Interface-engineering enhanced light emission from Si/Ge quantum dots

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Abstract

Si quantum dots (QDs) have a significant improvement in luminous efficiency compared with bulk Si, achieved by alleviating the forbiddance of no-phonon \(\Gamma - \Gamma\) radiative transition determined by the law of momentum conservation. Two divergent mechanisms have been proposed to account for the breakdown of momentum conservation in Si QDs, one is due to the space-confinement-induced spread of \(k\)-space wave functions associated with Heisenberg uncertainty principle \(\Delta r \cdot \Delta k > 1/2\), and the other is due to the interface-effect-induced intervalley mixing between indirect and direct bandgap states. Both mechanisms could cause a small overlap of the electron and hole wave functions in \(k\)-space and make vertical transitions allowed, which leads to the zero-phonon light emission. In this work, we unravel the hierarchical relationship between these two primary mechanisms in the process of zero-phonon light emission from indirect bandgap QDs, by performing semiempirical pseudopotential calculation including many-body interaction on the room-temperature luminescent properties of a series of Si, Ge, and Ge/Si core/shell QDs. We show that the space confinement mechanism is dominant in both Si and Ge indirect bandgap QDs, and the interface-induced intervalley coupling mechanism plays a minor role. While in Ge/Si core/shell QDs, the interface-induced intervalley coupling mechanism has a more pronounced contribution to enhanced light emission, implying one can further enhance light emission via engineering interface based on the intervalley coupling mechanism. Given this, we further engineer the Ge QD interface by bringing four motifs of Si/Ge multiple layers from previously inverse designed Si/Ge superlattices and core/shell nanowires for light emitters. We show that two out of four motifs always give rise to two orders of magnitude enhancement in light emission relative to the Ge and Si QDs. We demonstrate that the interface engineering can enhance light emission in indirect bandgap QDs substantially and regulate the intervalley coupling mechanism as the primary factor over the space confinement mechanism in breaking the momentum conservation law.

1. Introduction

The discovery of visible photoluminescence (PL) from porous Si [1–3] and diverse types of Si nanostructures [4–8] has stimulated tremendous interest in their optical properties, which bear the hope of overcoming the inefficiency of light emission of bulk Si [9, 10] for developing Si-based light sources towards integrating both electronic and photonic devices on a single Si chip [10–15]. Bulk Si is an indirect bandgap material with the valence band maximum (VBM) at the Brillouin zone (BZ) center (i.e., \(\Gamma\)-point), like in the most semiconductors, whereas, the conduction band minimum (CBM) settled at six equivalent \(\Delta\)-points at 0.85 × \((2\pi/a_0)\) from the \(\Gamma\)-point toward the X-point of the BZ \((a_0 \approx 5.43\ \text{Å}) is the lattice...
than Si QDs to archive high-efficiency light emission [32, 33]. In indirect bandgap Ge, the orders longer in the radiative lifetime than the first-order zero-phonon radiative recombination as occurred (threefold degenerate) of the constant of Si) [9]. For convenience, starting now, we refer besides the frequently observed radiative recombination transitions related to surface defect states [17, 18], in the direct bandgap semiconductors [16], indirect bandgap semiconductors are not efficient light emitters. Nanostructures still behave as indirect semiconductors even though their luminous efficiency is superior to the observed light emission from Si nanostructures [18–25]. Despite over 30 years of intensive research, Si it is now generally accepted that quantum confinement effect induced by the size reduction corresponds to unless phonons take part to supply the momentum difference between electron and hole to ensure the electrons usually sit at the CBM and free holes at the VBM. As a result, the optical transitions are forbidden unless phonons take part to supply the momentum difference between electron and hole to ensure the uncertainty principle [29, 31]. Subsequently, the surface perturbation potential representation derived from bulk k-space makes vertical transitions allowed (as illustrated in figure 1(a)), leading to the zero-phonon light emission [19, 20]. We call this mechanism the space confinement mechanism. The other mechanism, which we refer to as the intervalley coupling mechanism, is briefly described as follows. According to the zone folding theory, the BZ of QD shrinks into a single Γ-point [26, 27]. Once bulk Si X-valley folded onto I-point, the surface potential of QD deviated from the bulk Si crystal potential can probably induce mixing between the states belong to the same irreducible representation derived from bulk I- and X-valley [23, 24, 28]. In this way, incorporating I-component into the low-lying (in energy) X-derived QD electron states makes zero-phonon recombination with the I-derived holes possible. The spherical Si QDs centered on a Si atom have the symmetry of the Td point group [29–31]. The six lowest conduction band states folded from the six equivalent X-valleys of bulk Si transform according to irreducible representations ai (nondegenerate), e (twofold degenerate), and t2 (threelfold degenerate) of the Td point group (in the single group without considering spin–orbit coupling) [29, 31]. Subsequently, the surface perturbation potential HqD of QDs couples X-derived electronic states ψα (X) to high-lying I-derived electronic states ψα (I) if they belong to the same representation α, (here, α = ai, e, t2) [16]:

\[ S_{I-X}^{\alpha} = \frac{\langle \psi_{I}^{\alpha}(X) | H_{QD} | \psi_{X}^{\alpha}(I) \rangle}{E_{I} - E_{X}}. \]  

(1)

It is worth noting that without intervalley coupling (i.e., \( S_{I-X} = 0 \)), the zone-folding alone does not break the momentum conservation rule. The zero-phonon transition intensity is proportional to the I-component \( |S_{I-X}^{\alpha}|^2 \) in the X-derived QD electron state, which is inversely proportional to the square of energy separation \( E_{I} - E_{X} \) between X-valley and I-valley in bulk Si. In this respect, Ge QDs are more promising than Si QDs to archive high-efficiency light emission [32, 33]. In indirect bandgap Ge, the

![Figure 1.](image-url)
indirect bandgap (I-valley) is fairly close to the direct bandgap (Γ-valley) with a small energy separation \( E_\Gamma - E_L \approx 0.14 \text{ eV} \) relative to \( E_\Gamma - E_X \approx 2.38 \text{ eV} \) in Si (see reference [34], and figure 1(c)). Hence, even when Ge QDs are relatively large, I- and Γ-valley are anticipated to be strongly coupled [35], giving rise to intense zero-phonon transitions [33]. Unfortunately, such expected intense light emission in Ge QDs has not been confirmed experimentally. Specifically, the reported radiative recombination lifetime is about 18 \( \mu \text{s} \) for 3.5 nm Ge QDs [33], and in a 1–1000 \( \mu \text{s} \) wide range for Si QDs depending on particle size [20, 36, 37]. This unexpected result is probably because other factors hinder the luminescence of Ge QDs, such as the emission quenching from Ge QDs observed frequently in experiments is considered as a result of the presence of Ge oxide at QD surface [30, 43]. The lack of high-quality native oxide makes it formidable to passivate the dangling bonds of Ge QDs [44, 45]. The ambiguous surface chemistry leads to the studying of the effects of surface states and defects on the optical properties of Ge QDs in a greater challenge than those of Si QDs [46]. To eliminate this surface defect, researchers suggested covering the Ge core with a thin Si shell, which can enhance the luminescent performance by improving the surface passivation [38–43]. Nevertheless, the type-II band edge alignment in the Ge/Si heterojunction separates the electron–hole pairs (electrons in Si whilst holes in Ge), adding a factor obstructing the unraveling of light emission from Si and Ge indirect bandgap QDs [41, 43].

Distinguishing the divergent mechanisms underlying the light emission from indirect bandgap QDs is crucial to develop design principles for enhancing light emission toward Si QD-based light emitters. In this work, we study the intrinsic optical properties of Si and Ge QDs by performing semi-empirical pseudopotential calculations with ignoring the complex associated with surface defects. We find that the quantum-confinement-enhanced emission in Si QDs is similar to that in Ge QDs since the light emission intensity data of Si QDs plotted against the confinement energy crosses with that of Ge QDs. This finding implies that the space confinement mechanism dominates the optical emission from indirect bandgap Si and Ge QDs over the intervalley coupling mechanism. We further show that through interface engineering, we can enhance the light emission of Ge QDs utilizing Si/Ge multiple shells by two orders of magnitude in intensity without changing the confinement energy. This compelling enhancement arises from a significantly increased I’-component in the X-derived QD electronic states as a result of the interface-scattering-induced intervalley coupling. These findings shed new light on light emission from Si and Ge QDs.

2. Computational methods

To study quantum-confinement-induced optical properties of QDs, we consider nearly spherical QDs centered on an atom and embedded in the supercell composed of an artificial wide bandgap material with a lattice same as bulk Si or Ge [30]. These dots are generated by cutting out a sphere of a given radius in the fictitious matrix and replacing the atoms of artificial material within the sphere by Si or Ge. For Si and Ge QDs, all atoms are assumed to be in their ideal bulk positions. For the Si/Ge heterostructures, atomic positions are relaxed by minimizing the lattice-mismatch-induced strain energy based on the valence force field model [47, 48]. Since we focus on the near band edge states, the saturation of all dangling bonds at the surface is essential in order to remove the localized surface states associated with dangling bonds away from the bandgap [28]. Here, the fictitious lattice-match matrix material plays the role of saturating the dangling bonds. The conduction and valence band offsets of both Si/matrix and Ge/matrix are about 3.5 and 2.0 eV, respectively. It has been demonstrated that the effective mass of carriers in the artificial matrix is so large that the modest change in band offsets has little influence on the electronic state of QDs [30].

The single-particle energy levels \( \varepsilon_i \) and wave functions \( \psi_i \) of QDs are then obtained by solving the atomistic semi-empirical pseudopotential Schrödinger equation [30, 49]:

\[
-\frac{\hbar^2}{2m} \nabla^2 + V(r) + V_{NL} \psi_i(r, \sigma) = \varepsilon_i \psi_i(r, \sigma),
\]

here the local potential \( V(r) \) is the superposition of screened atomic potentials \( \tilde{V}_\mu \) of atom type \( \mu \) located at the relaxed atomic site \( R_{n,\mu} \): \( V(r) = \sum_{n,\mu} \tilde{V}_\mu (r - R_{n,\mu}) \), and \( V_{NL} \) represents the nonlocal potential that accounts for spin–orbit coupling [50]. To solve the system containing a large number of atoms efficiently and quickly, we adopt the folded spectrum method to calculate the electronic states right near bandgap instead of diagonalizing the entire matrix [51, 52].

After obtaining the single-particle electronic states, the configuration interaction (CI) method [30, 49] is used to account for the many-body effect to acquire the excitonic properties of QDs. The many-body exciton wave functions \( \Psi(\gamma) \) are the linear combinations of single-substitution Slater determinant basis set \( \{ \Phi_{\nu,\gamma}(r_1, \sigma_1), \ldots, r_N, \sigma_N) = A[\psi_1(r_1, \sigma_1) \cdots \psi_N(r_N, \sigma_N)] \} \) \( \gamma \) represents the exciton quantum number, and \( A \)
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... is the antisymmetrizing operator):

\[ \Psi^{(\gamma)} = \sum_{i=1}^{N_e} \sum_{c=1}^{N_h} C_{i,c}^{(\gamma)} \Phi_{i,c} \]

(3)

where \( N_e \) and \( N_h (N = N_e + N_h) \) are the numbers of electron and hole states included in the expansion of \( \Psi^{(\gamma)} \), respectively. The coefficients \( C_{i,c}^{(\gamma)} \) are the eigenstates of the CI Hamiltonian:

\[ \sum_{\nu'=1}^{N_e} \sum_{\nu=1}^{N_h} \hat{H}_{\nu',\nu} C_{\nu',\nu}^{(\gamma)} = E_{\nu} C_{\nu,\nu}^{(\gamma)}. \]

(4)

The CI matrix elements are expressed as:

\[ \hat{H}_{\nu',\nu} = \langle \Phi_{\nu',c} | \hat{H} | \Phi_{\nu,c} \rangle = (\varepsilon_{\nu'} - \varepsilon_{\nu}) \delta_{\nu',\nu} \delta_{c,c} - J_{\nu',\nu} + K_{\nu',\nu} \]

(5)

herein \( J_{\nu',\nu} \) and \( K_{\nu',\nu} \) are the Coulomb integrals and exchange integrals. The exciton transition energy \( E_0 \) is defined as the difference in the total energy of a QD in a dominant configuration of an electron in level \( \nu_0 \) and a hole in level \( h_0 \) and a QD in the ground state [53]:

\[ E_0 = E_{1,1} \left( \varepsilon_{\nu_0} h_0 \right) - E_{0,0}, \]

(6)

where \( E_{1,1} \left( \varepsilon_{\nu_0} h_0 \right) = \varepsilon_{\nu_0} - \varepsilon_{h_0} + K_{\nu_0 h_0} \) and \( \varepsilon_{\nu_0} \) and \( \varepsilon_{h_0} \) are the single-particle energy level of lowest unoccupied state (i.e., CBM) and highest occupied state (i.e., VBM), respectively. By directly diagonalizing the CI Hamiltonian, we are ready to get the excitonic eigenvalues \( C_{\nu,\nu}^{(\gamma)} \) and then the many-body optical transition dipole matrix elements [49],

\[ M_{\nu,\nu}^{(\gamma)} = \sum_{\nu',\nu} C_{\nu',\nu}^{(\gamma)} \langle \psi_{\nu'} | \hat{r} | \psi_{\nu} \rangle, \]

(7)

here \( \hat{r} \) is the position operator and \( \langle \psi_{\nu'} | \hat{r} | \psi_{\nu} \rangle \) is the single-particle transition matrix element.

The QD emission spectrum is calculated from Fermi’s golden rule occupying the lowest energy initial states according to the Boltzmann distribution at temperature \( T \) [54, 55]:

\[ I(E, T) = \frac{\sum f_{\lambda} e^{-\frac{E_0 - E + \lambda}{k_B T}} e^{-\frac{(E_0 - E)^2}{(\lambda k_B T)^2}}}{\sum e^{-\frac{E_0 - E + \lambda}{k_B T}}}, \]

(8)

wherein \( f_{\lambda} = \frac{2|C_{\nu,\nu}^{(\gamma)}|^2}{me} \) is the oscillator strength which is unitless, \( \lambda \) is the Gaussian broadening, and \( k_B \) the Boltzmann’s constant. At thermal equilibrium under temperature \( T \), photoexcited exciton occupies the exciton states unequally according to the Boltzmann distribution; the probability of an excitonic state of energy \( E_r \) relative to the probability of the ground exciton state of energy \( E_0 \) is determined by the Boltzmann’s factor \( \exp \left[ - (E_r - E_0) / k_B T \right] \). In the actual, the spectral line type should be the so-called Voigt profile, which is the convoluted form of either Gaussian broadening due to its own oscillations and Lorentz broadening due to natural lifespan and particle collision [56]. The broadening is temperature dependent as a result of phonon scattering and impacted by size distribution in a QD ensemble. In this work, for simplicity, we fix the spectral line to a Gaussian type with a broadening parameter of \( \lambda = 20 \) meV as usual [30, 57, 58].

3. Results and discussions

3.1. Size-dependent scaling law of optical bandgap of Si and Ge QDs

Before going to identify the real mechanism underlying the light emission from Si and Ge QDs, it is necessary to examine the variation of the bandgap as a function of dot size, which is one of the most famous scaling laws of semiconductor QDs [9, 35, 59, 60]. Emission photon energy is higher when electron–hole pairs are confined to a smaller volume [59, 60]. Many factors contribute to the precise scaling of bandgap versus QD size, including variations of the quantum-confinement-induced shift in electron and hole energy levels, intervalley and interband coupling, tunneling of electrons and holes through finite confinement barriers, and the Coulomb and exchange interactions between electron and hole [61]. These factors come into play in deciding the PL energy as well as light emission of a size tuning series of QDs [30, 31, 62]. Figure 2 presents the calculated optical bandgap as a function of dot diameter for both Si and Ge QDs, in comparison with the results obtained using the effective mass approximation (EMA) [60] and
Figure 2. Atomistic pseudopotential method calculated excitonic gap (or optical gap) against dot diameter $D$ for (a) single pure Si QDs and (b) single pure Ge QDs, in comparison with the corresponding experimental values. We use regular triangles for optical bandgap deduced from optical absorption data [4, 63, 71, 73], and inverted triangles for PL data [18, 63, 65–71, 73]. We also use solid triangles to indicate hydrogen passivated QDs, hollow triangles for QDs passivated by alkyl ligand, and striped triangles for passivated by OAM/ODE ligand. The dotted lines are the bandgap of the bulk materials, the dashed lines are the bandgap sizing curves calculated by the EMA model [60], and the solid lines are the fitting curves of our calculation results. Experimental data are taken from references [4, 18, 63–68] for Si QDs and references [69–74] for Ge QDs.

experimental data from various samples and groups [4, 18, 63–74]. Note that such a comparison has been repeatedly conducted out in considerable literature (for example, references [9, 30, 35, 59, 73]). However, the fundamental purpose here is to illustrate the reliability of the adopted semi-empirical pseudopotential method, which has been extensively used for a wide variety of semiconductors nanostructures [55], for prediction of optical properties of both Si and Ge QDs. Remarkably, in Ge QDs, besides the easily size-tunable red-NIR emission with microsecond to millisecond scale, the more frequently observed UV-green PL with nanosecond scale is less size-dependent [32, 35]. Such size-independent PL band has been well explained as the recombination of surface state electron with QD core hole or the directly radiative recombination of electron–hole pairs bonded on the surface [17, 18, 35, 36].

Our primary motivation in this work is to reveal the light emission from the QD core. Therefore, we chose the experimental data with reasonable size-dependent PL energy to avoid data associated with surface defects. From the bandgap–size relationship shown in figure 2, we can see that the effective mass model has a comparatively accurate description of the bandgap at larger QD sizes, but is significantly overestimated at smaller QD size. In striking contrast, our predicted optical gaps based on the semi-empirical pseudopotential method are consistent with the experimental results in the whole range of dot diameter $D$. The fitting curves of the calculation results are carried out according to the following expression proposed by Allen and Delerue [76]:

$$E_{QD}^g(D) = E_{bulk}^g - \frac{1}{aD^2 + bD + c}. \quad (9)$$

For Si QDs, $E_{bulk}^g = 1.12$ eV, $a = 0.109$, $b = 0.158$, and $c = 0.159$; and for Ge QDs, $E_{bulk}^g = 0.67$ eV, $a = 0.039$, $b = 0.153$, and $c = 0.223$. These good agreements establish that the atomistic pseudopotential method is a suitable choice for studying light emission from Si and Ge QDs.

Although the size scaling law has attracted much attention, the absolute QD size is not an appropriate parameter in the comparison of optical properties between Si and Ge QDs. For instance, as we mentioned in the introduction section, with the decrease of the size of indirect bandgap QD, the space-confinement-induced spread of the electron/hole wave functions in k-space increases, making the zero-phonon vertical transition more possible [19]. This phenomenon is more pronounced when the particle size is smaller than the exciton Bohr radius of the bulk counterpart as the quantum confinement effect emerges. Nonetheless, the Bohr radius of Ge (~11.5–24 nm) is much bigger than that of Si (~4.5 nm) [35]. Therefore, for Si and Ge QDs of the same size, the quantum confinement effect should be more significant in the latter. This expectation of energy is clearly illustrated in the sizing curve in figure 2. Bear this in mind: we will use the confinement energy $\Delta E = E_{QD}^g - E_{bulk}^g$ rather than the commonly used dot size as the measuring parameter for quantum confinement effect in different QDs.
Figure 3. Calculated optical properties of Si and Ge QDs with comparable quantum confinement energy. (Top) emission spectra at room temperature. The green profile represents the spectral line with a Gaussian broadening of 20 meV, and the orange vertical lines denote that without broadening. (middle) the absorption spectra without widening (black vertical lines) and the probability of an exciton state being thermally excited (red curve). The black dashed line marks the position of the first excitonic energy. (bottom) single-particle momentum matrix element of the transitions between the near band edge states (electron to hole).

3.2. Light emission from Si and Ge QDs

In bulk Si and Ge, zero-phonon radiative transitions are forbidden because both materials are indirect bandgap semiconductors [16]. As we discussed in the introduction section, no-phonon emission becomes possible in their nanocrystal counterparts [1–8]. In this case, the optical properties of Si and Ge QDs depend on the result of the competition between zero-phonon quasi-direct recombination and phonon-associated indirect recombination channels [9, 16]. Particularly, in Si QDs, the radiative transitions transform from being governed by phonon-associated indirect recombination to be dominated by no-phonon quasi-direct processes when confinement energy above 0.7 eV [20]. As we are interested in the mechanism underlying the quantum-confinement-enhanced light emission from Si and Ge QDs, we consider only the zero-phonon radiative recombination with neglecting the phonon-related recombination.

Figure 3 compares the calculated zero-phonon emission spectra of Si and Ge QDs with confinement energy slightly larger than 0.6 eV at room temperature. From the figure, one can see that two Si QDs with the same shape and lattice symmetry but tiny size difference have a considerable disparity in PL intensity (named as ‘QD-a’ for the one with stronger in PL and ‘QD-b’ for the one with weaker in PL). Moreover, the PL intensity of the Ge QD (designated as ‘QD-c’) is not stronger than that of QD-a. Regarding the intervalley coupling mechanism, the no-phonon transition intensity is inversely proportional to the square of the energy separation between direct and indirect bandgap of the bulk material [16]. Such an energy difference in bulk Ge is one order of magnitude smaller than that in bulk Si (0.14 vs 2.38 eV) [34]. Therefore, we may speculate that the space confinement mechanism is dominant over the intervalley coupling mechanism in no-phonon light emission from indirect bandgap QDs. Besides, we can see multiple peaks in the no-phonon PL spectra of both Si and Ge QDs at room temperature. Particularly in the Ge QD (QD-c), PL has two main peaks. Although the lower one has a much larger thermal occupation than the higher one, the latter even has a greater intensity than the former.
Table 1. Possible symmetry of the excitons (capital letters) formed from the CBM and VBM (lower case letters) of Si and Ge QDs with of $T_d$ symmetry in the single group notation by neglecting the spin–orbit coupling. The asterisk represents the exciton state being a ‘bright’ state.

| Exciton manifold | CBM |
|------------------|-----|
|                  | $a_1$ | $e$ | $t_2$ |
| VBM              | $t_1$ | $T_1 + T_2^*$ | $T_1 + T_2^* + E + A_1$ |
|                  | $t_2$ | $T_2^*$ | $T_1 + T_2^* + E + A_1$ |

According to the emission spectrum expression equation (8), the peak luminous intensity depends mainly on the oscillator strength $f_1$ of the corresponding energy states and the probability of these states being thermal accessed. As can be seen from the absorption spectra in figure 3, the apparent distinction (one order of magnitude) in PL intensity between two Si QDs of pretty close size about 3 nm in diameter must chiefly arise from the significant difference in the oscillator strength of the low energy transition. As we know, the transition matrix element $|M_\mu(\omega)|^2$ is the primary determinant of oscillator strength [16, 77]. In the framework of CI, the many-body transition matrix element is a linear combination of the single-particle transition matrix elements (See reference [49], and equation (7)). The lowest-energy many-body transitions are usually composed of the single-particle transitions between CBM and VBM.

For Si and Ge QDs with the symmetry of the $T_d$ point group, the VBM is threefold degenerate (without regard to spin–orbit coupling, otherwise splits into twofold and non-degenerate states [61]) with $t_2$ symmetry and occasionally with $t_1$ symmetry. Whereas the CBM could be an $a_1$, $e$, or $t_2$ state derived from six equivalent bulk $X$-valleys for Si QDs, or an $a_1$ or $t_2$ state derived from four equivalent bulk $L$-valleys for Ge QDs, depending on the QD size [28, 29, 31, 62, 78]. The resulting manifold of excitonic states is obtained in light of the multiplication table of the $T_d$ point group (e.g., $t_2 \otimes a_1 = T_2$, $t_2 \otimes e = T_1 \oplus T_2$, $t_2 \otimes t_2 = A_1 \oplus E \oplus T_1 \oplus T_2$, and more details see table 1) [31, 62]. Since the electric dipole transition operator $\hat{e}$ possesses $T_2$ symmetry, only the $T_2$ exciton is optically active or ‘bright’, and remaining excitons are optically passive or ‘dark’ [16]. The electron–hole exchange interaction will further split the bright exciton $T_2$ into a lower-energy spin-forbidden ‘dark’ triplet and a higher-energy spin-allowed ‘bright’ singlet [31, 62]. Many experiments evidence an anomalous lengthening of the decay times at low temperatures, attributed to such exchange-interaction-induced dark–bright splitting, which are greatly enhanced by quantum confinement [33, 79]. In our previous work, we have illustrated that in the direct gap QDs (such as InAs QDs), the electron–hole exchange interaction is dominated by the long-range component. In contrast, in the indirect gap QDs (such as Si QDs), only the short-range component survives. Consequently, the exciton dark/bright splitting scales as $\sim D^{-2}$ in InAs dots and $\sim D^{-3}$ (enlarge from 2 meV to 12 meV as dot size reduced from 4 nm to 2 nm) in Si dots [50].

Considering that the exchange-induced dark/bright splitting has a good relationship with dot size, it is unlikely to have a dramatic difference in the dark/bright splittings between two spherical QDs (made by the same material) with a similar size. In the case of two size-comparable Si QDs, as shown in figure 3, the large scatter in their PL intensity is mainly because of their substantial difference in the oscillator strength of the transitions between CBM and VBM. Since the CBM of both dots is $a_1$ state and VBM is $t_2$ state, the potential change of energy ordering of $X$-derived states does not occur here. Regarding the space-confinement-induced PL intensity depends only on dot size, the remarkable disparity between the oscillator strength of these two Si QDs with very similar size must be attributed to the effect of the intervalley coupling mechanism. More frankly, the surface potential between the two Si QDs may be different in atomic scale although they are both cut out using spheres with a tiny change in radius. In QD-b, the intervalley coupling mechanism cancels the contribution of the space confinement mechanism partially.

To disentangle the contributions from the space confinement mechanism and intervalley coupling mechanism to light emission, we have compiled a size series of spherical Si and Ge QDs. Figure 4(a) gathers the calculated PL intensity as a function of confinement energy in the range of 0–1.1 eV. This trend closely resembles that of the oscillator strength against quantum confinement energy in figure 4(b). The strong dependence of the oscillator strength on size and shape yields the large scatter, but a robust overall trend. This scatter has also been found in previous calculations of Si QDs [19, 28]. Besides the intervalley coupling induced remarkable change in oscillator strength, the change of energy ordering among the band edge states [28, 31] will influence the thermal occupation of bright states, as shown in figure 4(c), which may also yield fluctuation in PL intensity as varying dot size or shape. Both Si and Ge QDs sharing the same overall trend is in sharp contrast to the expectation of much stronger light emission occurred in Ge QDs relative to Si QDs according to the intervalley coupling mechanism. It thus rules out the mechanism of
Figure 4. (a) The calculated emission intensity, (b) the sum of the oscillator strengths of the transitions corresponding to the emission peak, (c) the thermal occupation probability of these excitonic states, (d) the $\Gamma$-component of conduction states that genuinely contribute to the luminescence at room temperature as a function of quantum confinement energy for spherical Si and Ge QDs, in comparison with the results of Ge/Si core/shell QDs as well as Ge/Si core/multishell QDs. Orange diamond: Si QD, violet square: Ge QD, green point: Ge/Si core/shell QD, and red hexagonal: Ge/Si core/multishell QD. The solid line is the result of a linear fitting of data from Si and Ge QDs. The QDs we focus on are marked.

3.3. Enhanced light emission from Ge/Si core/shell QDs

Figure 4(a) shows that some scatter points deviate from the overall trend of PL intensity, which should arise from the effect of surface-potential-induced intervalley coupling. These scatter points imply that one may engineer the crystal potential to enhance the light emission of Si or Ge QDs significantly. For instance, Dohnalova et al. [25] have demonstrated that replacing the oxygen or hydrogen surface termination by carbon surface termination can enhance the radiative rate of Si QDs by about two orders of magnitude. Moreover, Miyazaki et al. [39, 40] have also presented encouraging results in their experiments that cladding Ge QD with Si shell can improve the luminescence efficiency, despite the type-II band alignment (spatial separation of electrons and holes in the Si shell and Ge core, respectively) generally results in reduced emission intensity [80, 81]. Miyazaki et al. argued that the suppression of non-radiative recombination in Ge/Si core/shell QDs is the principal reason for the luminescence enhancement [39, 40]. An alternative explanation came up that the improved localization of electron and hole carriers in the Ge core is responsible for enhanced luminescence in Ge/Si core/shell QDs [39, 40, 82, 83]. But in our view, this argument does not hold water.

Figure 4(a) also presents the calculated emission intensity of Ge/Si core/shell QDs with total QD radius fixed to 16 monolayers (MLs) but varying the Si shell from 11 ML to 1 ML in a step of 1 ML (correspondingly, the Ge core radius increased from 5 ML to 15 ML). We name these 11 core/shell QDs as CS_05–CS_15, where CS is the abbreviation of ‘core/shell’ and the number is for Ge core radius units in ML. The confinement energy of the Ge/Si core/shell QDs is defined as the energy difference between the QD optical gap and Ge bulk bandgap. Here, we take the bulk Ge as the reference regarding the quantum confinement of Ge/Si core/shell QDs comes mostly from holes. The holes are highly confined in the Ge core region by the 0.5 eV valence-band offset between Si and Ge, while the electrons are rather delocalized with a slightly larger component in the Si region because of the small conduction-band offset (~5 meV). One can see from figure 4(a) that the calculated emission intensity changes by order of magnitude as varying Si shell
Figure 5. The real-space charge density of energy states with the principal contribution to the most potent transitions in four different core/shell QDs CS_08, CS_09, CS_10, and CS_11 with comparable diameter but different shell thickness. The cross-section contours are plotted on the [001] atomic plane, with the intensity increasing from blue to red. The boundary of quantum dots (QDs) is outlined with black dashed rings. Silicon and germanium atoms are represented by white and grey spheres, respectively. It also includes the moment transition matrix element between the electron state and the hole state in the figure.

Because the surface defects are absent in all calculated QDs, the enhanced emission intensity of Ge/Si core/shell QDs is not merely attributed to the suppression of non-radiative recombination, as suggested by Miyazaki et al [39, 40]. Meanwhile, Miyazaki et al [39, 40] also deemed that the localization of holes may lead to the enhancement of luminescence. But the nonmonotonic dependence of emission intensity on Si shell thickness further proves that this view is unreasonable. Figure 5 displays the wave function distributions of electron and hole of four selected Ge/Si core/shell QDs. We find that their small variation in wave function distributions is hard to yield several-fold differences in moment transition matrix element among the investigated Ge/Si core/shell QDs.

So far, we have demonstrated that there are two factors raised the variation in luminescence intensity around the strong overall trend: (i) the oscillator strength and (ii) the thermal occupation of the bright excitons, as shown in figures 4(b) and (c), respectively.

The oscillator strength is proportional to the overlap of wave functions of electron and hole in k-space. Given that the hole is most spread around the Γ-point in bulk BZ, we can analyze the oscillator strength by accessing the component of the QD electron state around the Γ-point. In doing so, we can project QD’s electron state $\psi_i(r)$ into the Bloch states $\varphi_{n,k}(r)$ of the underlying bulk crystal, say Si or Ge [24]:

$$\psi_i(r) = \sum_n \sum_k c_{i,n}^{\text{c}}(k) \cdot \varphi_{n,k}(r),$$

where $\varphi_{n,k}(r) = \exp(i k \cdot r) u_{n,k}(r)$, $k$ and $n$ are bulk wave vector and band index in the bulk BZ, respectively, and $c_{i,n}^{\text{c}}(k)$ is the expansion coefficient for QD energy level $i$. Consequently, the single-particle momentum matrix element in QDs is [24]:

$$\mathbf{P}_{\text{ev}} = \langle \psi_c | \hat{p} | \psi_v \rangle = \sum_n \sum_k c_{i,n}^{\text{c}}(k) \cdot \varphi_{n,k}(r) \cdot \langle \Psi_e | \hat{p} | \Psi_v \rangle,$$

where $\langle \Psi_e | \hat{p} | \Psi_v \rangle$ is the momentum matrix element of the bulk Bloch wave functions. A relationship between the momentum matrix element and the dipole matrix element is [75]

$$\langle \psi_c | \hat{p} | \psi_v \rangle = i m \omega_{\text{ev}} \langle \psi_c | \hat{r} | \psi_v \rangle.$$

$\hbar \omega_{\text{ev}}$ is the single-particle transition energy. According to equation (11), the quantum confinement effect causes a finite overlap between $c_{i,n}^{\text{c}}(k)$ and $c_{j,m}^{\text{v}}(k)$, as depicted in figure 1(a). This finite overlap is responsible for the quantum confinement effect induced breaking of the momentum conservation law $\delta_{k_c,k_v}$, and making the zero-phonon transition possible. Since the holes are mostly spread around the Γ-point, the

| QD   | Energy Shift (eV) | Wave Function
|------|------------------|---------------|
| CS_08 | 0.581            | ![Image of CS_08 wave function](image) |
| CS_09 | 0.563            | ![Image of CS_09 wave function](image) |
| CS_10 | 0.572            | ![Image of CS_10 wave function](image) |
| CS_11 | 0.587            | ![Image of CS_11 wave function](image) |
zero-phonon $\Gamma - \Gamma$ transition depends heavily on the $\Gamma$-component in the QD electron states. To quantify the weight of each bulk Bloch wave function mixed into the QD electron states, we use the ‘majority representation’ approach [84] with the projection technique:

$$p_i(k) = \sum_n |\langle \psi(r)|\varphi_{n,k}(r)\rangle|^2$$

Besides, we employ a more intuitive weight function $\omega_i^Γ(X,L)$ for estimating band mixing, by summing $p_i(k)$ of all $k$ points in a spherical region centered on $\Gamma(X,L)$ points [85]:

$$\omega_i^Γ(X,L) = \sum_{k\in(\Omega_\Gamma X,L)} p_i(k),$$

where the radii of the spheres $Ω_Γ$, $Ω_X$ and $Ω_L$ are identical.

Figure 4(d) depicts the $Γ$-component of the conduction band states (usually the CBM) that dominate the light-emitting for Ge/Si core/shell QDs as well as Si and Ge QDs. The overall trend of the $Γ$-component data points against the confinement energy for all investigated QDs is closely following the oscillator strength. This good agreement indicates a strong correlation between light emission and $Γ$-component of electronic states. Hence, we can attribute the enhancement of light emission in Ge/Si core/shell QDs to the increase in the $Γ$-component of band edge electron states. There is no need to invoke the real-space distribution of wave functions, and the suppression of nonradiative recombination associated with surface defects for the observed stronger light emission from Ge/Si core/shell QDs [39, 40].

We also note in figure 4 that, compared with the emission intensity, the oscillator strength and the $Γ$-component of electron states of Ge/Si core/shell QDs are more significant above the overall trend of Si and Ge QDs. This is because the transitions corresponding to the strongest PL peak in core/shell structures are often from the higher energy electron state with a smaller thermal occupation rather than CBM. The unsurprisingly reduced thermal occupation is presented in figure 4(c). For Si and Ge QDs, the data points are less scattered in $Γ$-component than those in the emission intensity. Specifically, the above discussed two Si QDs (QD-a and QD-b) have one order of magnitude difference in both emission intensity and oscillator strength but have similar $Γ$-component, implying the sum over $Γ$-point does not precisely reflect the detail overlap between electron and hole wave functions. The $Γ$-component data of QD-c is well above the overall trend, which is twice as large as that of QD-a, as shown in figure 4(d). However, the reduced thermal occupation renders it has a comparable light emission as the latter. These findings imply we can further enhance light emission via enhancing both the thermal occupation and CBM $Γ$-component.

### 3.4. Enhance light emission via interface-engineering in Ge/SiGe core/multishell QDs

In previous works, we have designed direct bandgap Si/Ge superlattices [58] and core/multishell nanowires [57] with substantially enhanced light absorption using a genetic algorithm inverse band structure design, which demands much more computationally cost for QDs. Specifically, we take $[\text{Si}_{1}\text{Ge}_{2}\text{Si}_{2}\text{Ge}_{2}\text{Si}_{1}]$ motif (motif-a) from direct bandgap Si/Ge superlattices [58], $[\text{Ge}_{4}\text{Si}_{2}\text{Ge}_{2}\text{Si}_{2}\text{Ge}_{1}]$ motif (motif-b) from inverse designed [100] oriented Ge/SiGe core/multishell nanowires, and $[\text{Si}_{5}\text{Ge}_{5}\text{Si}_{5}\text{Ge}_{5}]$ (motif-c) and $[\text{Ge}_{5}\text{Si}_{5}\text{Ge}_{5}]$ (motif-d) motifs from [110] oriented Ge/SiGe core/multishell nanowires [57].

First, we attach these four motifs to a Ge core with a size of 5 ML from the center atom to the interface, and vary $j$ in each motif to ensure 16 ML in total from the central atom to the outermost surface atom (the configuration space is illustrated in figure 6(a)). It will produce four Ge/SiGe core/multishell QDs (motif-a is shown as an example in figure 6(b)). We compare the light emission of these four core/multishell QDs with Si, Ge, and Ge/Si core/shell QDs in figure 4(a). Interestingly, motif-c and motif-d core/multishell QDs exhibit one order of magnitude enhancement in light emission relative to the Ge/Si core/shell QDs with the strongest luminescence. Whereas, motif-a and motif-b core/multishell QDs have comparable light emission with Ge/Si core/shell QDs.

As seen in figure 4, motif-c and motif-d with the strongest luminescence among the four core/multishell QDs have not only strong oscillator strength but also high thermal occupancy. The QD (motif-b) with the medium PL intensity possesses nearly the same thermal occupation probability as motif-c and motif-d. However, the oscillator strength is less than one-tenth of the latter two. As for the QD (motif-a) with the weakest luminescence, the thermal occupation probability is far less than that of motif-b, although their oscillator strengths are comparable. The comparison of the two factors, oscillator strength and thermal occupation, explains the light emission behavior of core/multishell QDs well, which is in line with our previous argument.
Nevertheless, we find in figure 4(d) that there is little variance in the \( \Gamma \)-component of the four core/multishell QDs, which cannot explain one order of magnitude differences in their oscillator strength. In the last paragraph of the previous section, we have pointed out that the \( \Gamma \)-component may fail to reflect the \( k \)-space distribution of the wave function accurately. In this paragraph, we will take core/multishell QDs motif-a and motif-c as examples to clarify this contradiction. Among the four core/multishell QDs, motif-a and motif-c have the closest quantum confinement energies, and the \( \Gamma \)-components of the electron states that dominate their respective light-emitting are nearly the same, while the corresponding oscillator strengths differ by more than one order of magnitude. Figure 6(c) exhibits a detailed comparison of the \( k \)-space wave functions of the electron states and hole states that are top contributors to the luminescence of motif-a and motif-c. One can find a stark contrast between the \( k \)-space wave functions of the two electronic states from the figure. In particular, the \( k \)-space wave function of motif-a displays a minor component with a uniform distribution around the \( \Gamma \)-point. Whereas, the \( k \)-space wave function of motif-c has a local maximum (with more substantial component) around the \( \Gamma \)-point, evidencing the effect of the intervalley coupling mechanism. In the computation of \( \Gamma \)-component, we may use too large integration radius \( \Omega \), so that a part of Bloch components in \( \Gamma \)-component do not give rise to no-phonon vertical transition with the hole. Subsequently, motif-a has a slightly larger \( \Gamma \)-component but one order of magnitude weaker in oscillator strength than motif-d. The same argument can also explain that the oscillator strengths in some core/shell QDs are less than one tenth of those in motif-c or motif-d, regardless of the advantage of the former in the \( \Gamma \)-component of the electronic state.

To access the robust of motif-c and motif-d for intense light emission, we increase the Ge core radius from 5 ML to 10 ML for motif-c and motif-d core/multishell QDs (labeled as motif-c-2 and motif-d-2). We also add six Ge MLs to the outermost of motif-c and motif-d core/multishell QDs (labeled as motif-c-3 and...
motif-d-3). Finally, we alternatively change the outermost six Ge MLs to two Si MLs (labeled as motif-c-4 and motif-d-4). Figure 7 depicts the calculated emission spectra of these modified QDs. Interestingly, we find a further enhancement in light emission from motif-c-2 and motif-d-2 core/multishell QDs. In other cases, the luminescence is reduced about three times but is still hundreds of times stronger than that of corresponding Ge QDs. In this way, we have shown explicitly that based on the valley coupling mechanism, the light emission can be significantly improved through interface engineering.

4. Conclusion

By performing atomistic semiempirical pseudopotential calculations, in this work, we attempt to unravel the hierarchical relationship between two primary mechanisms proposed to explain the light emission in both Si and Ge indirect bandgap QDs. We find that in both Si and Ge QDs, the space confinement mechanism originating from the Heisenberg uncertainty principle dominates the zero-phonon light emission. While the surface-potential-induced intervalley coupling mechanism plays a minor role, which causes scattering of QDs away from the strong overall trend of light emission intensity against the confinement energy. This implies that one may engineer the surface potential to enhance the light emission of Si or Ge QDs significantly. In Ge/Si core/shell QDs we discover that the emission intensity could indeed change by one order of magnitude as varying Si shell thickness. Because the surface defects are absent in all calculated QDs, and the emission intensity does not monotonically change with the Si shell thickness, the enhanced emission intensity in Ge/Si core/shell QDs is due to neither the suppression of non-radiative recombination nor the severe localization of holes, which are suggested by Miyazaki et al [39, 40].

We further engineer the Ge QD interface by bringing four motifs of Si/Ge multiple layers, which were designed to have intense light absorption for superlattices or nanowires. We find two out of four motifs always give rise to two orders of magnitude enhancement in light emission relative to the Ge and Si QDs. So far, we study ideal Si and Ge QDs in spherical shapes. Note that complex structures on QDs’ surfaces are reported in voluminous literature [86–89]. For instance, in our previous work [89], we have found that the surface of Si QDs embedded in an oxide matrix can contain numerous interface defects, which will strongly affect the QD PL efficiency and optical absorption. It indicates one may further enhance the light emission from Ge and Si QDs via surface engineering by considering these complex surface factors. Our findings shed new light on light emission from Si and Ge QDs and undoubtedly give good prospects to realize high-efficiency Si-based light sources.

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