

Temperature-induced crossover between bright and dark exciton emission in silicon nanoparticles

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Abstract – The excitonic fine structure of silicon nanoparticles is investigated by time-resolved and magnetic-field-dependent photoluminescence. The results are analyzed using the common model of an excitonic fine structure consisting of a bright and a dark exciton. We find that the radiative recombination rates of both excitons differ only by a factor of eight. Therefore, we observe a thermal crossover in the character of the emission from bright-exciton-like to dark-exciton-like. The validity of our model is further supported by magnetic-field-dependent measurements, in which effects of state mixing are observed.

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Introduction. – Silicon, which is the technologically most relevant semiconductor, has long been considered to be of little interest for optoelectronic devices. However, since the demonstration of efficient light emission from porous silicon by Canham *et al.* [1], nanostructured silicon (nano-silicon), especially nanoparticles, have drawn increasing attention as an optically active material. Extensive and in-depth investigations have been carried out in order to understand the origin of nano-silicon luminescence and to realize silicon-based optoelectronic devices. A complete understanding of the intricate excitonic structure in nano-silicon, however, is still missing. In particular, the exciton fine structure and the formation of a “dark exciton” are subjects of intense research in order to understand how they influence the photoluminescence properties of nano-silicon.

In this letter, we investigate the excitonic fine structure of silicon nanoparticles as a function of temperature, particle size and magnetic field. We observe that due to the thermal distribution a crossover between the bright and dark exciton recombination occurs. Surprisingly, we find that the radiative recombination rate from the dark exciton is only a factor of 8 lower than the bright exciton recombination rate. The results are discussed within the common model of the excitonic fine structure in nano-silicon. The interpretation is further substantiated

by magnetic-field-dependent data, which show that the photoluminescence life times can be tuned by mixing of the dark and bright exciton states.

Experimental. – The silicon nanoparticles are synthesized in a low-pressure microwave reactor. Silane (SiH_4) as a precursor gas, together with H_2 and Ar flow through a microwave resonator in which the silicon nanoparticles are formed by microwave-assisted decomposition of silane. Details of the reactor and the process parameters can be found in ref. [2].

The photoluminescence (PL) measurements are carried out using a Czerny-Turner monochromator (focal length $f = 500$ mm) with a LN_2 -cooled charge-coupled device as a detector. As an excitation source, a Nd:YVO₄ laser operated at $\lambda = 532$ nm, is used. The sample is mounted in a continuous-flow liquid-helium cryostat. For the time-resolved measurements, the laser is chopped by an acousto-optical modulator (AOM) and the decay of the PL is measured using a single photon counting module (Si-APD). The temporal resolution is 64 ns.

Results and discussion. – Typical PL spectra of the silicon nanoparticles for three different temperatures are shown in the inset of fig. 1(a). The spectra are obtained from an ensemble of particles with a mean diameter of $d \approx 4.8$ nm and a log-normal size distribution [2–4]. As the emission wavelength scales with the particle size,

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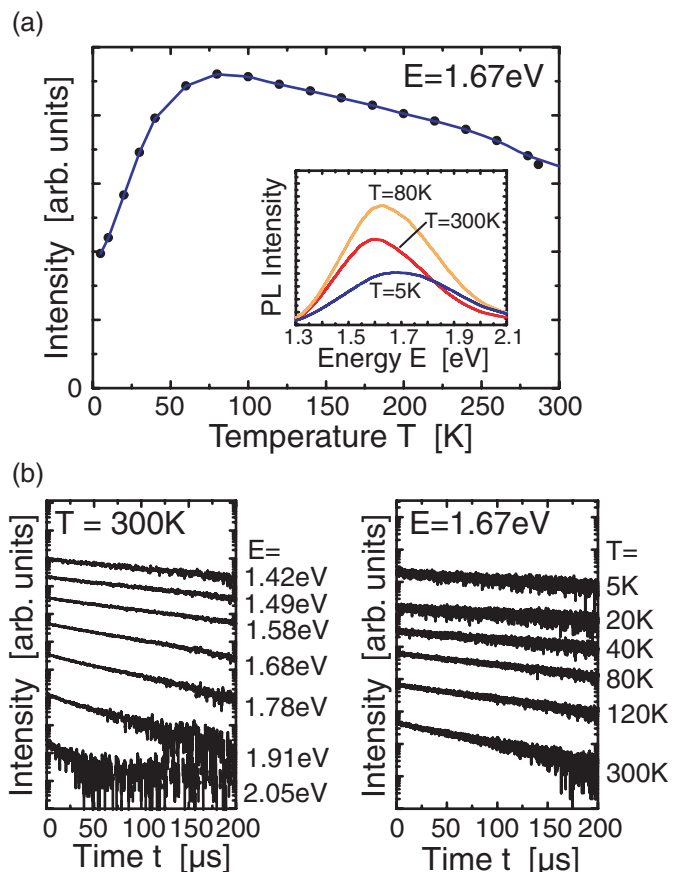


Fig. 1: (Color online) (a) Intensity of the PL as a function of temperature. Maximum intensity is found at $T \approx 80$ K. The inset shows the PL spectra for three different temperatures. (b) Decay of the intensity as a function of time for $T = 300$ K and several PL energies (left) and for $E = 1.67$ eV and different sample temperatures (right).

the spectra are inhomogeneously broadened (FWHM ≈ 430 meV). Both peak energy and peak intensity vary with the sample temperature.

The photoluminescence intensity as a function of temperature is shown in fig. 1(a). Starting at room temperature and lowering the sample temperature, the PL intensity first increases until it reaches its maximum at $T = 80$ K. As the temperature is further decreased, the intensity declines rapidly. However, even for the lowest temperature studied here ($T = 5$ K), no quenching of the PL is observed.

This non-monotonic behavior is in contrast to other nanoparticle systems such as CdSe [5], ZnSe/ZnS [6] or InAs [7], where a continuous increase of the PL intensity with decreasing temperature is observed. For nano-silicon, however, a similar characteristic has been observed by other authors, for systems with completely different fabrication routes [8–12]. This gives us confidence that the temperature dependence in fig. 1(a) is indeed an intrinsic property of the nanoparticles. It should also

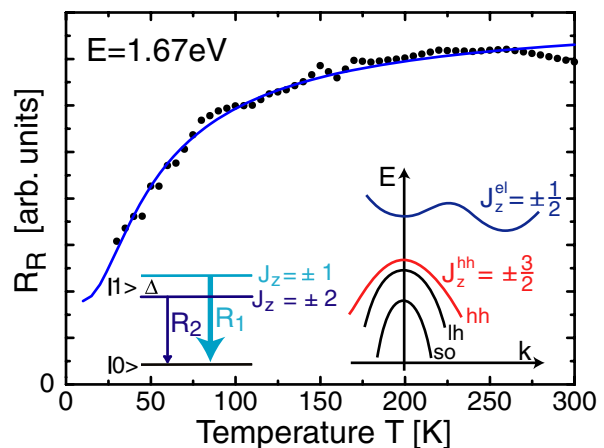


Fig. 2: (Color online) Radiative recombination rate R_R as a function of temperature (data points) and a fit using eq. (1) (solid line). The left inset is a sketch of the excitonic fine structure. The inset on the right shows the electronic bandstructure of nano-silicon. The spin-orbit band (so) as well as the light-hole band (lh) are split-off from the heavy-hole band (hh). The degeneracy is lifted by spin-orbit interaction and quantum confinement.

be pointed out that the PL time dependence is a single exponential for all energies and temperatures investigated (see fig. 1(b)). This shows that spurious effects from carrier diffusion in disordered systems [13,14], which would lead to a stretched exponential, can be neglected in our experiment.

An explanation for the non-monotonic PL temperature dependence was first proposed by Calcott *et al.*, who assumed an exchange interaction-induced splitting of the excitonic levels [15]. The upper and lower state exhibit different radiative constants R_1 and R_2 , respectively, with $R_1 \gg R_2$. The decrease of the PL intensity at low temperatures can then be explained by a freeze out of the upper state recombination (see also left inset in fig. 2). This model was used by many other groups to explain the temperature dependence of nano-silicon photoluminescence. Some disagreement exists, however, regarding the multiplicity of the states 1 and 2, which is given by the respective total exciton spin. As sketched schematically in the right inset of fig. 2, the highest valence band state is the heavy hole (hh), with a total angular momentum $J_z^{\text{hh}} = \pm 3/2$. The electron state is characterized by $J_z^{\text{electron}} = \pm 1/2$.

Therefore, the possible excitons can have total angular momenta of $J_z^{\text{exc}} = +2$ ($\uparrow\uparrow$), $J_z^{\text{exc}} = -2$ ($\downarrow\downarrow$), $J_z^{\text{exc}} = +1$ ($\uparrow\downarrow$) and $J_z^{\text{exc}} = -1$ ($\downarrow\uparrow$).

As calculated by Reboredo *et al.* [16] and in agreement with the experimental evidence [17], the $J_z^{\text{exc}} = \pm 1$ states are higher in energy than the $J_z^{\text{exc}} = \pm 2$ states (splitting Δ , see also inset in fig. 2). Since radiative recombination from the $J_z^{\text{exc}} = \pm 2$ states is dipole forbidden, they are generally labelled “dark” excitons, while the $J_z^{\text{exc}} = \pm 1$ states are called “bright”. The existence of these bright and dark

excitonic levels and their respective angular momentum was confirmed experimentally by Diener *et al.* [17] by one- and two-photon absorption measurements.

To obtain the total radiative transition rate R_R for a temperature T , we follow the approach of Brongersma *et al.* and calculate the weighted average of the two rates R_1 and R_2 , taking into account the thermal occupation of the states and their degeneracy [8,18]. Then, R_R can be written as

$$R_R = \frac{2R_2 + 2R_1 \cdot \exp\left(-\frac{\Delta}{k_b T}\right)}{2 + 2 \exp\left(-\frac{\Delta}{k_b T}\right)}. \quad (1)$$

The temperature dependence of R_R can be obtained from the PL decay measurements together with the intensity of the PL as a function of the temperature $I(T)$ [8]. $R_R(T)$ is plotted in fig. 2, which also shows a fit to the data using eq. (1).

The good agreement between fit and data, together with the fact that we observe only a single exponential decay, allows us to accurately determine $R_1/R_2 = 8$ and $\Delta = 5.8$ meV.

The splitting is mainly determined by the short-range exchange interaction, which is obtained from the probability of the electron and the hole being at the same position [19]:

$$\Delta \approx E_{ex} = E_{ex}^{bulk} \cdot \pi a_B^3 \cdot \int d^3r |\Psi_{exc}(\vec{r}_e = \vec{r}_h)|. \quad (2)$$

Here, E_{ex}^{bulk} is the bulk exchange energy, Ψ_{ex} is the wavefunction of the confined exciton and a_B is the bulk exciton Bohr radius.

For the present system the observed value of $\Delta = 5.8$ meV is in good agreement with theoretical predictions [20]. The value found here is higher than the exciton exchange splitting in bulk silicon (140 μ eV [21]). The reason for the enhancement of the exchange energy is quantum confinement, which leads to a localization of electron and hole wave function. The increase of the exchange energy with decreasing particle size has also been demonstrated experimentally by Brongersma *et al.* [8].

In view of the exciton model outlined above, the ratio between R_1 and R_2 is surprisingly low. As the dark exciton with $J_z^{\text{exc}} = \pm 2$ should not show any luminescence, the ratio R_1/R_2 is expected to be infinite.

To explain the fact that both recombination rates are of such similar magnitude, one has to take into account the indirect nature of the electronic bandgap of silicon. Optical recombination in silicon is a second-order process as it requires the involvement of an additional phonon to fulfill linear momentum conservation. The fact that we see in our experiments such similar recombination rates suggests that the conservation of both, linear and angular momentum is provided by the phonon bath with similar probabilities. For CdSe nanoparticles, angular momentum conservation by phonons has already been proposed by Efros *et al.* and Nirmal *et al.* [22,23].

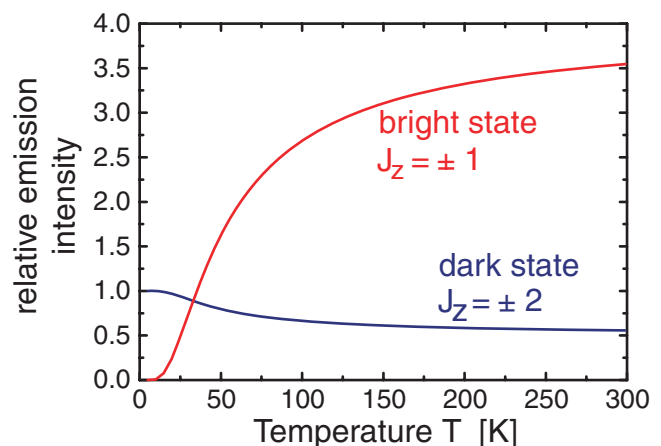


Fig. 3: (Color online) Normalized total recombination rate of the bright and dark state. Below $T = 35$ K more photons are emitted from the dark state than from the bright state.

Beside the phonon-assisted transitions also phononless transitions for silicon nanoparticles have been reported [24]. For these transitions the argument drawn before does not work. However, these transitions are much weaker than the phonon-assisted transitions.

Another important aspect is that in the silicon nanoparticles studied here, for the excitonic system a thermal equilibrium is reached by spin-scattering processes before the excitons decay radiatively or non-radiatively. For other nanoparticle systems, which exhibit an excitonic fine structure (such as CdSe and InAs [19,22]), the radiative recombination is completely masked by the fast bright exciton luminescence [25] in these systems and non-radiative processes.

It should be pointed out that the isolated silicon nanoparticles studied in this work form an ideal system to investigate the excitonic fine structure. In other systems, such as the nanocrystals used in [8] or [15], the recombination processes are subject to strong disorder, leading to a stretched exponential decay. In our particles, we observe a single exponential decay due to the high crystalline purity of the particles. This allows to determine the PL decay τ_{PL} unambiguously.

It is worth noting that the radiative recombination from the $J_z^{\text{exc}} = \pm 2$ states can directly be inferred from the low-temperature luminescence. If the transition from the dark exciton were forbidden, the intensity would quench for $T \rightarrow 0$ K.

Using the above model, the relative intensities from the dark- and the bright-state recombination can be calculated. The results are shown in fig. 3. At high temperatures, the PL emission is dominated by emission from the energetically higher bright state. As the temperature is decreased, the relative occupation of the dark state increases, and the emission character is more and more dominated by the emission from the dark state. The crossover point, below which more photons are emitted

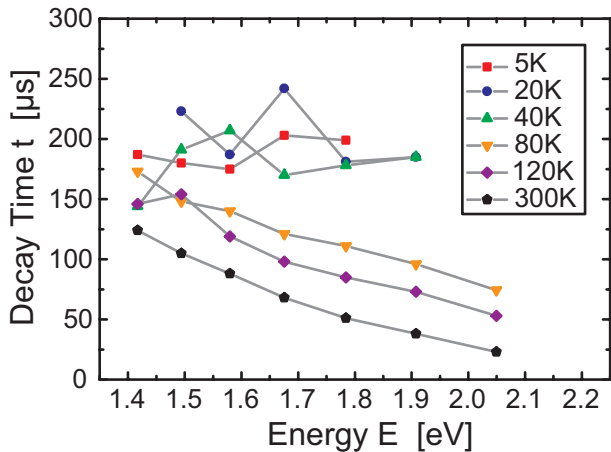


Fig. 4: (Color online) Decay time τ as a function of the emission energy for six different temperatures.

from the dark state than from the bright state is determined to be $T \approx 35$ K.

Our findings thus show, that there is a thermal crossover in the luminescence of silicon nanoparticles from dark-exciton to bright-exciton emission. This is the reason for the nonmonotonic temperature dependence of the PL intensity observed for silicon nanoparticles.

Figure 4 shows the decay time τ as a function of the emission energy E for various temperatures T . It can well be seen that for higher temperatures ($80 \text{ K} \leq T \leq 300 \text{ K}$) the decay time τ decreases with increasing emission energy. As the emission energy inversely scales with the particle diameter, this means that smaller particles exhibit shorter decay times. This is reasonable because in smaller particles the phonon-electron interaction is increased which scales inversely to the volume of the nanoparticles [24] and makes the phonon-assisted transitions more frequent. For the no-phonon transitions, the overlap of the electron and hole wave function in \vec{k} -space is relevant. This overlap scales with $(1/L)^6$ and is therefore also increased for small particles [26].

For lower temperatures, however, the decay time τ seems to be unaffected by the particle size. On the one hand, this behavior again indicates that the luminescence not just freezes out but indeed changes its character as the temperature is decreased. On the other hand, it is somewhat puzzling, since the arguments regarding the increased phonon-electron interaction and wave function overlap should apply to both bright and dark excitons. A possible explanation is a non-radiative decay time R_{NR} , which is longer than R_1 but shorter than R_2 . Then the PL lifetime would be limited by R_{NR} and the size effect would be masked. It should be stressed that the nonradiative decay processes are not responsible for the observed temperature dependence of the intensity $I(T)$. A quenching of nonradiative recombination centers at low temperatures can only lead to an enhancement

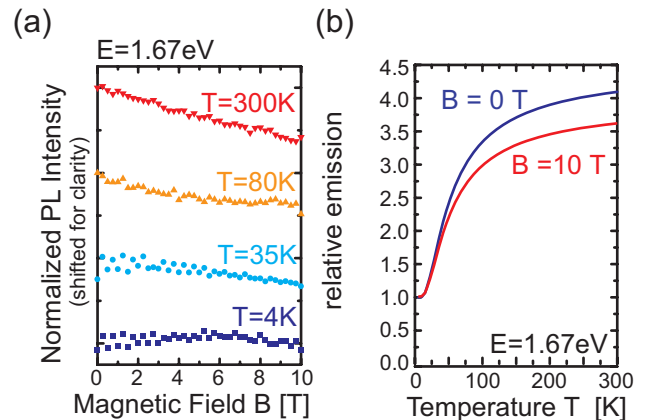


Fig. 5: (Color online) (a) Normalized PL intensity as a function of magnetic field. (b) Calculated normalized recombination rate from dark and bright excitons for $B = 0$ T and $B = 10$ T.

of the optical emission, which is not observed in the experiment. Instead, a decrease, both in intensity and decay rate with decreasing temperature is observed.

To further substantiate our findings and to investigate whether the exciton nature can be changed by parameters other than temperature, we have investigated the magnetic-field dependence of the PL. The normalized PL intensity as a function of the magnetic field is shown in fig. 5(a) for four characteristic temperatures. For $T = 300$ K, the intensity falls with increasing magnetic field. When the temperature is reduced to $T = 80$ K and $T = 35$ K, this effect becomes less pronounced, and at $T = 5$ K, almost no change in intensity is detectable.

To analyze our results, we have checked the influence of a Zeeman-splitting of the exciton levels. The external magnetic field B induces a Zeeman splitting of the excitonic levels with an energy shift of $\Delta E = g \cdot \mu_B \cdot J_z^{\text{exc}} \cdot B$. With this shift, the $J_z^{\text{exc}} = -2$ excitonic state becomes the lowest-lying state and the energetic differences to the other states increase with increasing magnetic field. A Boltzmann distribution over all four split states would therefore result in a decrease of the recombination rate. The influence of the Zeeman effect on the excitonic fine-structure states, however, is too small to be relevant in the present ensemble measurements. Using a Zeeman splitting of approximately $120 \mu\text{eV/T}$ [27,28], we only find a decrease of the PL intensity of about 0.1% at $T = 300$ K in a theoretical estimate.

Another magnetic-field-driven mechanism that affects the recombination rates is mixing of the dark $|\pm 2\rangle$ and bright $|\pm 1\rangle$ exciton states [22]. The energetically lower-lying mixed states

$$N_j[(|+2\rangle \mp |-2\rangle) + i\beta_j (|+1\rangle \pm |-1\rangle)] \quad (3)$$

gain some bright character and the energetically higher-lying mixed states

$$N_j[(|+1\rangle \mp |-1\rangle) + i\beta_j (|+2\rangle \pm |-2\rangle)] \quad (4)$$

gain some dark character [20,29,30]. Thus, the optical transition rate of the dark state increases whereas the recombination from the bright state is slightly suppressed [22].

Figure 5(b) shows the influence of the magnetic field to the total relative emission intensity calculated using our model. From our magneto-PL measurements we find that the emission from the bright state changes approximately 10 percent whereas there is only a slight increase of the dark-state emission.

In summary, we have investigated the excitonic fine structure of silicon nanoparticles using temperature-dependent, time-resolved and magnetic-field-dependent photoluminescence. We find a thermal crossover between the dark- and bright-exciton luminescence at $T \approx 35$ K. In time-resolved experiments we are able to show that both states exhibit a clearly different recombination behavior as a function of particle size, which supports the fact that the temperature determines the state from which luminescence is observed. The magnetic-field-dependent results presented demonstrate that the two states are split by exchange interaction. For temperatures above the crossover, the dark and the bright exciton states can be mixed using the magnetic field. This offers a potential opportunity to intentionally manipulate the different states, which may be of great interest for quantum information devices based on Si nanoparticles.

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