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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.

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 $E_g(T) = E_g(0) - a \cdot T^b + c$, 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 $\chi^2$ 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.3 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
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. 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 ~10%. According to our model, 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, 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 ~106 s⁻¹. The radiative rates of the several lowest excited states in methyl terminated SiQDs, on the other hand, are much higher.
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 increasing 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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References