Effects of inter-nanocrystal distance on luminescence quantum yield in ensembles of Si nanocrystals

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The absolute photoluminescence (PL) quantum yield (QY) of multilayers of Silicon nanocrystals (SiNCs) separated by SiO_2 barriers were thoroughly studied as function of the barrier thickness, excitation wavelength, and temperature. By mastering the plasma-enhanced chemical vapor deposition growth, we produce a series of samples with the same size-distribution of SiNCs but variable interlayer barrier distance. These samples enable us to clearly demonstrate that the increase of barrier thickness from ~1 to larger than 2 nm induces doubling of the PL QY value, which corresponds to the change of number of close neighbors in the hcp structure. The temperature dependence of PL QY suggests that the PL QY changes are due to a thermally activated transport of excitation into non-radiative centers in dark NCs or in the matrix. We estimate that dark NCs represent about 68% of the ensemble of NCs. The PL QY excitation spectra show no significant changes upon changing the barrier thickness and no clear carrier multiplication effects. The dominant effect is the gradual decrease of the PL QY with increasing excitation photon energy. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4904472]

Silicon nanocrystals (SiNCs) embedded in silicon dioxide (SiO_2) exhibited high photoluminescence (PL) quantum yield (QY) of the order of 10%, which is size tunable in the spectral region from orange to near infrared, i.e., about 650–1100 nm.[1] In case of colloidal suspensions of Si nanocrystals (NCs) passivated by different organic molecules (i.e., well separated NCs), the reported external PL QY can exceed 50%.[2,3] Such high QY can be potentially exploited to provide photon conversion, e.g., in lighting and photovoltaic devices.[4]

In this paper, we present a study of inter-nanocrystal distance effects on PL QY of $SiNC/SiO_2$ nanocrystalline multilayers. Our multilayer deposition technique provides unique opportunity to vary the vertical separation of nanocrystal layers while keeping the SiNC size distribution unaffected. We show that the PL QY increases about two-times when increasing the SiO_2 barrier from ~1 nm (or smaller) to thicknesses larger than 2 nm. The PL QY limiting mechanism is apparently related to the thermally activated carrier transport from a nanocrystal to silica defects or defective (dark) nanocrystals. Any effects of carrier multiplication (CM), like the so called space-separated quantum cutting (SSQC) which must be very sensitive to inter-nanocrystal distance,[5] have been found to be negligible in our superlattice samples.

The samples were deposited as alternating layers of silicon-rich silicon oxynitride (SRON; SiO_xN_y) and stoichiometric SiO_2 on fused silica substrates by the plasma-enhanced chemical vapor deposition (PECVD). On top and below the superlattice stack, 10 nm of SiO_2 were deposited as a buffer and capping layer, respectively, (see Fig. 1(a)). The samples were consequently annealed in a quartz tube furnace at 1150 °C for 1 h in high purity N_2 in order to achieve phase separation between Si and SiO_2, i.e., forming SiNCs and passivated by annealing in H_2 at 500 °C. In this study, we present results obtained on one series of *multilayer* (ML) samples and one series of *single-layers* (SLs) (i.e., a thick SRON monolayer without barriers), whose parameters are described in the Table I. The SRON stoichiometry parameter y was almost constant $y = 0.23 \pm 0.02$ in all samples and the x value is specified in Table I. Further details of the sample preparation as well as structural properties of the NC samples are given in our recent paper.[6]

The crucial point of the present study is that we can prepare (by adjusting the stoichiometry parameter x) a thick single-layer sample (S4), which has almost the same shape of PL spectrum as the ML samples (see Fig. 1(b)). This means that the size distribution of SiNCs in the sample S4 and M samples are very similar and the only different parameter is the absence or presence of a SiO_2 barrier with variable thickness.

PL QY was studied using a spectroscope with an integrating sphere (IS) designed and built in our laboratory. Both the set-up and the theoretical basis of the PL QY determination were described in our recent paper.[7] The IS has diameter of 10 cm and the internal coating by the Spectraflex® material. Samples are placed inside IS on one removable port in the position opposite to the excitation port where various light-emitting diodes (LEDs) are mounted to provide the PL excitation. Quite broad excitation range of 280–620 nm can be investigated using a set of more than 40 LEDs with various emission wavelengths. The LED output power is typically less than 1 mW, and it is not focused on the sample. Hence, we work several orders of magnitude below the saturating power density, which is about 1 W/cm^2 at room

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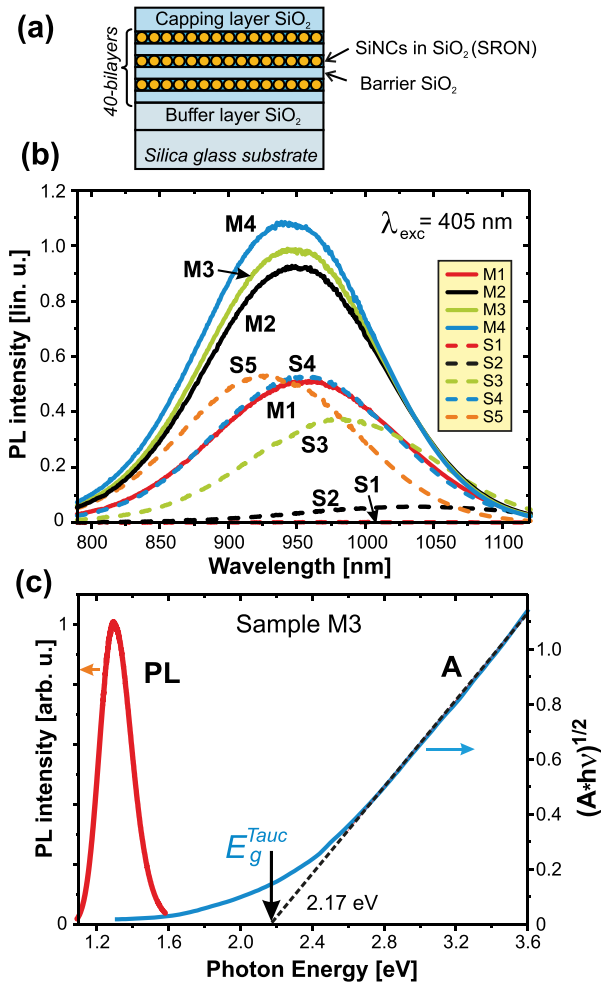

FIG. 1. (a) Schematics of a multilayer sample composition.[23] (b) PL spectra of all ML and SL samples under excitation by the 405-nm LED. (c) PL peak of the sample M3 transformed into the photon energy scale along with its absorbance. The optical gap is estimated from the Tauc plot of absorbance to be around 2.17 eV.

temperature for Si NCs in SiO_2 matrix.[8] The output signal from the IS is collected by a fused-silica fiber bundle and a liquid-nitrogen-cooled CCD camera is used for detection. The spectral sensitivity of the complete apparatus is calibrated over a broad spectral range (300–1100 nm) using two radiation standards (Newport Oriel): a 45 W tungsten halogen lamp (above 400 nm) and a deuterium lamp (below 400 nm). Special attention is paid to avoid stray light effects in the spectrometer.[7]

TABLE I. Description of the sample parameters.

Label	Layer stack	SiO_xN_y thick (nm)	SiO_2 thick (nm)	Stoichiometry x-value
M1	40 bilayers	4.5	1.0	0.93
M2	40 bilayers	4.5	1.6	0.93
M3	40 bilayers	4.5	2.2	0.93
M4	40 bilayers	4.5	2.8	0.93
S1	Single layer	200	…	0.64
S2	Single layer	200	…	0.93
S3	Single layer	200	…	1.05
S4	Single layer	200	…	1.10
S5	Single layer	200	…	1.15

PL QY is determined as a ratio of emitted and absorbed photon rate for the whole investigated sample—it means that we are characterizing the *external quantum yield* (EQY). In case that an ensemble of Si NCs contains some "*dark*" NCs (which absorb but do not emit photons due to the presence of a very fast and efficient non-radiative center), EQY will deviate from the *internal QY* (IQY), which concerns only *bright* NCs (see, e.g., Ref. 9). IQY can be measured in special samples from variation of PL decay rates under different local density of optical states (variable near-field distance from a reflecting surface), which enable to decouple radiative and non-radiative rates. Such experiments were reported only by two groups; while the experiment by Walters *et al.*[10] on implanted SiNCs show QY up to 60% almost independent on wavelength, Miura *et al.*[11] reports different IQY for different sputtered samples reaching up to 100% for well isolated big NCs emitting at wavelengths above 850 nm.

The temperature variation of PL QY was determined indirectly by measuring temperature evolution of PL intensity $I_{PL}(T)$ and absorption cross section (ACS) $\sigma(T)$ of a sample placed in a cryostat and excited by a 405-nm laser whose continuous wave emission was modulated with an acousto-optical modulator (the leading and the trailing edge of the "rectangular" excitation pulses is about 0.1 μs, frequency 900 Hz and the duty cycle is 40%). ACS is calculated from the intensity dependence of the PL onset and decay rate as described, e.g., by Kovalev *et al.*[12] The relative temperature changes of PL QY $\eta(T)$ are then calculated from the following relation:

$$I_{PL}(T) = N\, I_{ex}\, \sigma(T)\, \eta(T), \tag{1}$$

where N is the density of absorbing SiNCs, which is unknown but supposed to be independent of T, and I_{ex} is the excitation photon flux which is kept constant. The relative change of PL QY with temperature $\eta(T) \sim I_{PL}(T)/\sigma(T)$ is converted to absolute PL QY using the room temperature QY value determined with the integrating sphere setup.

The room temperature PL QY for samples M1 to M4 with increasing thickness of SiO_2 barriers is compared with the appropriate single-layer sample S4 in Fig. 2 for two

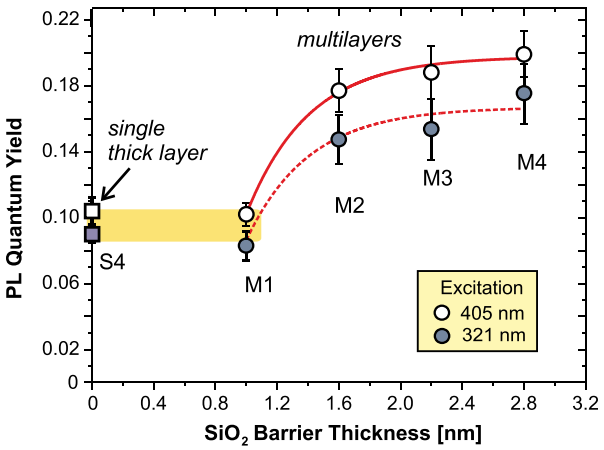

FIG. 2. PL QY (excited at 405 nm and 321 nm) as function of the barrier thickness for ML samples and the S4 sample (the extreme left points). The lines are fitted exponential decays with decreasing barrier thickness.

excitation wavelengths (321 and 405 nm). PL QY clearly grows with increasing barrier thickness. The experimental points can be fitted well by an exponential function with the characteristic distance of 0.4 nm (the barrier thickness for which PL QY drops to 1/e of the maximal value). Interestingly enough, the single-layer sample S4 has almost the same value of PL QY (~10%) as the multilayer sample M3, which has narrow barriers of 1 nm. Therefore, we can state that: (i) The transition from a thick SiNC layer (containing random distributed NCs) to the well separated (>2 nm) stack of confined layers increases the PL QY to approximately double value and (ii) the barrier of 1 nm or thinner becomes ineffective and the PL QY of ML structures is equal to those of the equivalent SL sample.

In the Fig. 1(b) one can see that the decrease of barrier thickness (from the sample M4 to M1) is accompanied by a small red-shift. Such effect can be due to the easier quenching of excitons by neighbor NCs in case of small NCs (there is energy gain when exciton transfers to a bigger NC). At the same time, the presence of barriers alters the distribution of Si excess concentration in multilayer-structures via the diffusion of Si atoms from SRON layers into silica barriers. The diffusion-related loss of Si from the SRON layers must be compensated by a certain increase of the Si excess concentration ($x = 0.93$) in ML samples compared to the SL sample S4 ($x = 1.10$) with equivalent size distribution. Interestingly, for the thermal budget employed, the calculated Si diffusion length in SiO_2 turned out to be about 2 nm. Consequently, the SiO_2 barrier thickness larger than 2 nm reduces the coupling between SiNC layers as the silica barrier contains less excess Si atoms and the barrier height is bigger. However, the nature of the transport (e.g., exciton migration or carrier tunneling) cannot be revealed from data in Fig. 2 due to the NC-size distribution and the barrier control limited to one dimension. Finally, we note that the doubling of PL QY by introducing barriers in the ML structure can be related to the change of number of neighbouring NCs: Supposing that an ensemble of Si NCs can be idealized as the hexagonally close packed (hcp) structure, then a NC has 6 close neighbors in its layer and 3 neighbors in both upper and lower layer. It means that the transition from a thick layer to a monolayer decreases the number of close neighbors to half.

Determination of the PL QY temperature dependence (presented in Fig. 3 for samples M4 and S4) reveals that both ML and SL samples have approximately the same PL QY for T below ~100 K. The PL QY peak of about 32% is around $T = 120$ K from which the PL QY slowly decreases toward lower T. The decrease of PL QY with T increasing above 120 K is more important for the S4 sample and gives hints to the origin of the observed room temperature difference in PL QY. This observation suggests that the QY reducing mechanism is thermally activated, for example, carrier diffusion or dispersive motion of excitons.[8,13] Let us suppose that the peak PL QY of 32%, common for SL and ML samples, corresponds to the situation where no carrier transfer out of a NC is allowed, then the observed EQY is limited by non-radiative losses of excitation in dark NCs and the fraction of bright NCs can be estimated by dividing EQY and IQY. If we suppose that the IQY was 100%,[11] then the

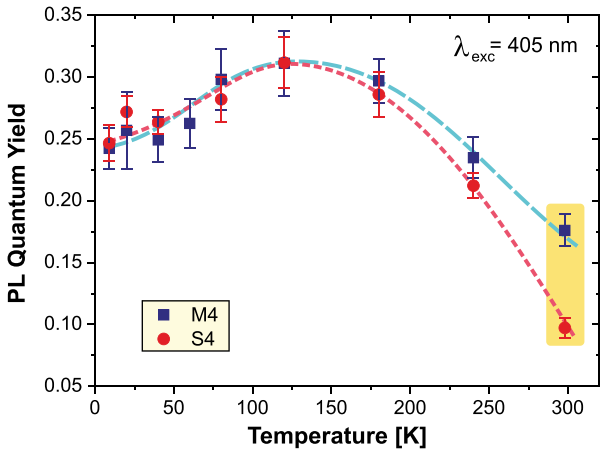

FIG. 3. The temperature changes of PL QY for samples M4 and S4 determined from temperature variation of PL intensity and absorption cross section using the calibration by the PL QY value obtained at room temperature in the integrating sphere setup (highlighted rectangle). The dashed lines are just guides for the eye.

fraction of bright NCs is 0.32. Even if this is a very rough estimation, it is in surprisingly perfect agreement with data published recently by Limpens and Gregorkiewicz[9] who reported 68.5% dark SiNCs in passivated $SiNC/SiO_2$ samples, when taking IQY data from Miura *et al.*[11] as we do. The question of whether the dark NCs are permanently off due to presence of a quenching center (structural defect) or some NCs can switch between bright and dark state is very interesting but cannot be answered using the present PL QY experiments.

Luminescence QY values are usually measured (and reported in literature) for only one excitation wavelength as it is generally supposed that the so called *Kasha-Vavilov* (KV) *rule* is fulfilled. The KV rule (formulated originally for organic chromophores) says that both the luminescence spectral shape and its QY do not depend on the applied excitation wavelength.[14] However, there may be exceptions from the KV rule. In general, for a semiconductor, one tends to expect a decreasing PL QY for excitation addressing higher states above the band gap as more non-radiative paths can be opened for relaxation of hotter carriers. It was also theoretically proposed and experimentally observed that absorption of one high-energy photon can produce two (or more) low energy photons which is called quantum cutting (so giving a IQY above 1 but the energy efficiency below or equal to 1).[15] In organic materials, an analogous process called singlet fission generates two triplet states from one singlet excited state.[16] For bulk semiconductors a high-energy excitation can create multiple excited electrons by impact ionization and the equivalent effect in nanocrystals is called carrier multiplication. However, multiple excitation of a single SiNC is believed to induce fast and efficient quenching by Auger recombination. Despite of this fact, some experiments suggested that high photon energy excitation can improve luminescence yield in closely packed SiNCs and a model of the SSQC was proposed.[5,17]

In order to reveal the possible variation of PL QY with excitation photon energy we measured the PL QY

excitation spectrum using an excitation by a set of LEDs. In Fig. 4, we compare the PL QY excitation spectrum for one ML sample (M3, however, other samples give very similar results) and the single-layer samples S4 and S2 (which has low QY of about 1%). The PL QY of sample M3 varies between 11% and 22% with three characteristic features superposed on the background QY value (light blue line in Fig. 4) slowly decreasing toward higher excitation photon energy:

(a) The rapidly decreasing QY below 2.2 eV is proposed to be due to preferred absorption into defect states. Such absorbing states located close to the optical gap can be sometimes observed with the photo-thermal deflection spectroscopy.[18] Similar decrease of QY at the long-wavelength edge was observed in porous Si.[13,19]

(b) The PL QY peak around 3.3 eV seems to correspond to the direct $\Gamma'_{25} \rightarrow \Gamma_{15}$ absorption, which is about 3.5 eV in bulk Si but shrinks due to the quantum confinement in SiNCs.[20] The mechanism of boosting the radiative recombination probability by such resonant absorption is not clear but a similar QY peak can be found in some literature data on SiNCs (e.g., Refs. 13 and 21) and we observed similar effects also for other materials like PbS nanocrystals (Σ-point transitions) in liquid suspension.

(c) Finally, the increase of QY for excitation with high energy photons (above 3.9 eV) could be related to the onset of CM—generation of two electron-hole pairs after absorption of a single photon.[17] Unfortunately, the experimental uncertainty of QY values for energies above 4 eV is very large - due to the low UV-sensitivity of the CCD[1]—and the observed QY increase is practically within the error bars. The optical band gap of the studied Si NC sample is estimated from the absorption Tauc plot ($(A^*h\nu)^{1/2}$ vs. $h\nu$) where the linear part of the curve is extrapolated and its intersection with the abscissa is found at about 2 eV. Please note that this is a very rough estimate as the "linear" part of the curve is not clearly defined and there is also a possible influence of the NC size distribution, see Fig. 1(c). Then the QY increase at high energy side occurs above the double of the Tauc gap energy. Alternative explanation of the high energy peak is that it is a part of a peak with maximum around 4.4 eV, which is close to the E_2 critical point resonance in Si and was also observed in some PL excitation spectra.[22]

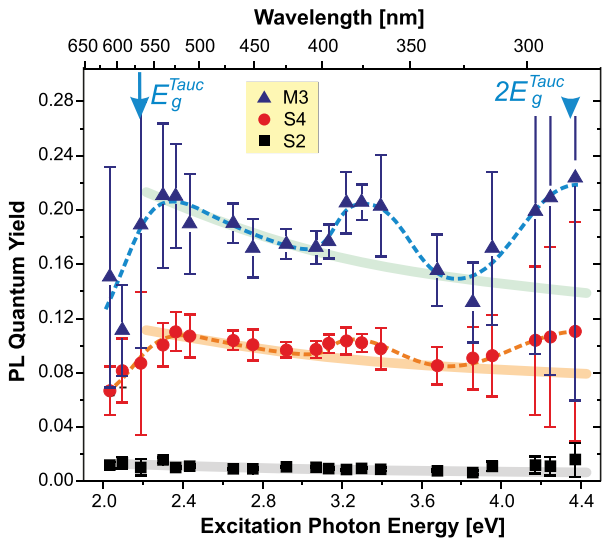

FIG. 4. PL QY excitation spectra for the samples M3, S4, and S2 (points with error bars). The dashed lines are just guides for the eye and the broad semi-transparent lines highlight the general slow decrease of QY with increasing photon energy. The arrows indicate energy 2.2 eV corresponding to the optical gap and its double value of about 4.4 eV derived from the absorption edge (Fig. 1(b)).

Finally, we have to point out, that the above mentioned spectral features in PL QY excitation spectra are not sensitive to the changes of the barrier thickness which excludes any important role of the SSQC processes.

In conclusions, using a special set of SiNC/SiO_2 multilayers, we demonstrated an increase of the luminescence QY at room temperature from ~10% to ~19% for an interlayer barrier thickness of 2 nm or larger. A barrier of 1 nm or narrower is shown to be ineffective and such multilayer samples behave like a thick single-layer of SiNCs. The temperature evolution reveals a merging of the PL QY values of ML and SL samples for temperatures below ~120 K. This fact indicates that the room temperature differences of PL QY are due to the thermally activated transport of excitation into non-radiative centers in dark NCs or in the matrix. We can estimate that dark NCs represent about 68% of the ensemble. The PL QY excitation spectra show no significant changes upon changing the barrier thickness and no clear carrier multiplication effects, like SSQC.

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