

Single dot optical spectroscopy of silicon nanocrystals: low temperature measurements

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Abstract

Single dot spectroscopy allows studying properties of a single nanocrystal avoiding inhomogeneous broadening of the emission band. Here, data obtained by this technique for Si nanocrystals fabricated by electron beam lithography, plasma etching and subsequent size-reduction by oxidation are presented. First, blinking (on–off intermittence) of the luminescence was observed for most individual nanocrystals, although some exhibited relatively stable luminescence. As a result of the quantum confinement effect spectra with different emission wavelengths for different nanocrystals were recorded. While at room temperature the full width at half-maximum of the nanocrystal emission peaks was measured to be ~ 100 – 150 meV, at 80 K the linewidth for some dots appeared to be about ~ 25 meV only. The observed temperature dependence of the homogeneous linewidth may lead to an understanding of the exciton–phonon interaction in indirect band-gap quantum dots.

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1. Introduction

Si nanocrystals are receiving widespread interest because of their potential ability to combine electronic and optical functionality in Si-based devices. Recently, optical gain in silicon nanocrystals was reported [1], which may open a way to the fabrication of a Si-based laser. So far energy selective spectroscopy [2] and PL hole burning [3] have been the main techniques to investigate properties of this low-dimensional structure. The main drawback of the mentioned methods is the fact that an ensemble of quantum dots is addressed rather than a single nanocrystal during measurements. Related inhomogeneities in the ensemble lead to the smearing of unique features of a nanocrystal thus screening valuable

data on its level structure and emission band. The homogeneous emission linewidth of quantum dots is one of its most important parameters, while temperature dependence of the band reflects unique dephasing mechanisms of quantum states by phonons.

Although single dot spectroscopy technique was used in characterization of direct bandgap semiconductor dots [4], it has been difficult to employ this method for indirect bandgap materials, such as silicon. A controllable space separation of silicon nanocrystals and their low emission rate are the major issues one needs to overcome in order to carry out such an experiment.

In our previous work [5] it was shown that electron beam lithography combined with plasma etching and subsequent size-reduction by oxidation may provide necessary means to isolate silicon nanocrystals spatially well enough for far-field single dot spectroscopy to be applied. Since a conventional optical microscope is used in this technique, single dots can be resolved when their area concentration is $\sim 1/\mu\text{m}^2$ and less. These studies

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showed a single dot linewidth of 125–150 meV with peak energy varying from dot to dot.

To gain further insight into the emission mechanism and to reveal the single dot character, low temperature measurements are needed. On this route additional experimental problems were encountered. First, thermal expansion/shrinking effects had to be reduced to a micron scale not to blur images during long data acquisition. Secondly, image distortion due to the cryostat window had to be solved maintaining a high numerical aperture, crucial for detection of the low emission intensity.

Here we demonstrate successful linewidth measurements at 80 K, also revealing participation of TO-phonon modes in the emission.

2. Sample preparation and experimental setup

An N-type Si wafer having a 25 nm thermal oxide layer was used as a substrate. Electron-beam lithography (Raith TurnKey 150) was used to create holes with a diameter of ~ 100 nm in a positive type of resist. Then reactive ion etching was performed to etch through the SiO_2 layer and into the Si substrate. As a result, ~ 200 nm tall Si pillars were obtained. Subsequent thermal oxidation at 900°C led to shrinking of the Si cores of the pillars. The temperature variations at different areas on the sample give a slightly different consumption of Si. In addition, the initial range of different diameters results in Si cores of different sizes ranging down to few nanometers. A phenomenon of self-limiting oxidation [6] plays an important role in the formation of a Si nanocrystal from a pillar. The rate of oxidation is significantly reduced on a few nanometer scale when the surface has a large curvature, due to stress build up at the silicon-oxide interface. For pillars, the largest curvature is at the top and one may expect than an isolated SiO_2 sembedded Si nanocrystal could remain here while other parts of the silicon core have been oxidized.

The sample was mounted on the cold finger of a liquid nitrogen flow cryostat. The light emitted from a sample was collected by a window-correction objective Olympus LCPlanF1 (NA = 0.65). An Imaging spectrometer coupled to a liquid nitrogen cooled CCD was employed to detect luminescence. The PL was excited by the UV line (325 nm) of a cw He–Cd laser with a pumping intensity of $\sim 1 \text{ W/cm}^2$. Two different gratings provided optical spectral resolution of 3 or 0.8 nm. The laser beam was directed towards the sample through the gap between the objective and the sample surface at grazing incidence. To get an acceptable signal to noise ratio each spectra acquisition lasted for 30 min. All spectra were corrected with the system response curve.

3. Results and discussion

Several indications of the observation of single emitters have been found and we start by outlining a few observations in support of this. First of all, emission photon energies from different nanocrystals lie in the range from 1.5 to 2.0 eV (see Fig. 1). According to the

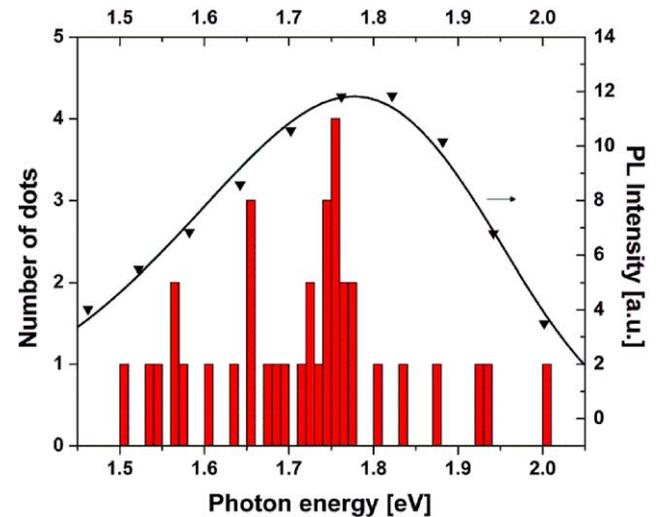


Fig. 1. Statistical breakdown of the number of dots with different emission photon energies (step 0.1 eV) measured at 80 K. Black triangles—results of previous PL measurements on an ensemble of nanocrystals embedded in silicon dioxide (solid line—Gaussian fit) [8], when 160 keV Si ions were implanted into SiO_2 films of ~ 100 nm thickness and underwent annealing at 1100°C .

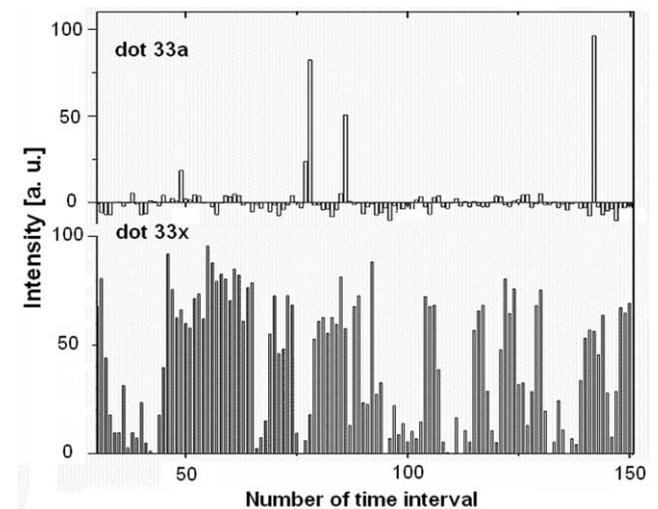


Fig. 2. Luminescence trajectories for two different dots at RT (upper and lower panels). A blinking phenomenon (switching between “on” and “off” states) can be seen with different on and off periods. Note that the integration interval (40 s) to get an acceptable signal/noise ratio was quite long ($\sim 10^5$ exciton lifetimes in a Si nanocrystal), which may result in some intermediate values of the “on” intensity per interval.

quantum-confinement theory and the size-separation experiment [7, and references therein] this range corresponds to Si nanocrystals embedded into a SiO₂ matrix with sizes less than 6 nm in diameter. In Fig. 1 we have also included a typical emission spectrum from Si nanocrystals embedded in oxide [8] for comparison. Secondly, blinking (on–off intensity fluctuations) phenomenon was observed for most individual nanocrystals (see Fig. 2). This phenomenon is known to be a hallmark of single fluorescent nano-objects [9]. Here we show the intensity traces for two different dots, one of which is off most of the time and the other is on for more than 50%. Note the similar intensities during on-times, scaling with the inverse of the emission lifetime. In addition, it was shown that quantum dots possess

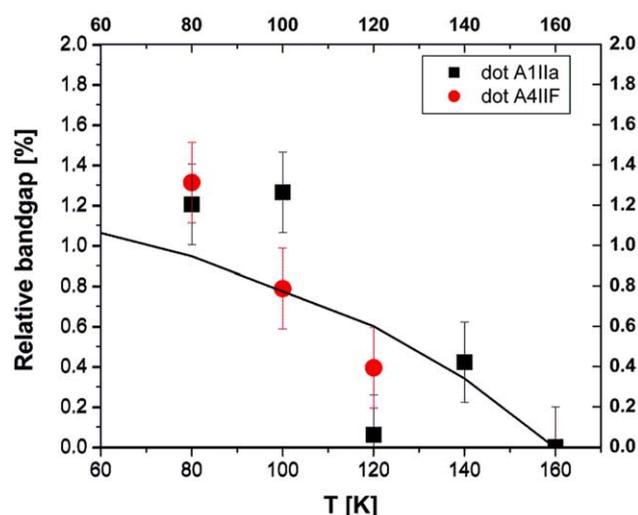


Fig. 3. Bandgap narrowing effect for Si nanocrystals. Emission photon energies observed for two different dots at several temperatures normalized to the value at 160 K are plotted with experimental error bars. Comparison is made with the bandgap narrowing effect for bulk Si (solid line, calculated by semi-empirical Varshni formula: $E_G(T) = E_G(0) - aT^2/(b + T)$, where $E_G(0) = 1.17$ eV, $a = 7.02 \cdot 10^{-4}$ eV/K, $b = 1108$ K). Band-to-band transition is assumed to be responsible for the observed PL from single Si nanocrystals.

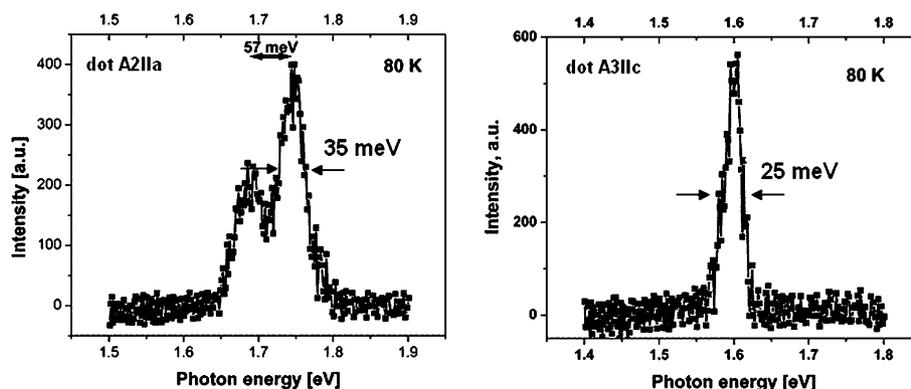


Fig. 5. PL spectra for two different single Si nanocrystals measured at 80 K under 325 nm cw excitation.

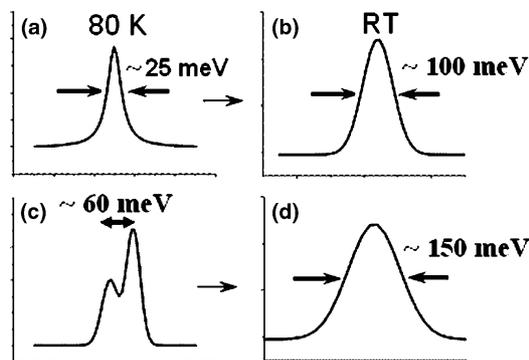


Fig. 4. Observed temperature evolution of silicon nanocrystals emission line, shown schematically for the range of temperatures from 80 K to RT (see text).

such property of the bulk material as bandgap narrowing [10]. Here the temperature dependence of the nanocrystal emission photon energy has also been detected for two different dots (see Fig. 3).

The observed temperature evolution of the emission line for different nanocrystals is shown schematically in Fig. 4. At 80 K some fraction of the nanocrystals revealed a second peak standing ~ 60 meV apart from the main one (c). This group of quantum dots exhibits quite a broad featureless emission line at RT (d). At the same time, the rest of the investigated nanocrystals showed a gradual broadening of the main emission line with no other lines appearing (a). At RT the linewidth of these dots is somewhat narrower than those with a side band (b).

In Fig. 5 two PL spectra of different Si nanocrystals measured at 80 K are presented. A TO-phonon replica is clearly seen for the dot on the left panel, while the other nanocrystal does not exhibit any satellites. It was shown [11] that the emission linewidth of CdSe nanocrystals at this temperature is ~ 20 meV. This result was obtained experimentally and accounted theoretically taking into consideration the exciton–phonon interaction in direct band gap nanocrystals. Although to draw analogues

between these two materials is not correct because of the fundamental difference in zone structure, it is interesting to note that absolute values of the linewidth are very similar. Also it is worthwhile to notice that, according to the effective mass approximation theory [12], two main parameters determining excitonic states in a nanocrystal—Rydberg energy and Bohr radius—are very close for these materials (15 and 16 meV, 4.3 and 4.9 nm for Si and CdSe correspondingly).

Recently, by PL decay experiments a drastic PL lifetime increase for Si nanocrystals at cryogenic temperatures was revealed [13]. This fact makes PL characterization of single Si quantum dots at lower temperature even more difficult. The ultra low emission rate (~ 50 times less than at RT) of Si nanocrystals at liquid helium temperature range seems to be below detection capabilities of our measuring system. Furthermore, nanocrystals may become trapped in a non-luminescent state during cool down (off blinking state).

Zero-phonon optical transition was reported earlier for Si nanocrystals [2], which appears as a result of the spatial confinement of the electron and hole wave functions and this effect is size-dependent. This dependence has not been observed in present single dot spectroscopy experiments for dots with a TO-phonon replica. Perhaps, the investigation of the emission line at even lower temperatures will help to find out if the observed main peak corresponds to no-phonon or TO-phonon assisted optical transition. Further experiments are under way.

4. Conclusions

Single dot spectroscopy has been successfully applied to the investigation of properties of Si quantum dots down to 80 K. For the first time it was shown that the emission linewidth of Si nanocrystals can be, at least, as sharp as for direct bandgap materials quantum dots, which confirms the atomlike nature of these low-dimensional entities. Also exciton–phonon interaction in Si

nanocrystals was revealed as a TO-phonon replica was observed at 80 K. Its influence on the emission band was discussed. The interaction with a TO-phonon mode results in an extreme broadening of the emission linewidth for some nanocrystals. This effect leads to a very broad photoluminescence spectrum from a single silicon nanocrystal at room temperature, as reported earlier.

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