Absence of redshift in the direct bandgap of silicon nanocrystals with reduced size

To the Editor — Silicon is an indirect-bandgap semiconductor and thus an inefficient light emitter, a fact that has posed a serious impediment to the long-standing dream of integrating Si electronics with Si photonics into a combined dual-functional monolithic platform[1,2]. An encouraging experiment that held promise of creating a breakthrough for large-scale integrated complementary metal-oxide–semiconductor-based optoelectronics was published in this journal by de Boer *et al.*[3], who observed, in an ensemble of Si nanocrystals, a high-energy direct transition that rapidly lowered its energy (redshifted) with decreasing nanocrystal size, projected to lead at sufficiently small sizes to a Si nanocrystal with a truly direct gap. The authors observed a hot photoluminescence band and wrote, "…we assign this band to no-phonon hot carrier radiative recombination at levels in the vicinity of the Γ-point in the Brillouin zone, with a red spectral shift that can be regarded as a reduction of the direct bandgap energy due to quantum confinement." They added, in discussing the hot photoluminescence, "This will induce enhancement of PL [photoluminescence] intensity due to radiative recombination via the direct channel." Kovalev, writing in the News and Views of the same issue[4], shared the opinion that this was excellent news for the Si optoelectronic community: "Can silicon ever be a true direct-bandgap semiconductor? The first observation of a new, short-lived photoluminescence band from silicon nanocrystals offers fresh hope."

Because of the great difficulty of performing a single-dot spectroscopy experiment in an indirect-gap material, at that time de Boer *et al.* had to perform

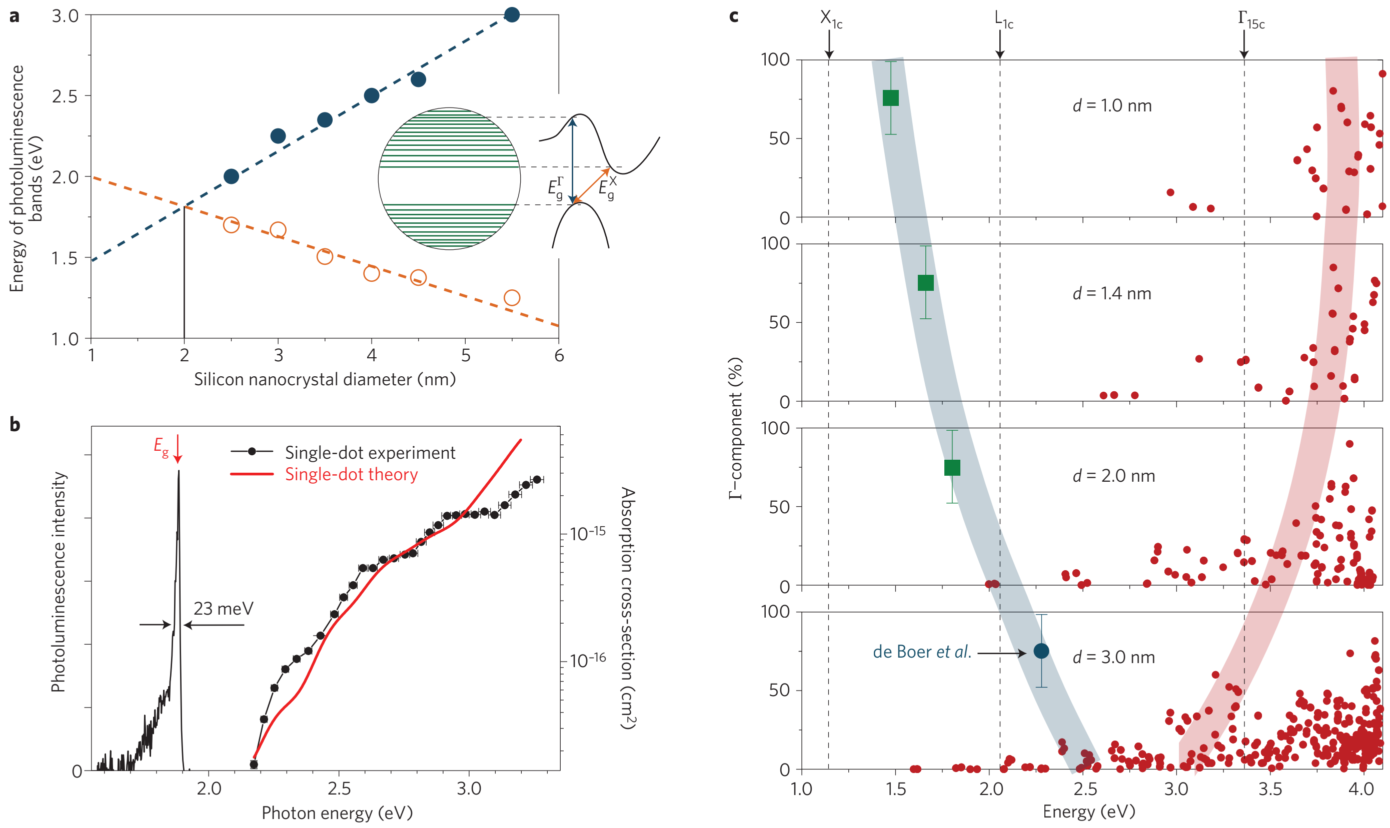

Figure 1 | Photoluminescence of bulk and nanocrystalline silicon. **a**, Energy of photoluminescence bands as a function of nanocrystal diameter, based on experimental data from de Boer and colleagues[3]. Blue filled circles: the ground photoluminescence band arising from bulk Si Γ–X indirect bandgap transition. Orange empty circles: hot photoluminescence band, assigned to bulk Si Γ–Γ direct bandgap transition. **b**, Photoluminescence spectrum (linewidth indicated) and absorption curve measured for a single Si nanocrystal at 70 K together with a atomistic pseudopotential method calculated absorption curve (red) of a Si nanocrystal 3 nm in diameter. **c**, Calculated and measured Γ-component in Si nanocrystal electron states. Whereas the redshift was found by de Boer *et al.*[3] (the blue filled circle), and is also given by the green squares that represent our extrapolation of their data to smaller nanocrystal sizes (d = 1, 1.4 and 2 nm as in **a**), as well as calculations using the effective mass approximation[5] (blue band), we observe a slight blueshift with reducing nanocrystal size (red points and red band).

an ensemble experiment in which they observed many different sizes[3]. Also, the theoretical calculations had to be done at the time by deducing the nanocrystal energy levels from the simplified effective mass approach[5] rather than by the more accurate (but demanding) method of considering a finite nanocrystal as a giant molecule in its own right[6,7]. We have recently overcome both difficulties and were able to combine our well-tested[6,8–10] atomistic pseudopotential theory of single passivated Si nanocrystals[7,11], including excitonic effects, with our newly developed single-dot absorption spectroscopy to reveal the origin of the redshifted transition in Si nanocrystals. These advanced theoretical and experimental methods enabled us to question the main points of the original paper[3], as we found no significant redshifted direct-bandgap transitions in Si nanocrystals that could be attributed to the effects of decreasing size at the nanoscale.

Bulk crystalline Si is characterized by an indirect Γ–X bandgap of 1.1 eV with the valence-band maximum (VBM) located at the centre of the Brillouin zone, whereas the conduction-band minimum (CBM) occurs near the X-point (X-valley). The conduction band at the Γ-point (Γ-valley) is high-lying and marks the direct Γ–Γ bandgap of 3.32 eV (Fig. 1a). The breaking of translational symmetry in the finite nanocrystal and the existence of interfacial discontinuities at the nanocrystal surface[11–13] promote inter-valley coupling. The electron states of Si nanocrystals therefore represent a superposition of 3D bulk X-like and Γ-like (and other) Bloch states, rather than being modified single-valley states as depicted in simplified perturbation approaches[5]. In the modern theory of nanostructures[6,8–10], we solve the atomistic Schrödinger equation explicitly for thousand-atom to multimillion-atom nanocrystals, treated as a giant molecule without reference to the bulk states, with atoms located at specific positions, each carrying its own (screened) pseudopotential[6,7,14]. The ensuing nanocrystal wavefunctions are then projected onto bulk Bloch states[7,8] (see Supplementary Eq. (2) for details), as shown in Fig. 1c. We see an appreciable Γ-component in the nanocrystal electron states below 3.3 eV. But despite this enhancement of the Γ-component in the low-energy nanocrystal electron states, the lowest-energy nanocrystal state with significant Γ-component (about 50%) lies as high as 3.1 eV relative to the bulk Si VBM, well above the proposed[3] direct bandgap of about 2.2 eV (see Fig. 1c) and much higher than the X-valley-dominated nanocrystal CBM at 1.6 eV for a Si nanocrystal of 3-nm diameter. Reducing the nanocrystal size from 3 nm down to 1 nm, we find no significant redshift of the Γ-dominated nanocrystal electron states, unlike the previous interpretation[3] (blue band in Fig. 1c) and calculations using the effective mass approximation[5]. Instead, we observe a slight blueshift of the Γ-dominated nanocrystal electron states with reducing nanocrystal size (red band in Fig. 1c).

We have compared the calculated absorption spectrum with the measured single-dot absorption curve in a wide spectral range (Fig. 1b) for a Si nanocrystal of 3-nm diameter embedded in a silica matrix (see Supplementary Information for experimental details). The measured peak position of the excitonic photoluminescence spectrum, corresponding to the fundamental bandgap for the nanocrystal, fits our calculation for a dot of 3-nm diameter. Figure 1b shows good agreement between experimental and theoretical results over nearly three orders of magnitude in absorption intensity, where a growing curve with several discernible steps is predicted theoretically and observed experimentally (interference effects are excluded; see Supplementary Information). Small differences between the calculated and measured curves are attributed to variations in nanocrystal shape, which can slightly affect the exact position and amplitude of absorption peaks. One can distinguish four broad peaks in the absorption spectra of Si nanocrystals, and their positions do not vary significantly within the measured energy interval (see Supplementary Fig. 1), providing additional support to our atomistic calculations. Although the emission efficiency from the 'redshifted' direct states was claimed to be low[3,5], the presence of such truly direct transitions would be clearly visible in the single-dot absorption spectrum, as in bulk Si (ref. 15), where a sharp jump at about 3.3 eV arises from the direct band transitions[15]. Here, we observe no redistribution of the absorption intensity towards lower energies as the 'direct-bandgap redshift' hypothesis suggests[3,5], but instead a steadily growing curve all the way to the bulk direct Γ–Γ bandgap, well described by the atomistic calculations (Fig. 1b).

The redshifted hot photoluminescence band was argued by de Boer *et al.*[3] to reflect the Γ–Γ direct-bandgap transition[3], and an effective mass approximation was used to corroborate this claim based on an assumed negative effective mass for electrons in the Γ-valley of the Si conduction band[5,16]. As shown in Supplementary Fig. 2, the conduction-band Γ-valley in bulk Si is the threefold degenerate Γ_{15} state, whose degeneracy is lifted by spin–orbit interaction. One branch of bands moves up and the other moves down in energy as the crystal momentum moves away from the Γ-point, giving rise to negative and positive mass, respectively, on a large energy scale (see the lower panel of Supplementary Fig. 2). However, if we examine the conduction bands closer to the Γ-point, we see that the lower branch with assumed negative mass is not a simple parabolic curve. The actual state at the Γ-point is a saddle point with a large positive effective mass. This result is confirmed by a comparison to the first-principles approach calculation, including the treatment of spin–orbit interaction, as shown in Supplementary Fig. 2 (left). Such subtle features of the Si conduction band are missed on the large energy scale in effective mass calculations[5]. This explains why the effective mass model with an assumption of negative effective mass predicts redshift of the direct bandgap in Si nanocrystals, but the atomistic method does not.

We propose instead the possibility that state filling assisted by strong pumping with subsequent fast recombination of multi-excitons may be responsible for the measured emission, as has been demonstrated for Si nanocrystals[17]. The redshift would then correspond to the multi-exciton depopulation due to an enhanced recombination rate at the fundamental bandgap of smaller nanocrystals. This would lead to a redshifted spectrum for the hot photoluminescence as higher states are emptied faster for smaller nanocrystals. Thus, the nanosecond-scale, 'direct-like' recombination observed in ref. 3 could be an effect of Auger or multi-exciton recombination, not a shifting of the Γ-energy (see Supplementary Information for details).

To conclude, a combination of single-dot spectroscopy with single-dot atomistic electronic structure theory is able to decipher the mystery of the redshifting band in Si nanocrystals with reduced size, finding that, disappointingly, it is not the long-sought intrinsic direct-band transition. ❐

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Additional information

Supplementary information is available in the online version of the paper.

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, Colorado 80309, USA.
*e-mail: jwluo@semi.ac.cn; Alex.Zunger@Colorado.edu