Absence of red-shift in the direct bandgap of silicon nanocrystals with reduced size

Jun-Wei Luo[1,2]*, Shu-Shen Li[1,2], Ilya Sychugov[3], Federico Pevere[3], Jan Linnros[3], and Alex Zunger[4]*

[1]*State Key Laboratory for Superlattices and Microstructures, Institute of Semiconductors, Chinese Academy of Sciences, PO Box 912, Beijing 100083, China*
[2]*Synergetic Innovation Center of Quantum Information and Quantum Physics, University of Science and Technology of China, Hefei, Anhui 230026, China*
[3]*Materials and Nano Physics Department, KTH – Royal Institute of Technology, Kista, Stockholm, 16440, Sweden*
[4]*Renewable and Sustainable Energy Institute, University of Colorado, Boulder, CO 80309, USA*

*Email: jwluo@semi.ac.cn; Alex.Zunger@Colorado.edu

Methods

; ( )} of the Si nanocrystals from direct diagonalization, in a basis set of plane-wave functions, of the Schrödinger equation[1]:

(1)

where the crystal potential of the nanocrystal plus its matrix are both described as a superposition of atomic screened (semi-empirical pseudopotential) potentials of atom type at each atomic site , within the lattice site *n* ( ) = ∑ , −

coupling (coupling between different parts of the Brillouin zone), and spin-orbit coupling. This approach frees us from relying on the simplified effective-mass based (continuum) approximations for describing electronic levels. The well-known density functional errors in band gaps and effective masses[3], both rather detrimental to obtaining a physically correct description of quantum confinement, were corrected by applying small adjustments in the pseudopotential in the core region. We calculated the energy states in a wide energy window from the conduction-band minimum (CBM) up to states with energy of ~ 4 eV above the bulk Si valence-band maximum (VBM) and the absorption spectra for Si nanocrystals. For the purpose of analysis only, we expand nanocrystal wavefunctions by a set of Bloch states of underlying perfect Si crystal: $(\ ) = \sum_{,} \ (\ , \ ) \ _{,} (\ )$, and we obtain the “majority representation” decomposition of the nanocrystal silicon-on-insulator wafers by thermal oxidation (900^{o}C for 30 seconds) [5]. Silicon dioxide thickness was 1.1 µm. Nanocrystals are close to spherical or faceted in shape as revealed by TEM imaging [6]. A laser-driven Xe lamp with an attached monochromator ensured stable and tunable excitation with ~ 6 nm spectral bandwidth (20-60 meV in the experimental energy range). A thermoelectrically cooled (-100 ^{o}C) CCD camera with electron gain was used to detect weak single-dot luminescence in epifluorescence configuration with a wide-field microscope. To obtain the absorption spectra the measured photoluminescence signal was corrected for the excitation power recorded for each excitation wavelength. To calibrate obtained absorption curves a modulated excitation by a 405 nm laser diode was used, where the luminescence rise time provided information of the absolute value of the absorption cross-section [7]. The single dot absorption spectra reveal several prominent peaks. Optical interference effects can be ruled out due to poor temporal and spatial coherence of the excitation light at the sample position. The 6 nm bandwidth of the spectrally-filtered lamp corresponds to ~ 20 µm coherence length, while here the beam travelled 2-3 meters to the sample. Since the beam was expanded to a several mm waist and then focused to a ~ 30 µm spot to feed it to the sample through the microscope the lateral (spatial) coherence is also destroyed. As a practical manifestation we note that different numerical aperture objective lenses were used for room and low temperature measurements (0.9 and 0.75, respectively). Those would be expected to produce different interference patterns because of different effect on lateral coherence, but instead

red-shifted PL peak by de Boer *et al.* is a radiative channel from surface localized states. In our previous work[12,13], we have shown that the surface of Si nanocrystals embedded in an oxide matrix can contain numerous interface defects that strongly affect the Si nanocrystal photoluminescence efficiency. Specifically, red-shift of PL band arising from surface-defect related transitions was observed in several experiments[14-16]. Owing to the small joint density of states of surface defect related transitions, these transitions are usually masked by ũ-X mixing enhanced band-to-band intrinsic transitions and are hardly been observable in absorption spectrum of Si nanocrystals[11] (see also Fig. 1b in main text). Therefore, it is generally accepted whether the origin of high efficient PL from extrinsic localized defect states or not, they are always present in Si nanocrystals and may affect their high excited transitions. Finally, we note the very good agreement between the single-dot absorption spectrum and the atomistic calculations (Fig. 1b in main text) over several orders of magnitude confirming the high degree of accuracy for these calculations.

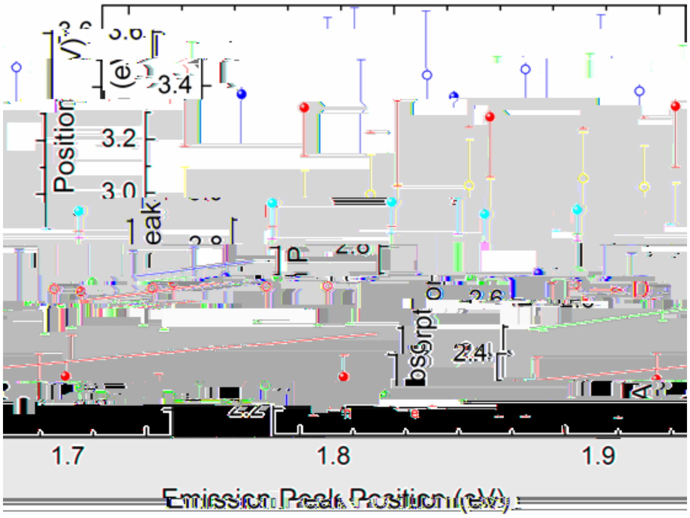

Figure S1. Positions of detected absorption peaks as a function of emission energy for 9 nanocrystals measured at room temperature (open circles) and at 70 K (filled circles). Error bars represent width of the measured peaks obtained by deconvolution. Lines show calculated energy dependence for some identified quantum dot transitions.

References:

1 Wang, L.-W. & Zunger, A. Solving Schrodinger's equation around a desired energy: Application to silicon quantum dots. *The Journal of Chemical Physics* **100**, 2394-2397, doi:10.1063/1.466486 (1994).

2 Luo, J.-W., Stradins, P. & Zunger, A. Matrix-embedded silicon quantum dots for photovoltaic applications: a theoretical study of critical factors. *Energy & Environmental Science* **4**, 2546-2557 (2011).

3 Wang, L. W. & Zunger, A. Local-density-derived semiempirical pseudopotentials. *Physical Review B* **51**, 17398-17416 (1995).

4 Wang, L. W., Bellaiche, L., Wei, S. H. & Zunger, A. Majority Representation of Alloy Electronic States. *Physical Review Letters* **80**, 4725-4728 (1998).

5 Sychugov, I., Nakayama, Y. & Mitsuishi, K. Sub-10 nm crystalline silicon