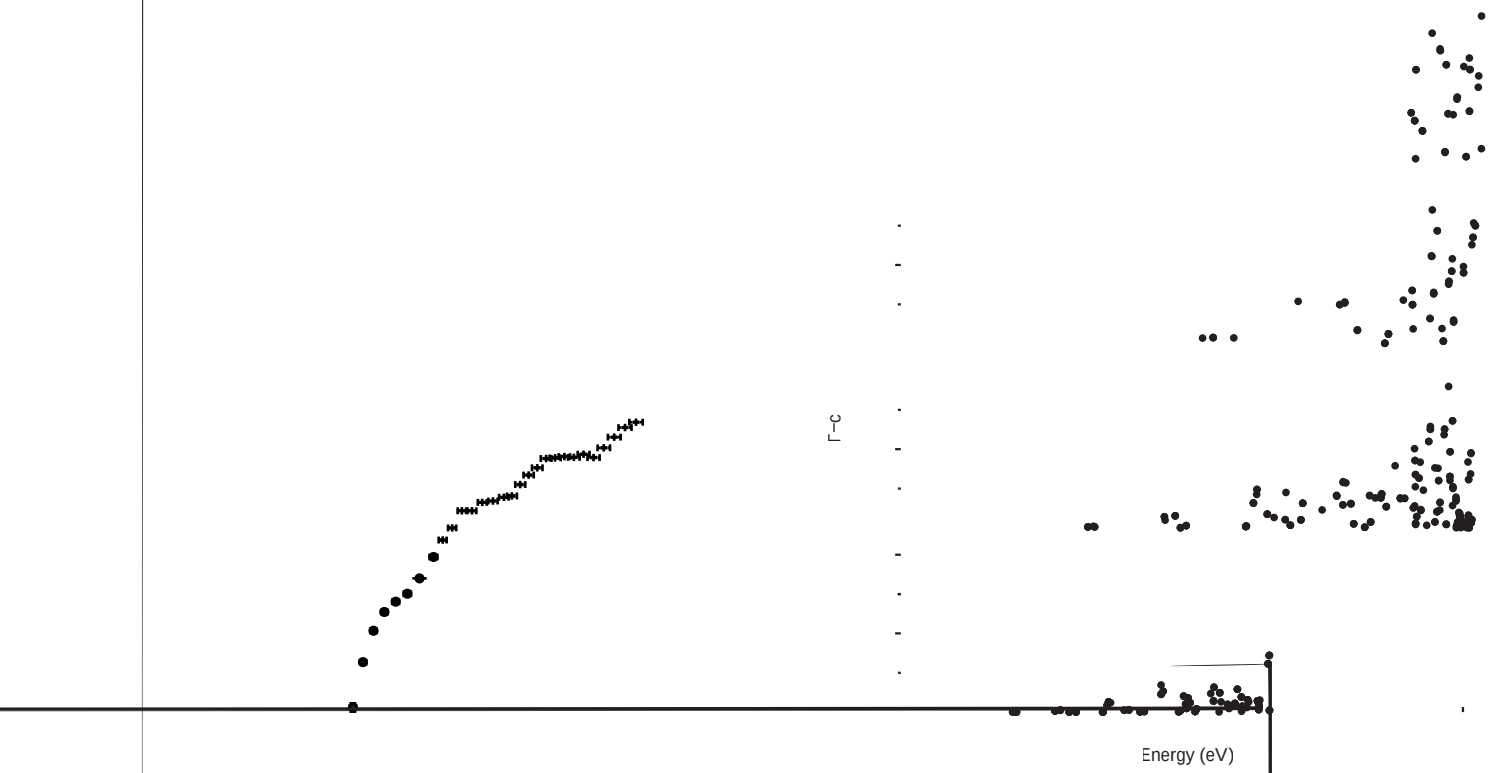
— Silicon is an indirect-bandgap semiconductor and thus an ine cient light emitter, a fact that has posed a serious impediment to the long-standing dream of integrating Si electronics with Si photonics into a combined dual-functional monolithic platform[1,2]. An encouraging experiment that held promise of creating a breakthrough for large-scale integrated complementary metal-oxide–semiconductor-based optoelectronics was published in this journal by de Boer *e al.*[3], who observed, in an ensemble of Si nanocrystals, a high-energy direct transition that rapidly lowered its energy (redshi ed) with decreasing nanocrystal size, projected to lead at su ciently small sizes to a Si nanocrystal with a truly direct gap. e authors observed a hot photoluminescence band and wrote, "…we assign this band to no-phonon hot carrier radiative recombination at levelr(.3 00(su2kq2m1n5DC BT9.3 0 0 9.3 36 525.8622 Tm(An encr8.8622 Tm(its(en4-[ng (en-GB)MC



an ensemble experiment in which they observed many di erent sizes[3]. Also, the theoretical calculations had to be done at the time by deducing the nanocrystal energy levels from the simpli ed e ective mass approach[5] rather than by the more accurate (but demanding) method of considering a nite nanocrystal as a giant molecule in its own right[6,7]. We have recently overcome both di culties and were able to combine our well-tested[6,8–10] atomistic pseudopotential theory of single passivated Si nanocrystals[7,11], including excitonic e ects, with our newly developed single-dot absorption spectroscopy to reveal the origin of the redshi ed transition in Si nanocrystals. ese advanced theoretical and experimental methods enabled us to question the main points of the original paper[3], as we found no signi cant redshi ed direct-bandgap transitions in Si nanocrystals that could be attributed to the e ects 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). e conduction band at the Γ-point (Γ-valley) is high-lying and marks the direct Γ–Γ bandgap of 3.32 eV (Fig. 1a). e breaking of translational symmetry in the nite nanocrystal and the existence of interfacial discontinuities at the nanocrystal surface[11–13] promote inter-valley coupling. e electron states of Si nanocrystals therefore represent a superposition of 3D bulk X-like and Γ-like (and other) Bloch states, rather than being modi ed single-valley states as depicted in simpli ed 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

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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]*
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M , I
C A , B 12, B 1000 3, C . [2] I C , I , C A 23002 , C . [3] M D , K H , K , , 1 440, . [4] E I , C , B , C 030 , A.
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