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Effect of substrate proximity on luminescence yield from Si nanocrystals

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The influence of the proximity of a high refractive index substrate on the luminescence of Si nanocrystals was investigated by time-integrated and time-resolved photoluminescence. The luminescence yield was found to be ~ 2.5 times larger for emitters distanced from the substrate compared to those in proximity with the substrate, while luminescence decay measurements revealed only a slight increase in the luminescence lifetime ($\sim 15\%$). Results are discussed in terms of local density of optical modes surrounding a pointlike light emitter with important implications for the collection efficiency of luminescence and the estimation of internal quantum efficiency for a quantum dot. © 2006 American Institute of Physics. [DOI: 10.1063/1.2226976]

Light emission from a pointlike source, such as an atom or a molecule, depends not only on the intrinsic properties of the source but also on the optical properties of the surrounding media or, more specifically, on the available optical modes. This is governed by Fermi's "golden rule" and, in general, the emission can be highly anisotropic. Modification of the luminescence due to the proximity of materials with different optical properties is of interest from both fundamental and practical standpoints.¹ For example, the spontaneous emission rate of Er^{3+} ions can be enhanced by the proximity of a high refractive index substrate,² an effect of particular interest for application in Si-based optoelectronics.³

Quantum dots (QDs), which typically have dimensions of several nanometers, can also be treated as subwavelength light sources, and there is considerable interest in methods to improve the light collection efficiency or enhance the spontaneous emission rate from such structures. One of these is the utilization of metallic, nanostructured layers placed in close proximity to the QDs,⁴ which has been demonstrated to enhance the luminescence yield by a factor of ~ 4 . A more geometric approach is the use of a solid immersion lens, an approach that has been reported to yield a factor of 5 improvement in collection efficiency.⁵

The characterization of semiconductor QDs often involves analysis of dots residing on a planar substrate at the interface with air. An example would be self-assembled In-(Ga)As quantum dots, where the substrate is typically a bulk semiconductor (e.g., GaAs). Such substrates normally absorb luminescence in the visible range, and the light emission is routinely collected in the upper hemisphere. In this geometry, the proximity of a high refractive index substrate ($n \approx 3.5$ for most semiconductors) quite markedly changes the spatial distribution of luminescence, and therefore disregarding this effect can lead to an underestimation of a QD's internal quantum efficiency.

Here we report results from measurements of the luminescence yield as a function of distance between a pointlike emitter (an ensemble of Si nanocrystals) and a high- n Si substrate. The main objectives are to determine the effective distance of the coupling and to estimate the total change in the yield that can be achieved by distancing the emitter from the interface. In addition, we compare the effects of lifetime modification and spatial redistribution of light on the luminescence yield change.

Silicon nanocrystals were created by implantation of Si^- ions into SiO_2 with subsequent annealing.⁶ The nanocrystals were formed in a 20 nm layer of SiO_2 on top of an n -type $\langle 100 \rangle$ Si wafer. Electron-beam lithography was then employed to define dots in the SiO_2 with diameters from 100 to 400 nm. In order to vary the distance between the Si nanocrystal emitters in SiO_2 and the substrate, reactive-ion

FIG. 1. [(a) and (b)] Pillars of different heights with 20 nm luminescent dioxide islands on top, etched in silicon substrate. [(c) and (d)] Corresponding time-integrated photoluminescence images, taken with the same exposure time. (a) Closer proximity of the luminescent layer to the substrate leads to (c) less collected signals. Irregular bright spots are conglomerates of nanocrystals left on the surface after the etching.

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FIG. 2. (Color online) Luminescence yield as a function of pillar height for (a) pillars with diameters less than a wavelength for two excitation regimes and (b) large structures with sizes much more than a wavelength; here the effect of height is not seen because of very small aspect ratios. A PL spectrum from the nanocrystals is shown in the inset.

etching (RIE) of the Si substrate was carried out for different times, resulting in different heights (up to 370 nm) of Si pillars with thin “active” SiO₂ layers on top. The height of pillars was measured with scanning electron microscopy (SEM). Annealing in a mixture of H₂:N₂ at 1:9 at 400 °C for 30 min was performed to passivate defects, including those introduced during RIE and SEM exposures.⁷ Time-integrated PL measurements were carried out using the 325 nm line of a cw He–Cd laser as the excitation source. Time-resolved PL measurements were performed using a pulsed YAG laser at 355 nm with 3 ns pulse and 90 Hz repetition rate and photoluminescence (PL) emission was detected during a 10-μs-wide gate. Both experiments were performed at room temperature and detected by the same charge-coupled device (CCD) imaging system.

Figure 1 shows results of SEM and PL imaging of 20 nm SiO₂ islands containing Si nanocrystals, which are 300 nm in diameter and at different distances from the substrate: 110 nm [Figs. 1(a) and 1(c)] and 370 nm [Figs. 1(b) and 1(d)]. The difference in the luminescence yield for the structures of different heights is clearly seen. In the context of such measurements it is important to note that the luminescence properties of a single nanocrystal exhibit variations from one particle to another due to effects such as emission anisotropy, which can be caused by the shape of a quantum dot, or the phenomenon of blinking, due to the interaction of a single nanocrystal with its local environment.⁸ Here, in order to average these individualities the measurements were performed on structures containing an ensemble of nanocrystals.

In Fig. 2 we plot the normalized luminescence yield as a function of the distance between the emitter and the substrate. This was obtained by averaging the intensity data shown in Figs. 1(c) and 1(d) and normalizing to the signal from structures of the same diameter residing at the interface.

FIG. 3. (Color online) Luminescence decay measurements: (a) stretched-exponential decay is seen with different parameters for nanocrystals on the substrate and on top of the highest pillars; (b) instantaneous lifetime is extracted from (a); the relative change is shown on the inset and reveals a value of ~15%.

In Fig. 2(a) we show the measured dependence for small structures with diameter $D < \lambda$. When excited below saturation, the yield change is more pronounced than when nanocrystals are pumped deep into saturation. We attribute this difference to the scaling of the excitation field with pillar height; the grazing geometry of the incidence excitation together with the high reflection coefficient of bulk Si ($R = 0.6$ for UV light) suggests a possible contribution of the reflected component to the excitation process. Nanocrystals are sensitive to variations in excitation power only below saturation, while deep in saturation the luminescent intensity is basically independent of the pumping power. From Fig. 2(a) one can also assess the effective coupling length to be ~250 nm, which is about λ/π and compares well with the calculations in Ref. 9.

Significantly, no dependence on pillar height is observed for structures with a size much larger than the wavelength $D > \lambda$ [Fig. 2(b)]. This result is not surprising, considering that the geometry of these small aspect ratio structures closely matches that of nanocrystals located directly at the interface.

Time-resolved PL measurements revealed a stretched-exponential decay of luminescence for both nanocrystals on the substrate and away from it [Fig. 3(a)]. This behavior is typical for these nanostructures.⁶ Instantaneous lifetimes as a function of time, $\tau_{0i}(t)$ and $\tau_i(t)$, derived from the corresponding decay transients, are presented in Fig. 3(b).

Generally, several different processes can manifest the substrate proximity effect. For small distances d ($d \ll \lambda$, $\lambda = 850$ nm) between the nanocrystals and a semiconductor, nonradiative transfer of the excitation to the bulk material is possible. However, in the geometry used in the present experiment, as far as nonradiative energy transfer is concerned, the distance from nanocrystals to the substrate remains the same for all pillars irrespective of height. Indeed, in all cases

nanocrystals reside in a 20-nm-thick SiO₂ layer directly on top of a silicon trunk.

On the other hand, purely optical processes of a radiative nature have characteristic distances in the order of the wavelength: $d \sim \lambda$. In this case the etched area around the SiO₂ islands represents a change in the local density of states of optical modes [LDOS(**r**)] in the hemisphere with radius $\sim \lambda$ below the nanocrystals. To a first approximation, the LDOS(**r**) away from the interface is proportional to the refractive index n of the medium.⁹ We consider a point light source at the interface between two media: $n=1$ in the upper half space and the variable refractive index in the bottom half space, ranging from $n_2=3.7$ to $n_1=1$. Then

$$\eta_{\text{space}} \equiv Y/Y_0 = \left(\frac{n}{n_1 + n} \right) / \left(\frac{n}{n_2 + n} \right) \equiv \frac{n_2 + n}{n_1 + n} = 2.35, \quad (1)$$

where Y_0 and Y are the fractions of luminescent power reaching the detector for nanocrystals at the interface and remote from the substrate, respectively. At the same time a lifetime shortening effect acts to counterbalance this effect under strong excitation. Indeed, a faster decay enhances the yield when the luminescence is lifetime limited. From Fig. 3(b), using measured instantaneous lifetimes at the interface τ_{0i} and away from it τ_i , one can estimate the ratio of emission rates caused by the substrate proximity effect in time domain:

$$\eta_{\text{time}} \equiv \frac{\Gamma}{\Gamma_0} = \frac{\tau_{0i}}{\tau_i} \approx 0.87. \quad (2)$$

The total change in the yield is then, from Eqs. (2) and (3),

$$\eta \equiv \eta_{\text{time}} \eta_{\text{space}} \approx 2.05, \quad (3)$$

which is consistent with the measured value in Fig. 2(a) for excitation of nanocrystals in the saturation regime.

It is seen that the lifetime effect has far less impact on the luminescence yield than the spatial redistribution of light. In order to assess the former in more detail we use a qualitative approach and consider both radiative and nonradiative recombination channels inside nanocrystals. Away from the interface, the experimentally observed decay rate:

$$\Gamma = \Gamma_{\text{nr}} + \Gamma_{\text{rad}} = \Gamma_{\text{nr}} + \Gamma_{\text{rad}}^{\uparrow} + \Gamma_{\text{rad}}^{\downarrow} = \Gamma_{\text{nr}} + \text{QE} \times \Gamma, \quad (4)$$

where $\Gamma_{\text{nr,rad}}$ are the nonradiative and radiative recombination rates, respectively, $\Gamma_{\text{rad}}^{\uparrow,\downarrow}$ are the radiative rates to the upper and lower half spaces, respectively, and $\text{QE} \equiv (\Gamma_{\text{rad}}^{\uparrow} + \Gamma_{\text{rad}}^{\downarrow})/\Gamma$ is the internal quantum efficiency of a QD suspended in air. Although the radiative rate has a complex direction dependence here, we use terms of radiative rate to the upper and lower half spaces in order to distinguish between light emission to the detector and substrate sides. At the interface the radiative rate to the lower half space is enhanced due to larger density of optical modes below the nanocrystals: $\Gamma_{\text{orad}} = \Gamma_{\text{rad}}^{\uparrow} + n_2 \Gamma_{\text{rad}}^{\downarrow}$. Assuming that the nonradiative channel is determined only by the intrinsic properties of a QD, we can assess the experimentally observed decay rate at the interface:

$$\Gamma_0 = \Gamma_{\text{nr}} + \Gamma_{\text{orad}} \equiv \Gamma_{\text{nr}} + \text{QE} \times \Gamma + (n_2 - 1) \Gamma_{\text{rad}}^{\downarrow}. \quad (5)$$

Then, the relative change in the luminescence yield, caused by the lifetime effect, can be obtained from Eqs. (4) and (5):

$$\eta_{\text{time}} \equiv \frac{\Gamma}{\Gamma_0} = \frac{1}{1 + \text{QE} \times (n_2 - 1)/2}. \quad (6)$$

Substituting the measured value of η_{time} into this equation, the internal quantum efficiency of the silicon nanocrystals can be estimated as $\text{QE} \approx 11\%$. This value is similar to that previously measured for single Si nanocrystals in a SiO₂ shell, distanced from the substrate.⁸ In the case of nanocrystals at the interface, the quantum efficiency can be defined as

$$\text{QE}_0 = \frac{\Gamma_{\text{rad}}^{\uparrow} + n_2 \Gamma_{\text{rad}}^{\downarrow}}{\Gamma_{\text{nr}} + \Gamma_{\text{rad}}^{\uparrow} + n_2 \Gamma_{\text{rad}}^{\downarrow}} \equiv \frac{1 + n_2}{2/\text{QE} - 1 + n_2} \approx 22\%. \quad (7)$$

So, the quantum efficiency here is twice as high as for isolated nanocrystals but solely due to the leaking of luminescence to the high- n substrate.

Finally, the total change in the luminescence yield with substrate recession, from Eqs. (1) and (6), is

$$\eta = \eta_{\text{space}} \eta_{\text{time}} = \frac{n_2 + n}{(n_1 + n)[1 + \text{QE} \times (n_2 - 1)/2]}. \quad (8)$$

From Eq. (8) it is seen that at $\text{QE}=100\%$ the two effects compensate each other yielding $\eta=1$, while for $\text{QE}<100\%$ the luminescence yield increases with substrate recession.

In summary, it has been shown that the luminescence yield from a quantum dot is influenced by the local density of optical modes around it. Namely, a high refractive index substrate in proximity to the quantum dots leads to an enhanced emission into the substrate, lowering the collected emission in the upper half space. A corresponding lifetime shortening, associated with the enhanced emission rate for QDs at the substrate, is, however, masked by concurrent non-radiative recombination within nanocrystals. Such a substrate proximity effect has straightforward implications for the collection efficiency of light. Another important implication is the assessment of a QD's internal quantum efficiency.¹⁰ When geometric factors are considered they should include the corresponding optical properties of the surrounding materials rather than assume isotropic luminescence.

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