

Single-dot absorption spectroscopy and theory of silicon nanocrystals

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Photoluminescence excitation measurements have been performed on single, unstrained oxide-embedded Si nanocrystals. Having overcome the challenge of detecting weak emission, we observe four broad peaks in the absorption curve above the optically emitting state. Atomistic calculations of the Si nanocrystal energy levels agree well with the experimental results and allow identification of some of the observed transitions. An analysis of their physical nature reveals that they largely retain the indirect band-gap structure of the bulk material with some intermixing of direct band-gap character at higher energies.

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Finite-sized nanostructures and bulk random alloys lack the translational symmetry of the underlying bulk-periodic solids they are drawn from. Therefore their wave functions represent a mix of bulk bands over different wave vectors and band indices [1,2]. The additional shift in energies present in nanostructures due to quantum confinement and enhanced many-electron interactions in confined space lead to clear spectroscopic manifestations in nanostructures relative to the reference bulk material [3]. This includes changing of a bulk indirect transition to a nanostructure quasidirect transition [4], as well as more exotic effects such as Coulomb and spin blockade, appearance of many-electron multiplets, violations of Hund's rule and the Aufbau principle, etc. [5]. The modern theory of nanostructures treats such single nanostructures atomistically as a giant molecule rather than via continuum-based effective mass methods [3,6]. However, such high-resolution theoretical calculations cannot be compared with experimental data from ensemble measurements, where size (and shape) dispersion even at a very small scale smears out discrete features both in emission and absorption. Single-dot spectroscopic techniques have been previously applied to self-assembled and colloidal direct band-gap material quantum dots (QDs) of III-V [5,7,8] and II-VI group elements [9]. They have indeed revealed, in conjunction with theory, significant novel nanostructure effects forming the basis for the current understanding of QD physics.

Experimentally, the spectrum of nanocrystals can be probed by emission and absorption spectroscopy. While the emission peak position corresponds to the effective optical band gap, the absorption measurements can provide information over a wide energy range, allowing for a more detailed comparison to calculations. So far only ensemble studies were performed on the absorption spectrum of Si nanocrystals by photoluminescence excitation (PLE) or transmission methods [10,11], preventing us from observing single Si nanodot features. PLE of individual quantum dots was demonstrated for direct band-gap materials [12–14], but it is much more difficult to perform on single Si nanocrystals due to their low emission rate, stemming from $\sim\mu\text{s}$ exciton lifetimes [15]. At the same time, understanding the electronic structure of Si nanocrystals

relevant for light absorption is central to their application as phosphors [16], biolabels [17], sensitizers [18], downshifters [19], or photon multipliers [20].

In this Rapid Communication we report successful single-dot spectroscopy studies of silicon quantum dots, revealing the absorption states above the emission level. The experimental difficulty of detecting weak PLE signals from single Si nanocrystals under varying excitations was solved by introducing a stable, focusable, and tunable light source to the sensitive detection system, as described in the Supplemental Material [21].

Previously we could access only the emission state of individual Si nanocrystals in photoluminescence [4,22] and decay measurements [15,23]. The Si quantum dot origin of the emission was evidenced by the observed variation in emission peak position and lifetime, the sharp narrowing of the linewidth at lowered temperature, a signature of biexciton recombination at high excitation, and a Si transverse optical (TO)-phonon sideband in the spectra. Here we present spectroscopic results over a broad energy range (1.5–2.0 eV above the emission state) for Si nanocrystals. A typical spectrum is shown in Fig. 1 (circles, right), where several distinct absorption features can be identified, which are not seen in ensemble absorption measurements (dashed line).

We have calculated the energy states and absorption spectra of Si nanocrystals using a set of well-tested theoretical tools based on the empirical pseudopotential method [25]. By employing this atomistic method one no longer needs to use the effective-mass based (continuum) approximations, with their significant flaws [26–28]. Unlike the (atomistic) local density approximation (LDA) methods, the theory discussed here is free from the well-known LDA errors on band gap and effective masses [29], both rather detrimental to obtaining a physically correct description of quantum confinement. In this “modern theory of QDs” one includes a fairly complete description of single-particle effects (multiband interactions; multivalley coupling; spin-orbit interactions; surface or interface effects) [3,28,30]. We solved the atomistic Schrödinger equation explicitly for QD architecture consisting of a thousand to multiple millions of atoms, with the atoms located at specific positions, each carrying its own (screened) pseudopotential [25]. These semiempirical pseudopotentials were obtained

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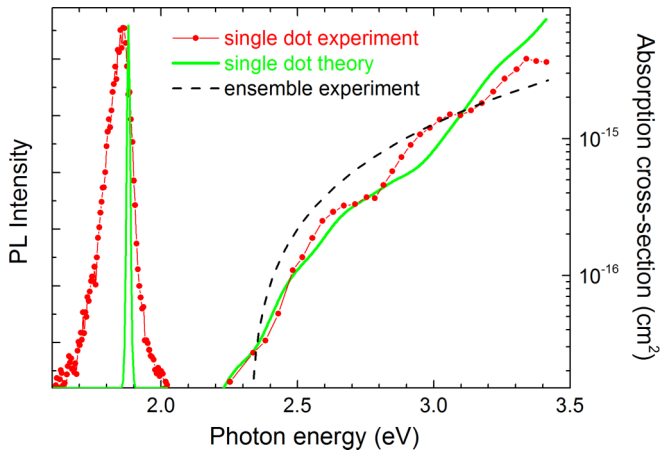


FIG. 1. Comparison of the experimentally obtained absorption curve (red circles to the right) with a calculated one (broadening 50 meV) for a ~ 3 nm diameter Si nanocrystal (green curve) exhibiting best agreement. The room-temperature photoluminescence spectrum (PL) of this nanodot is presented as red circles to the left. The PL peak position is close to the calculated band gap (green peak at 1.88 eV). A typical featureless ensemble absorption [24] is also given for comparison (dashed line).

from fitting to the experimental parameters of the bulk material [29]. The no-phonon optical absorption spectrum in a single-particle basis was then calculated using Fermi's golden rule, where many-body effects are solved using a configuration interaction (CI) approach [3]. Such an approach will help us to understand the origin of the spectral features observed experimentally in Si quantum dots. This theoretical method is summarized in the Supplemental Material and has been tested extensively over the past two decades for a broad range of spectroscopic quantities in colloidal as well as self-assembled nanostructures from the atomistic point of view [3,25–30].

In this work, theory and experiment are compared in a wide spectral range, from the emission peak position to the highest-energy absorption, pertaining to direct transitions. This is illustrated in Fig. 1 by comparing the measured (red) and the calculated (green) absorption curves for a ~ 3 nm Si nanocrystal. This nanodot has a calculated band gap of

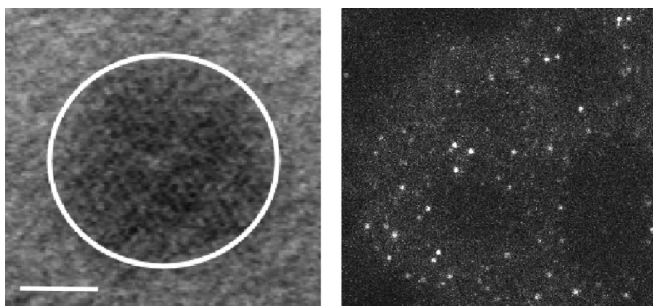


FIG. 2. Left: Cross-sectional TEM image of a silicon nanocrystal taken along the [110] direction from an SOI sample. Si (111) plane lattice fringes visible (scale bar 2 nm). Right: Photoluminescence image of $\sim 50 \times 50 \mu\text{m}^2$ sample area. Bright points correspond to luminescence from individual Si quantum dots, formed randomly in a thinned SOI layer.

~ 1.88 eV (green peak), similar to the measured PL peak position of ~ 1.86 eV (red peak). Indeed, one can notice a good agreement over nearly three orders of magnitude in absorption intensity, where a growing curve with several discernible steps is predicted and observed experimentally. In this way, single-dot spectroscopy and atomistic calculations allowed us here to identify and analyze light absorbing states in indirect band-gap material nanocrystals.

The samples were fabricated by etching and short oxidation of silicon-on-insulator (SOI) wafers resulting in close to spherical, as well as faceted, silicon nanocrystals in an amorphous oxide matrix [4,31]. A typical transmission electron microscopy (TEM) image of such nanocrystals is shown in Fig. 2 (left). Interplane distance analysis reveals no significant

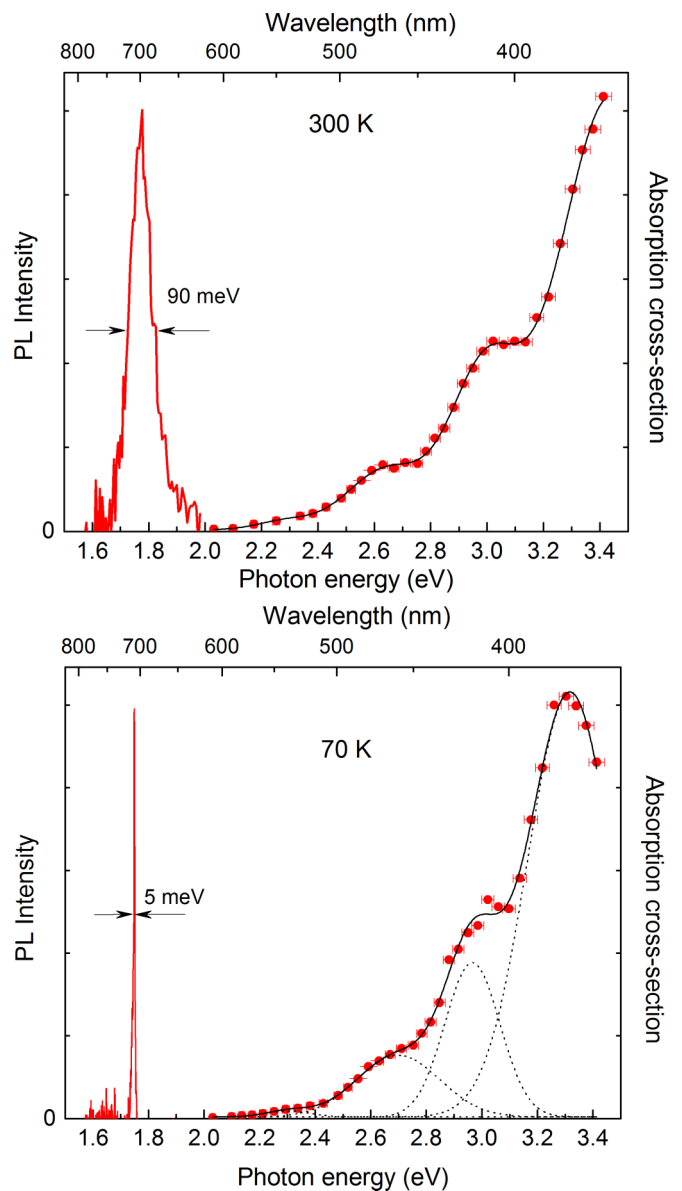


FIG. 3. Typical (top) room-temperature and (bottom) low-temperature photoluminescence (linewidth indicated) and absorption spectra of two different individual silicon quantum dots. Four steps on the absorption curves can be distinguished and the black line is a fit based on four Gaussians (see text).

TABLE I. Summary of the observed and calculated absorption peak parameters: E_0 is the peak position; ΔE is the full width at half maximum. Experimental peak parameters represent average over all dots measured at low temperature (see Table S1). Peak parameters for the theory curve are from the fitting shown in Fig. S2.

Parameter	Peak 1		Peak 2		Peak 3		Peak 4	
	E_0 (eV)	ΔE (meV)	E_0 (eV)	ΔE (meV)	E_0 (eV)	ΔE (meV)	E_0 (eV)	ΔE (meV)
Experiment	2.29	210	2.67	340	2.94	230	3.33	460
Theory	2.27	110	2.45	180	2.80	410	3.45	500

strain (Fig. S1). The PLE measurements were carried out in a microphotoluminescence setup using epifluorescence excitation geometry. A laser-driven xenon lamp with an attached monochromator was used as a wavelength-tunable excitation source from 350 to 620 nm with ~ 6 nm spectral resolution. The nanocrystals emitting in the range from 1.7 to 1.9 eV could be probed in this experiment and only nonblinking particles were considered. For low-temperature measurements the samples were mounted on a cold finger of a cryostat, and a typical PL image of such samples is shown in Fig. 2 (right). Absorption curves were obtained by correcting the detected PL signal to the excitation intensity for every wavelength. Absolute values of the absorption cross section were found using luminescence rise time measurements under a modulated laser diode excitation at 405 nm. Since the exact information on the nanocrystal shape and size is difficult to obtain, measured emission peak positions served as an experimental input to the calculations, indicating a typical size of the nanocrystals studied in this work of ~ 3 nm. Further experimental details are provided in the Supplemental Material.

Figure 3 shows typical absorption spectra recorded at 300 K (top) and 70 K (bottom), together with the corresponding emission lines for two different nanodots. Altogether, nine such silicon nanocrystals were probed, revealing a similar pattern in the absorption curves, which consists of several steps. One can identify four absorption peaks from the multicomponent Gaussian fitting (black curves in Fig. 3), and the averaged peak parameters are presented in Table I (a breakdown over individual dots is given in Table S1). It is seen from Fig. 3 that temperature has little effect on the absorption curve, although at 70 K the first peak at ~ 2.3 eV becomes somewhat clearer. The emission linewidth narrows from ~ 100 meV at 300 K to ~ 5 meV at 70 K, which is as sharp as we have ever observed for a Si QD at

this temperature and clearly less than $k_B T$. This effect was studied in detail previously, where it was attributed to the exciton phonon coupling [22]. The calculated absorption peak parameters for a ~ 3 nm nanodot (obtained by deconvolution of the calculated curve from Fig. S2) are also included in Table I for comparison, revealing reasonable quantitative agreement with the experiment.

The absolute values of the absorption cross section, measured for three nanocrystals at 300 K, yielded values in the range $0.8 - 1.9 \times 10^{-15} \text{ cm}^2$ under 405 nm excitation. Such values are typical for Si nanocrystals in an oxide matrix [32]. Thus we can define the average value of the absorption cross section at this excitation energy (3.06 eV) as $\sigma_{\text{avg}} \approx 1.5 \times 10^{-15} \text{ cm}^2$, which was used to normalize the measured curve in Fig. 1. Some variations of the absorption cross-section values were found even for nanocrystals with a similar emission energy. As revealed by the shape-dependent calculations shown in Fig. 4 (left), it can be attributed to slight structural nonuniformities among the probed nanoparticles. Such shape variations can also explain the small discrepancies in the calculated curves with the experiment (cf. Table I and Fig. 1), where the exact shape of the probed nanocrystals may vary slightly from dot to dot.

After establishing good agreement between the measured and calculated transition energies, we can interpret theoretically the origin of the transitions. For that we performed many-body calculations, which include electron-hole Coulomb interactions and correlation effects as described in the Supplemental Material. The resulting excitonic spectrum for nanodots with slightly different geometries is shown in Fig. 4 (right), where individual transition peaks are marked for the 3 nm nanodot. We identify the first peak in the experimental absorption curve at ~ 2.3 eV (cf. Fig. 3) as a combination of $S_h \rightarrow D_e$ and $P_h \rightarrow P_e$ transitions (S , P , and D are notations

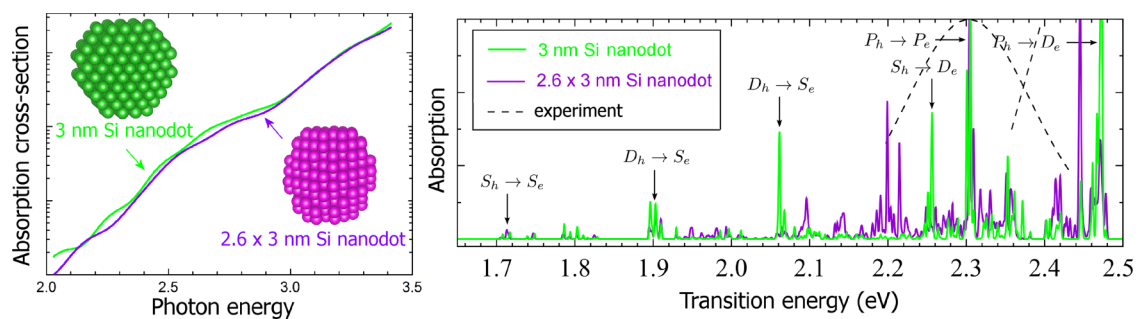


FIG. 4. Left: Calculated absorption curves (broadening 50 meV) for a nanodot of $2.6 \times 2.6 \times 3$ nm dimensions (purple) and for a 3 nm diameter nanocrystal (green) on a log scale. Small shape variations slightly modify the absorption curve. Right: The exciton spectrum counterpart including many-body effects (broadening 1 meV). Dashed lines represent the experimentally obtained peaks.

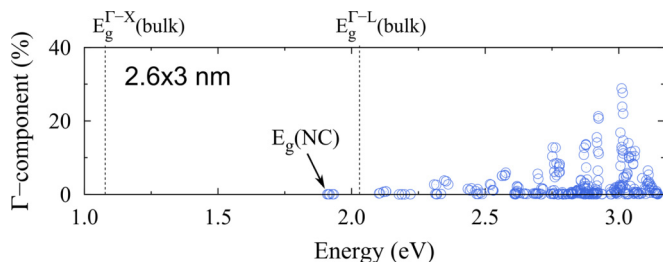


FIG. 5. Projections of the calculated conduction band states to bulk directlike Bloch functions for a $2.6 \times 2.6 \times 3$ nm Si nanodot in oxide matrix. The intermixing of Γ and X components is stronger for higher energy.

of the envelope functions with orbital angular momentum 0, 1, and 2 for holes and electrons in a silicon quantum dot). The next broad peak at ~ 2.65 eV partially consists of the $P_h \rightarrow D_e$ family of transitions. Higher-energy states of such nanodots were not analyzed in detail as they appear to consist of several mixed transitions from numerous, densely spaced electron and hole states. These states are highly quasidegenerate [25], and transitions between different sublevels result in broad experimental peaks (shown as a dashed line in Fig. 4, right), limited by the probe energy resolution and thermal broadening.

When analyzing these results we first notice that the absorption is very weak in the vicinity of the emission line (cf. Fig. 3). Indeed, the signal count rate for red light excitation was about two orders of magnitude lower than for blue light excitation, requiring a much longer time to get a measurable signal. To understand the nature of the absorbing states we calculated the conduction state wave-function projections to bulk Bloch functions (see the Supplemental Material). Since the initial valence band states are mostly localized around the Γ point, the Γ component of these projections represents the direct band-gap character of the transitions (Fig. 5). Indeed, the levels close to the emission energy retain the indirect nature of the bulk $\Gamma'_{25}-\Delta_1$ band gap (only $\sim 10^{-3}$ admixture of the Γ component), while at higher energies a strong intermixing of X and Γ states occurs (up to 30%). This situation is different from direct band-gap quantum dots, where strong direct band-gap related absorption peaks are located right next to the emission line [12–14].

This fact has a positive effect for the application of Si nanocrystals as phosphors in white-light emitting devices

[16]. Indeed, from Fig. 3 one can see that within at least ~ 300 meV next to the emission peak (~ 110 nm for 1.8 eV) Si nanocrystals are nearly absorption free. The optimum positions of the trichromatic source for the generation of white light with a high color rendering index are at 450, 540, and 610 nm [33]. While the blue light in most modern white light-emitting diodes (LEDs) comes from an (In)GaN diode, the red and green bands originate from light converting phosphors. The ~ 70 nm difference between the red and green bands is well within the poor absorption interval of Si nanocrystals. Thus the reabsorption for the green-red phosphor combination, which is a common problem for direct-band-gap nanocrystals [34], can be significantly reduced. Second, quantum dots have been recognized as superior biomarkers for multiplexing applications in biolabeling [35]. Here we note that the absorption at high energies is quite strong for Si nanocrystals due to the direct band-gap character admixture (Fig. 5), regardless of the emission energy, as shown recently for ensembles of ligand-passivated Si nanocrystals [36]. Such a large Stokes shift makes these nanoparticles good candidates for this application, considering the high natural abundance and the low toxicity of silicon.

In conclusion, we have measured absorption spectra of individual silicon nanocrystals in the visible range and found an energy structure consisting of several broad peaks, successfully reproduced by atomistic calculations. The origin of some peaks was identified as a convolution of transitions from different electron and hole states, including corresponding sublevels. The physics revealed by this single nanodot study of silicon is that the absorption states next to the emission level are still of an indirect band-gap nature, while at higher energies some intermixing with direct band-gap states occurs. For the application part, this large Stokes shift makes silicon nanocrystals attractive as phosphors and biolabels, where material abundance and nontoxicity are clear advantages.

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