ pair) and N_2 (containing two $e-h$ pairs), we obtain the system of states filling equations:

$$\begin{aligned} \dot{N}_0 &= -N_0 I_{\text{ex}} \sigma(\hbar\omega_{\text{ex}}, \hbar\omega_{\text{det}}) + \frac{N_1}{\tau_R(\hbar\omega_{\text{det}})}, \\ \dot{N}_1 &= N_0 I_{\text{ex}} \sigma(\hbar\omega_{\text{ex}}, \hbar\omega_{\text{det}}) - N_1 I_{\text{ex}} \sigma(\hbar\omega_{\text{ex}}, \hbar\omega_{\text{det}}) \\ &\quad - \frac{N_1}{\tau_R(\hbar\omega_{\text{det}})} + \frac{N_2}{\tau_A}, \\ \dot{N}_2 &= N_1 I_{\text{ex}} \sigma(\hbar\omega_{\text{ex}}, \hbar\omega_{\text{det}}) - \frac{N_2}{\tau_A}, \\ N_T &= N_0 + N_1 + N_2. \end{aligned} \quad (1)$$

Here N_T is the total number of luminescing nanocrystals, $\tau_R(\hbar\omega_{\text{det}})$ is the radiative lifetime of an $e-h$ pair, $\sigma(\hbar\omega_{\text{ex}}, \hbar\omega_{\text{det}})$ is the cross section for absorption of photons with an energy $\hbar\omega_{\text{ex}}$ in a nanocrystal with a ‘‘gap’’ $\hbar\omega_{\text{det}}$, and I_{ex} is the intensity of the exciting light expressed in an areal flux of incident photons. We assume that the Auger recombination time τ_A is much shorter^{4,5} than $\tau_R(\hbar\omega_{\text{det}})$ and that the presence of one $e-h$ pair in a nanocrystal does not significantly modify the absorption of the second one. We

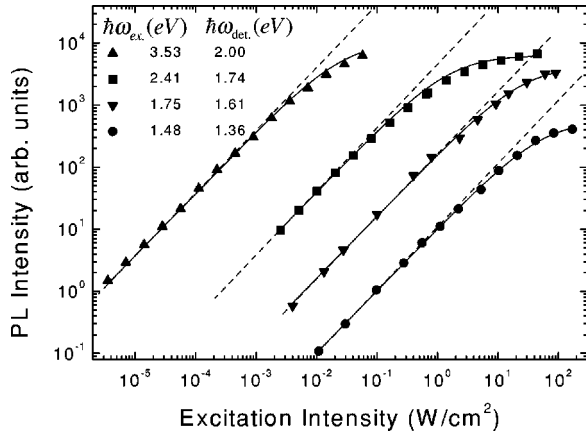


FIG. 1. The dependencies of the PL intensity versus excitation intensity. Excitation and detection energies are indicated. Solid lines are fits according to Eq. (2). Dashed lines are linear power laws. The data sets are arbitrarily scaled for clarity.

neglect here the fact that light emission at $\hbar\omega_{\text{det}}$ originates from crystallites with gaps $\hbar\omega_{\text{det}}$ (via a no-phonon process) and $\hbar\omega_{\text{det}} + \hbar\Omega_{\text{phonon}}$ (via a phonon-assisted emission).^{3,8}

The PL intensity power law according to these equations is

$$I_{\text{PL}} = \frac{N_1}{\tau_R(\hbar\omega_{\text{det}})} = \frac{N_T \sigma(\hbar\omega_{\text{ex}}, \hbar\omega_{\text{det}}) I_{\text{ex}}}{1 + \sigma(\hbar\omega_{\text{ex}}, \hbar\omega_{\text{det}}) I_{\text{ex}} \tau_R(\hbar\omega_{\text{det}})}. \quad (2)$$

One can see that at low excitation intensities, when $\sigma(\hbar\omega_{\text{ex}}, \hbar\omega_{\text{det}}) I_{\text{ex}} \tau_R(\hbar\omega_{\text{det}}) \ll 1$ the PL intensity is a linear function of the excitation intensity while at high excitation levels the PL saturation behavior is expected. The maximal emissivity of nanocrystals is limited by one photon per nanocrystal per $e-h$ pair lifetime. Since the areal photon flux and the radiative time of $e-h$ pairs can be experimentally measured, there is only one parameter that defines the PL power dependence: the absorption cross section $\sigma(\hbar\omega_{\text{ex}}, \hbar\omega_{\text{det}})$.

In Fig. 1 we show some examples of the measured PL intensities at different excitation and detection energies as a function of the excitation intensity. At low excitation levels the PL intensity is a linear function of the exciting light power while at higher intensities the PL saturation regime occurs. The excitation levels at which a transition to the PL saturation is observed is extremely sensitive to the excitation energy. The solid lines represent fits according to the steady-state solution of equations with only one adjustable parameter $\sigma(\hbar\omega_{\text{ex}}, \hbar\omega_{\text{det}})$. We found that all experimental curves can be fitted very precisely at all excitation and detection energies used.

The verification of our model comes from studies of the PL kinetics under a steplike excitation function. The temporal solution of the state-filling equations

$$I_{\text{PL}}(t) = I_{\text{cw}} \left\{ 1 - \exp \left[-t \left(\frac{1}{\tau_R(\hbar\omega_{\text{det}})} + \sigma(\hbar\omega_{\text{ex}}, \hbar\omega_{\text{det}}) I_{\text{ex}} \right) \right] \right\} \quad (3)$$

predicts that the transient time to the PL steady-state conditions (I_{cw}) has to be extremely excitation power dependent and is smaller for higher pumping rate.

In Fig. 2 we show the temporal kinetics of the PL at

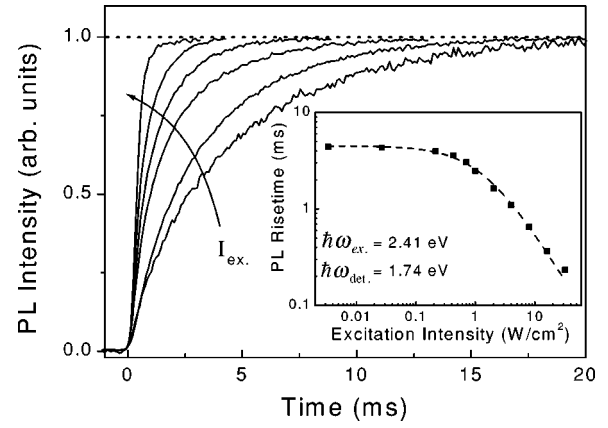


FIG. 2. Temporal response of the PL on a steplike optical excitation. $T = 4.2$ K, $\hbar\omega_{\text{ex}} = 2.41$ eV, $\hbar\omega_{\text{det}} = 1.74$ eV. Excitation intensities are 0.003, 0.7, 2, 4, 8, and 32 W/cm^2 , respectively. Dotted line shows the cw PL level. Inset: the PL rise time as a function of the excitation intensity. Dashed line shows the fit according to the time-dependent solution of the state-filling equations written in the text.

different excitation intensities. The onset of the excitation step is at the time $t = 0$. At very high intensity the time evolution of the PL practically coincides with the excitation onset while at low excitation level the rise time is identical to the PL decay time. The decay time is found to be almost independent on the excitation intensity. This arises from the fact that all Auger events take place only during the illumination period while after switching off the exciting light the remaining $e-h$ pairs recombine with the constant decay time $\tau_R(\hbar\omega_{\text{det}})$. In inset of Fig. 2 we show the values of the rise time versus excitation intensity. The dashed line is a theoretical fit according to Eq. (3) with the same value of $\sigma(\hbar\omega_{\text{ex}}, \hbar\omega_{\text{det}})$ that has been used to fit the PL power law at the same excitation and detection energies. We found that by using only one fitting parameter $\sigma(\hbar\omega_{\text{ex}}, \hbar\omega_{\text{det}})$, it is possible to describe very accurately both the PL power law and transient time dependence at any excitation and detection energy used.

In general, the absorption cross section $\sigma(\hbar\omega_{\text{ex}}, \hbar\omega_{\text{det}})$ is a function of $\hbar\omega_{\text{ex}} - \hbar\omega_{\text{det}}$ and $\hbar\omega_{\text{ex}}$. In indirect semiconductors the density of electronic states is proportional to $(\hbar\omega_{\text{ex}} - \hbar\omega_{\text{gap}})^2$, where $\hbar\omega_{\text{gap}}$ is the fundamental band-gap energy.⁹ PLE studies have shown that this is the case for Si nanocrystals.^{6,10} Therefore at each specific detection energy $\hbar\omega_{\text{det}} = \hbar\omega_{\text{gap}}$ the magnitude of σ has to be a strong function of $\hbar\omega_{\text{ex}} - \hbar\omega_{\text{gap}}$. At the same time at larger $\hbar\omega_{\text{ex}}$ the oscillator strength of the optical transitions is strongly enhanced mainly due to the breakdown of the \mathbf{k} -conservation rule.^{11,8} Finally, $\sigma(\hbar\omega_{\text{ex}}, \hbar\omega_{\text{det}})$ is affected by the reduction of the density of electronic states towards higher confinement energy.

In Fig. 3 we show the values of $\sigma(\hbar\omega_{\text{ex}}, \hbar\omega_{\text{det}})$ deduced according to the procedure described above in a wide range of $\hbar\omega_{\text{ex}}$ and $\hbar\omega_{\text{det}}$. Depending on both values, $\sigma(\hbar\omega_{\text{ex}}, \hbar\omega_{\text{det}})$ varies over nearly 5 orders of magnitude from 10^{-19} cm^2 under low-energy resonant excitation to 10^{-14} cm^2 under excitation above the bulk Si direct band gap. At resonant excitation the value of $\sigma(\hbar\omega_{\text{det}})$ is a very strong function of $\hbar\omega_{\text{ex}} - \hbar\omega_{\text{det}}$. The energy dependence of

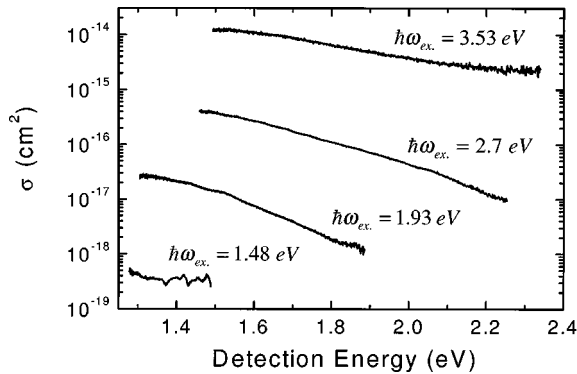


FIG. 3. Absorption cross sections of Si nanocrystals versus detection energy. Excitation energies are indicated in the figure.

$\sigma(\hbar\omega_{\text{ex}}, \hbar\omega_{\text{det}})$ reflects the increase in the density of electronic states with increasing energy above the “gap” and, to a large extent, follows the spectral dependence of the absorption coefficient of bulk Si.¹² At high energy of excitation ($\hbar\omega_{\text{ex}} = 3.53$ eV) these values vary significantly weaker due to a large energetic distance between $\hbar\omega_{\text{ex}}$ and $\hbar\omega_{\text{det}}$.

To separate contributions of the oscillator strength of optical transitions and the density of states to the value of σ it is necessary to compare those for different $\hbar\omega_{\text{ex}}$ simultaneously, keeping $\hbar\omega_{\text{ex}} - \hbar\omega_{\text{det}}$ fixed. The lifetime of the allowed exciton state and therefore its oscillator strength in the considered emission range vary over one order of magnitude.³ Nevertheless the values of $\sigma(\hbar\omega_{\text{ex}} = 1.93$ eV, $\hbar\omega_{\text{ex}} - \hbar\omega_{\text{det}}$) are even higher than those for ($\hbar\omega_{\text{ex}} = 2.7$ eV, $\hbar\omega_{\text{ex}} - \hbar\omega_{\text{det}}$) under equal energetic distance between excitation and detection. Combining these two observations we conclude that the density of electronic states is significantly reduced towards higher confinement energies. We believe that the most natural reason for that is an increased spacing between quantized energy levels in smaller nanocrystals.

The variation of σ at fixed $\hbar\omega_{\text{ex}}$ is a very strong function of $\hbar\omega_{\text{ex}} - \hbar\omega_{\text{det}}$. It is similar to the spectral dependence of the absorption coefficient¹² of bulk Si and reflects the indirect nature of optical transitions in Si nanocrystals. However, the relative variation of $\sigma(\hbar\omega_{\text{ex}} - \hbar\omega_{\text{det}})$ due to a reduction

of the density of states is significantly smaller than in bulk Si. From the comparison of $\sigma(\hbar\omega_{\text{ex}} - \hbar\omega_{\text{det}})$ with the spectral dependence of the bulk Si absorption coefficient in the vicinity of the fundamental gap we estimate for $\hbar\omega_{\text{ex}} = 1.93$ eV the reduction factor is of the order of 5. Only at high excitation energy (excitation in a high density of states region) does the spectral dependence of σ become almost identical to that of the absorption coefficient of bulk Si.

Up to now we neglected the fact that light emission at certain $\hbar\omega_{\text{det}}$ originates from crystallites with gaps $\hbar\omega_{\text{det}}$ (via a no-phonon process) and $\hbar\omega_{\text{det}} + \hbar\Omega_{\text{phonon}}$ (via a phonon-assisted emission).^{3,8} This is a good approximation under high excitation energy. For resonant excitation, however, the peak structure of the PL spectra⁸ complicates the evaluation procedure described above. Each phonon-assisted PL replica represents the contribution of phonon-assisted recombination of excitons excited via electronic states having low density and a certain oscillator strength. These replicas are superimposed on a background of the PL excited via no-phonon transitions between states having higher density and other oscillator strengths. This results in a fine structure of the spectral dependence of σ and therefore the evaluation procedure described above is not straightforward (see Fig. 3, $\hbar\omega_{\text{ex}} = 1.48$ eV).

We believe that our measurements have important implications for the understanding of fundamental optical properties of Si nanocrystals. First, a comparison between the porous Si “absorption edge” and PL peak position has been widely discussed in the literature (see, for instance, Refs. 13 and 14). An experimentally found variation of $\sigma(\hbar\omega_{\text{ex}}, \hbar\omega_{\text{det}})$ within 5 orders of magnitude shows that for indirect-gap nanocrystal assemblies such a correlation obviously can never be observed. Second, it shows that there is no Stokes shift between absorbing and luminescing states. The usually observed significant Stokes shift between the “absorption edge” and the PL band peak energy is an artificial fact arising from a very small density of electronic states in the vicinity of the energy of the exciton ground state. Third, it naturally explains the inefficiency of resonantly excited PL from porous silicon.¹⁵

Finally, the same studies could be successfully used to explore the optical properties of other nanocrystal assemblies.

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