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Thermally Activated Emission from Direct Bandgap-Like Silicon Quantum Dots

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Due to the covalent character of silicon-carbon (Si-C) bond, C-linked molecules on the silicon quantum dot (SiQD) surface lead to dramatic changes in wavefunctions of the excited electron-hole pairs. Some of the optical transitions are strongly modified and attain direct bandgap-like character, giving rise to bright phonon-less fast decaying emission, while many other transitions keep their typical indirect bandgap character. It appears that in C-terminated SiQDs, with diameter larger than ~2 nm, the most efficient recombination occurs from states slightly above the ground state. This leads to thermal activation of the fast emission, dominating the photoluminescence from these SiQDs. On the other hand, in the smallest SiQDs of less than 2 nm, the lowest excited states have the direct bandgap-like character and therefore their emission becomes gradually dominant at lower temperatures, as indeed supported by our experimental observations.

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Indirect band gap limits optical applications of bulk silicon and silicon nanostructures. Low radiative rate compared to fast nonradiative recombination rate leads to a very low internal quantum efficiency of emission. Therefore in silicon, emission efficiency is much more sensitive to the presence of nonradiative channels than for direct bandgap materials. In order to improve the optical faculty of Si many approaches have been explored, with the most prominent ones being optical doping,^{1,2} nanostructuring³ and a combination of the two.⁴ In particular, SiQDs turn out to offer many opportunities, either in form of oxygen passivated SiQDs⁵ or with customizable organic passivation,⁶⁻¹⁷ achieved via various techniques of chemical synthesis. Apart from excellent photostability and lack of aggregation, organic passivation also leads to intriguing optical properties - visible emission with fast decay,¹⁰⁻¹⁵ not understood for a long time.¹⁶ In Ref. 16, it has been reported that the particular surface chemistry, in combination with quantum confinement, could lead to dramatic improvement of the radiative rate, to a level comparable with those of the direct bandgap materials, such as, e.g., CdSe QDs. In particular, the organic termination of SiQDs enhances the radiative rate up to 10^7 - 10^9 s⁻¹, provided that organic molecules are C-linked and that the presence of oxygen is strictly eliminated. The absorption cross-section at the band edge is also increased, by a factor 10-100, but remains lower than for the direct bandgap materials. The reason is that only some of the optical transitions attain the direct bandgap-like character, while most of them remain indirect bandgap-like. This is confirmed by the anomalous temperature behavior of photoluminescence (PL) spectra and intensity reported in this work.

Experimental

The investigated samples were prepared by wet chemical synthesis.⁸ SiQDs with mean diameter (2.2 ± 0.5) nm, are butyl capped and deposited densely on quartz substrate by drop-casting. Exclusion of oxygen on the SiQD surface was assured by careful synthesis of SiQDs in argon atmosphere. Dense covalently bonded organic layer on the SiQD surfaces assures excellent chemical stability and prevents aggregation. Lack of oxygen on the SiQD surface has been confirmed from optical properties.^{16,17} When non-oxidized, sample exhibits blue-green PL band with nanosecond decay and 10% external quantum efficiency, upon surface passivation with oxygen, we have shown transformation of such PL into microsecond decaying red PL band, which is not observed in the results presented here. Besides that, also Si-O vibration phonon replicas are missing in the single QD PL spectra, whereas Si-C vibration mode is present.¹⁷ More details on the sample preparation and optical properties can be found in

Refs. 8, 16, 17. The PL experiment was performed under 355 nm pulsed excitation (3rd harmonic of Nd:YAG laser, 100 Hz repetition rate, 7 ns pulse duration). The samples were placed in a continuous-flow He-cryostat (Oxford Instruments Optistat CF) and the measurements were taken at temperatures ranging from 4.2 to 290 K. The PL signal was detected by CCD (Hamamatsu S10141-1108S, 200-1100 nm) coupled to a spectrometer (Solar M266). For PL lifetime, the photomultiplier tube (Hamamatsu R9110, 185-900 nm) in time-correlated single-photon-counting mode was used.

Experimental Results

PL emission spectra measured at different temperatures between 4.2 and 290 K are shown in Fig. 1a. The integrated PL intensity (Fig. 1b) drops by a factor ~1.6 within the investigated temperature range. PL spectra show slight blue-shift and broadening on the high energy side. This is shown in detail in Fig. 2, where thermal dependence of the peak position (black) and FWHM (gray) are plotted. The inset of Fig. 2 shows comparison of the normalized PL spectrum measured at 4.2 K (gray) and 290 K (black). Above ~50 K, PL peak shift follows the typical bulk Si dependence of the bandgap energy on temperature $E_g(T) = E_g(0) - a \cdot T^2/(T+b)$, with $E_g(0) = 2.52$ eV and fixed bulk Si values for $a = 4.73 \times 10^{-4}$ eV.K⁻¹ and $b = 636$ K.^{18,19} However below 50 K, PL peak position deviates from the bulk Si dependence and appears to increase linearly with lower temperatures $E_g(T) = E_g'(0) - c \cdot T$, with $E_g'(0) = 2.57$ eV and $c = 9.44 \times 10^{-4}$ eV.K⁻¹. PL lifetime at the peak maxima of ~2.5 eV for temperatures between 4.2 and 290 K shows only a weak temperature dependence (Fig. 3). PL lifetimes are obtained by fitting the signal decay (Fig. 3a, black) with convolution of the system response function (laser pulse and detection temporal resolution) and mono-exponential decay function, exhibiting the minimal χ^2 values.

Discussion

Temperature dependence of the integrated PL intensity as observed in Fig. 1 is not very usual for SiQDs, which typically show PL intensity maximum between 100 and 200 K, such as reported from, e.g., porous silicon²⁰ or sputtered multilayers of SiNCs in SiO₂.²¹ However these, and many other similar reports, have in common microsecond PL lifetimes.⁵ The microsecond lifetime is characteristic for hydrogen- or oxygen-terminated SiQDs. For small QDs (with sizes below ~3 nm), the origin of this typical red microsecond decaying emission from oxygen terminated SiQDs is usually ascribed to recombination from carriers trapped in oxygen related defect states.²² The temperature dependence of PL intensity could then be interpreted in terms of thermal activation from these defect states. However this is not the case

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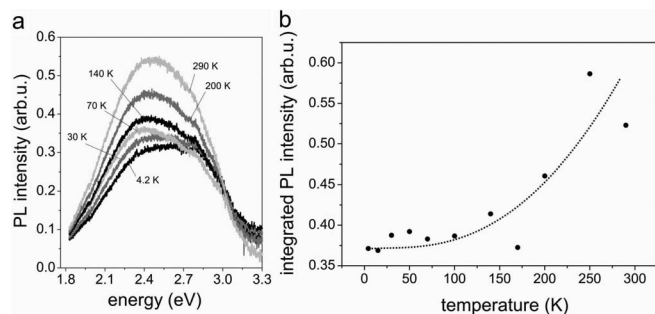


Figure 1. PL at different temperatures: (a) PL emission spectra for selected temperatures; (b) Integrated PL intensity. Dotted line is guide to the eye.

in the present study, where we show temperature dependence of PL from SiQDs terminated by butyl chains (C-linked molecules) with the typical PL lifetime of a few nanoseconds.^{16,17} In past, we have shown that this fast lifetime is not the result of strong nonradiative quenching, which is evidenced by the high external quantum yield of $\sim 10\%$.¹⁶ According to our model,¹⁶ the fast radiative rate can occur as a result of critical modifications in wavefunctions of electron and hole in excited states both in the real and the k-space, caused by the C-atoms linked to the SiQD surface via covalent Si-C bonds. In particular, this leads to the enhanced density of both electron and hole wavefunctions in Γ point of k-space. In result, many of the lowest energy optical transitions attain direct bandgap-like character with large transition rates, and C-linked SiQDs become “direct bandgap-like” material. The rate of phonon-less radiative transitions is enhanced ~ 100 –1000 times when compared to same size hydrogen- or oxygen-terminated SiQD, up to the same level as in direct bandgap materials. Fast radiative rate results in typically nanosecond PL lifetime, observed in various organically terminated SiQDs. However, this effect is very sensitive to the presence of oxygen, minimal amounts of which can slow down the emission back to microseconds.¹⁶

Contrary to oxygen termination, carbon does not limit the spectral tunability of the PL with SiQD size, allowing to obtain emission from near IR to near UV. Here, the size distribution (previously reported in¹⁶) is estimated from the TEM measurements (Fig. 4a), and shows Gaussian profile with mean diameter of (2.2 ± 0.5) nm (Fig. 4b). Fig. 4c shows transition energies and radiative rates calculated for all possible combinations of excited electron-hole states, for SiQD sizes between 1.8 and 2.7 nm. For more details on the tight-binding simulation used here see Ref. 16. The energy of the excited electron-hole pairs are calculated for spherical SiQDs, terminated by hydrogen (black) and methyl group (red). The lowest excited states are marked by orange and blue circles for hydrogen and methyl passivation,

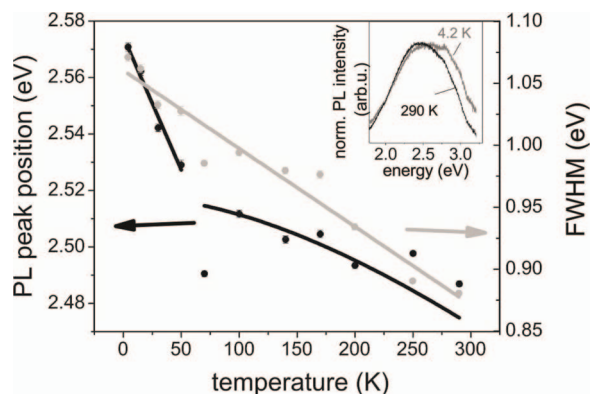


Figure 2. PL peak position (black) and FWHM (gray, line is guide to the eye) at different temperatures. Inset: Normalized PL emission spectra measured at 4.2 K (gray) and 290 K (black).

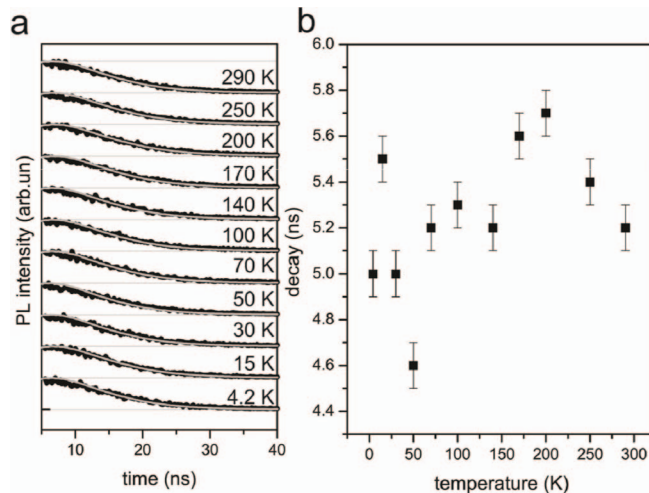


Figure 3. (a) Time dependence of the PL signal at the peak maxima of ~ 2.5 eV (black). Fitting function (gray) is convolution of the measured system response function and mono-exponential decay, giving minimal χ^2 . (b) Thermal dependence of PL lifetimes obtained from the convolution with minimal χ^2 .

respectively. As can be seen in Fig. 4c, the hydrogen terminated SiQDs show low radiative rates (similar to oxygen terminated SiQDs (not shown here)), up to only $\sim 10^6$ s⁻¹. The radiative rates of the several lowest excited states in methyl terminated SiQDs, on the other hand, are much higher.

Now we turn our attention to the possible explanation of temperature dependence observed in our material, taking into account the above mentioned results of the tight-binding calculations. It is instructive to compare our samples with amorphous SiQDs in silicon nitride matrix, which also show nanosecond PL lifetime.²³ Both materials demonstrate nearly identical PL dependence with temperature, which could be an indication of a similar origin – direct bandgap-like transitions with enhanced radiative rates. Interestingly, besides SiQDs, such a dependence has been observed also from Si dislocation loops²⁴ and in amorphous hydrogenated Si,²⁵ where PL intensity change could be caused by quenching. However, these systems are dramatically different from the material in the present study, where PL lifetime (Fig. 3) is nearly independent of temperature. Therefore, nonradiative quenching cannot be behind the observed PL intensity drop. Taking into account our tight-binding model and the transition rates calculated for different sizes of SiQDs (Fig. 4c), we conclude that, on average, the lowest excited states in methyl-terminated SiQDs have slightly lower radiative rates than the states slightly higher in energy. As a result, bright fast decaying emission will be thermally activated. However, we might not be able to actually measure this activation energy due to QD dependent spread in the sample. The reason behind different activation energies could be the broad size distribution of QDs, small variations in their shape, crystallinity or/and surface reconstruction. These will lead to a gradual decrease of the total PL intensity, as indeed confirmed by our experimental observation in Fig. 1b.

We might also notice that in the case of the smallest SiQDs, it is the lowest excited state, which exhibits one of the fastest radiative rates (Fig. 4c). This could explain the observed peak shift dependence. For temperatures above ~ 50 K, PL peak position (i.e. optical bandgap energy) follows precisely the typical bulk Si dependence. However this dependence deviates strongly for temperatures below ~ 50 K. This could be related to the inhibited thermal activation of the higher states with faster radiative rates and therefore dominant emission from more direct bandgap-like smaller SiQDs within the system. We should mention here that similar peak shifting was observed also for SiQDs embedded in silica matrix,²¹ and ascribed to an abrupt switch between the thermally activated excitonic migration amongst all nanocrystals at higher temperatures to the preferential small-to-large nanocrystals

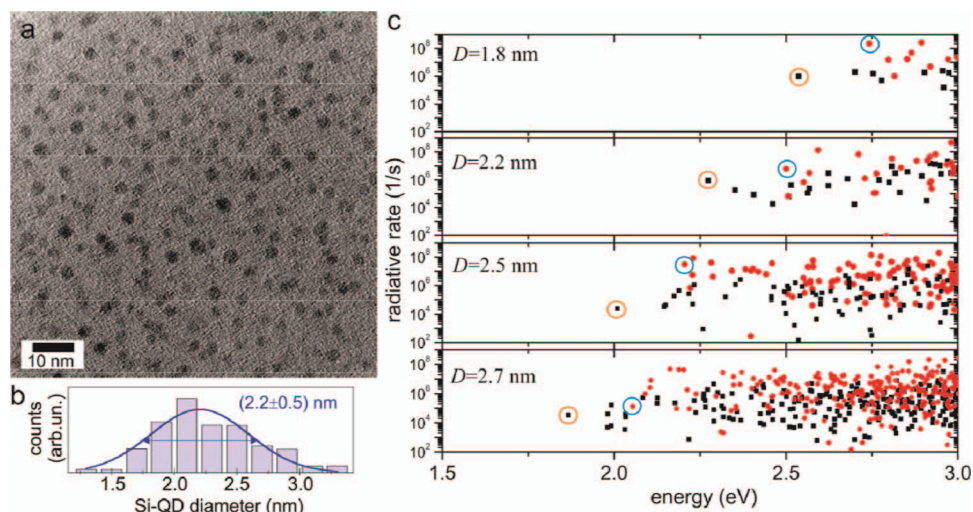


Figure 4. (a) TEM picture of the butyl-capped SiQDs. (b) Size distribution derived from the TEM measurement, fitted by a Gaussian profile of mean diameter (2.2 ± 0.5) nm. (c) Rates of phonon-less optical transitions calculated by tight-binding model for spherical SiQDs terminated by hydrogen (black) and methyl (red) for diameters between 1.8-2.7 nm. The lowest excited states are circled in orange for hydrogen and blue for methyl capping.

migration at lower temperatures. However, excitonic transfer is quite unlikely to happen in the free-standing SiQDs with butyl shells, as investigated here, with the minimal distance between SiQDs surfaces of more than 1.5 nm.

Our interpretation of the peak shift dependence for the lower temperatures is further supported by FWHM dependence (Fig. 2, gray), which gradually increases. This could be again related to the gradually increasing contribution from the smallest SiQDs (or, rather, the decreasing contribution from larger SiQDs), giving rise to a slight blue shift of the PL spectrum (Fig. 1a), and also broadening the ensemble PL spectrum. Similarly, the small decrease of PL lifetime at lower temperatures could be related to an enhanced contribution from the smaller SiQDs on the high energy side of the spectrum.

Conclusions

We have shown that the direct bandgap-like emission from SiQDs ensemble exhibits minor spectral changes with decreasing temperature from 290 to 4.2 K, with only slight enhancement of emission on the high energy spectral wing. Efficiency of the PL from this material is the highest near the room temperature. This is in agreement with the theoretical model, which shows that the lowest excited states in carbon-terminated SiQDs have on average slightly lower radiative rates than the nearest higher excited states. Therefore the direct bandgap-like emission is thermally activated. Due to the broad size distribution, there is no distinct thermal activation energy for the ensemble, but rather an inhomogeneous distribution. For temperatures below ~ 50 K, we have observed also an interesting change in PL peak position, deviating from the typical bulk Si dependence observed at higher temperatures. This together with the temperature dependence of the FWHM, PL lifetime and spectra indicates that when the thermal activation of the fast radiative rate transitions is not possible, emission becomes dominated by smaller SiQDs, which have the higher radiative rates for the lowest excited states.

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