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Direct band gap silicon quantum dots achieved via electronegative capping

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We propose a theoretical concept of switching between direct and indirect band gap character in silicon quantum dots (SiQDs) by the use of surface potential induced by the ligands or environment in which SiQDs are immersed—both cases are studied. Theoretical simulations show that the density of states of confined electrons in both real and k space can be dramatically altered by engineering the local electrostatic field. Especially interesting is modification of the lowest excited states, which appear in the Γ valley for electronegative field that “pulls” electrons towards the SiQD surface. Opposite sign of the field does not have such effect at all. Hence we conclude a general trend of promotion of directlike radiative transitions by electronegative capping/environment. The rates are enhanced by more than two orders of magnitude compared to “normal” SiQDs, which can be as high as the values characteristic for direct band gap semiconductors. This model is in agreement with observed experimental properties of SiQDs with covalently bonded electronegative ligands.

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I. INTRODUCTION

Switching between the direct and indirect band-gap-like radiative transitions could be very useful for tuning optical qualities of quantum dots (QDs) of many important semiconductor materials, such as, e.g., silicon. Light emission from silicon based materials is of great interest for monolithic integration of optoelectronics and photonics with microelectronics [1–3]. Indirect band gap bulk silicon is not suitable for this purpose and the most promising platform towards efficient and tunable emission is silicon QDs (SiQDs) whose optical and electronic properties are modified by the quantum confinement. Size-tunable optical band gap allows for emission spectrally tunable in wide UV-to-IR regions (260–1100 nm), attractive for the currently developing market of QD-based light-emitting diodes and displays [4–6]. Nontoxicity [7–9], biodegradability [10], and superior photo- and pH stability [11] of SiQDs open opportunities in traditionally high health risk areas such as medicine or cosmetics. However, even though quantum confinement in SiQDs leads to considerable improvement in radiative rates, their magnitude remains still very low (e.g., 10^4 s^{−1} for small ~ 2.5 nm H-capped SiQD), compared to direct band gap semiconductors utilized for light emitter and laser applications (of the order of 10^7 – 10^9 s^{−1}). The reason for this low radiative rate is in phonon assisted radiative transitions, resulting from an indirect band gap of bulk silicon. As has been shown recently using Fourier transform of atomistically calculated wave functions, even small SiQDs have a persistently indirect character of the “fuzzy” band structure [12]. On several occasions, bright fast emission with high rates of 10^7 – 10^9 s^{−1} has been reported experimentally from various chemically synthesized SiQDs with organic capping [13–19]; however, a clear understanding and underlying physical model has been missing, leaving the speculation over the origin of the fast emission unresolved. Needless to say, the physics of emission of SiQDs is, in general, challenging and not yet fully controlled due to the complex interplay between the core and surface chemistry. Furthermore, approaches leading to emission improvements in

terms of emission efficiency or color tunability using surface engineering are understood even less. For the latest developments in this field we also recommend a recent review, Ref. [3].

Partial explanation of the observed enhancement of the radiative rates appeared only very recently in Refs. [20,21] as related to an appearance of new electron states in the Γ valley of the Brillouin zone at the SiQD band edge. Even though a similar result has been achieved by both models, agreement on the origin has not been reached. While the tight-binding calculations of Ref. [20] indicate that the carbon atoms at the QD surface may lead to an appearance of the electron states in the Γ valley in the absence of strain, Refs. [12,21] suggest that this effect can only arise as a result of a relatively large ($\sim 3\%$) ligand-induced strain [21] and as such is not necessarily *per se* linked to the carbon atoms on the surface. Furthermore, the strain induced by ligands was found not to be enough to induce observed enhancement in rates on its own. Hence, the origin of the fast emission in the particular case of carbon capping is not completely clear and no further implications of this effect have been obtained.

In this paper, we suggest a general effect that in our understanding stands behind the observed fast radiative rate and we offer far-reaching implications to open possibilities of manipulation of electronic density in QDs in real and k space by surface charge. The effect we describe is, in essence, independent of the used QD material, but its greatest practical implications are obtained for indirect band gap materials, such as silicon, where enhanced light emission is one of the long-term desired properties. We found that specifically for the case of SiQDs, an electronegative type of ligand or environment leads to a direct band gap character, which is not the case for the field of opposite sign (electropositive). By tuning the electronegativity magnitude and character, we are able to suggest “ideal” conditions to obtain direct band gap SiQDs, and our theoretical findings are in agreement with the experimental observations of various research groups and could therefore serve as the underlying mechanism that has been missing up until now.

II. MODEL

SiQDs of different sizes (1.8–4 nm) are simulated using an $sp^3d^5s^*$ empirical tight-binding (TB) approach [22]. Optical transitions are calculated in the diagonal approximation for the coordinate matrix element [23] neglecting the assistance of phonons. For the purpose of tight binding, electronegativity χ_{spec} is described as a weighted average of s - and p -orbital energies (ϵ_p and ϵ_s , respectively) [24] by equation

$$\chi_{spec} = (m\epsilon_p + n\epsilon_s)/(m + n), \quad (1)$$

where m and n are the number of electrons in the p and s orbitals, respectively. Hence, the more electronegative elements have lower orbital energies. Electronegative ligand $R^{\delta-}$ on top of the QD is simulated as a virtual atom with lowered energies of valence s and p orbitals with respect to the bulk Si $E_p(\text{Si})$ by a variable $|\Delta_{s,p}|$. In a general case, both s - and p -orbital energies should be shifted, however, it appears that shift of the s -orbital energy has only negligible influence on the final results. Hence, in the following we will refer only to the p -orbital energy shift $|\Delta_p|$. Obviously, this is a very crude approximation and the rigorous modeling of the charge transfer effects between the QD core and the surface/ligand is to be performed only using self-consistent approaches rather than by introducing *ad hoc* energy shifts. Still, self-consistent *ab initio* simulations remain quite challenging up to now. On the other hand, the tight-binding procedure offers an efficient approach to analyze the wide range of nanocrystal sizes and capping energies. By comparing these results to the available experimental data one can obtain important insights into the actual physics of the problem which will provide the basis for the following analysis by a more advanced technique. Moreover, the chosen definition of electronegativity also allows straightforward interpretation of our results in terms of the “ideal” capping element for enhanced emission in the SiQD system by comparing obtained ideal s - and p -orbital energies with existing materials (reverse engineering).

We also consider another model system—H-capped SiQD immersed in an electronegative environment in close proximity to the SiQD core. In the tight-binding model, the effect of the electronegative environment is simulated phenomenologically by the gradual change in the p -orbital energies of the Si atoms through the whole SiQD, following the general equation $E_p(r) = E_p(\text{Si}) + U(r/R_{\max})^2$, where $E_p(r)$ is energy of the p -orbital level for the Si atom on position r , $E_p(\text{Si})$ is the energy of the p orbital in bulk Si, U is the variable factor defining the magnitude of the electronegative effect (local field), and $R_{\max}$ is the radius of the SiQD. This effect is similar to what is known as “band bending” on semiconductor-oxide interfaces as a result of localized surface charges. Such analysis allows us to see the influence of the spatial profile of the field on the changes observed in band structure, relevant for future experimental realization of the “ideal” system.

After the energy spectrum is obtained, we proceed to the fuzzy band structure calculation [12]. In particular, for each confined state $|n\rangle$ with the energy E_n we find the Fourier component $C_{\nu}(\mathbf{k})$ and sum the squared absolute values of the Fourier components for different orbitals, $\rho_n(\mathbf{k}) = \sum_{\nu} |C_{\nu}(\mathbf{k})|^2$. The probability $\rho_n(\mathbf{k})$ is averaged over equivalent Δ directions of the vector $\mathbf{k}$. To calculate the total wave

vector resolved density of states, we multiply $\rho_n(\mathbf{k})$ by the Gaussian $\exp[-(E - E_n)^2/\delta E^2]$ with $\delta E = 30$ meV and sum over all the states $|n\rangle$. This is a very powerful technique to analyze the entire spectrum of confined carriers. The real-space density $|\Psi(r)|^2$ is obtained by adding the absolute values of the tight-binding expansion coefficients $|C_{\nu}(\mathbf{a})|^2$ for different s, p, d, s^* orbitals ν ($\mathbf{a}$ is the atom coordinate), convoluting in real space with a Gaussian with the dispersion ~ 0.3 nm and averaging over the angle of the vector $\mathbf{r}$.

III. RESULTS

The main result of our simulations is presented in Fig. 1, where we show the wave vector resolved density of carrier states, Figs. 1(b) and 1(c), and the real-space wave functions, Fig. 1(d), for the Si QDs covered with electronegative ligand (lower panels) and for the Si QD passivated with hydrogen (upper panels). Figure 1(b) demonstrates that electronegative ligand leads to the formation of new states in the Γ valley located at the bottom of the conduction band (as in direct band gap materials)—compare panels (b) and (c) in Fig. 1—and dramatically enhances the phononless radiative transition rates from ground states (from $2.5 \times 10^4 \text{ s}^{-1}$ to $3.1 \times 10^7 \text{ s}^{-1}$ for ~ 2.5 diameter QD in Fig. 1). The opposite sign field, i.e., electropositive, does not have such impact. It is very interesting to compare the real-space densities for H-capped SiQD and electronegative ligand in Fig. 1(d), showing that the real-space “pull” effect on the electronic density $|\Psi_e(r)|^2$ by the electronegative capping is present as we would intuitively expect.

In the following Secs. III A and III B we elaborate on the effect of the electronegative field induced in two different scenarios: (i) SiQDs capped with covalently bonded electronegative atom/ligand and (ii) SiQDs capped with hydrogen and immersed in an electronegative environment. Both systems are compared to a reference H-capped SiQD system, calculated using the hydrogen parameters from Ref. [25].

A. Electronegative ligand

The general effect of the electronegativity, represented by $|\Delta_p|$, on a SiQD band gap and radiative rate of the HOMO-LUMO transition is shown in Fig. 2 for SiQD diameters between 1.8 nm and 4 nm. Band gap shows nonmonotonous dependence on the shift Δ_p [Fig. 2(a)]. This is caused by the fact that for small negative values of Δ_p , the electron ground energy appears to be only weakly affected while the hole energy decreases faster and for large negative Δ_p , corresponding to the strong surface electronegativity, and the electron energy decreases fast, while the hole energy saturates. The band gap values are peaking at $\Delta_p \approx -2$ eV and rapidly decrease for larger shifts. This narrowing of the band gap for strong electronegative capping is consistent with the results obtained for ultrasmall Si clusters covered with F and Cl in Refs. [26–29].

Our central result is the strong modification of the phononless radiative rate for the electron-hole pair ground state (HOMO-LUMO) transition shown in Fig. 2(b). This dependence shows prominent maximum for $-6 \text{ eV} < \Delta_p <$

FIG. 1. (Color online) Summary of the effect of the electronegative field on the electronic system of SiQD with diameter 2.5 nm. Top row: Hydrogen-capped SiQDs; Bottom row: SiQD capped with a covalently bonded electronegative element. (a) Scheme of the system. (b) Wave vector resolved electronic density (fuzzy band structure) with indicated radiative recombination rate for the HOMO-LUMO phononless transition. (c) Wave-vector-resolved electronic density for the two lowest HOMO and LUMO states (energy of the states is indicated). (d) Real-space-resolved electronic density of the HOMO and LUMO states.

FIG. 2. (Color online) General influence of the covalently bonded electronegative capping for various sizes of SiQDs (1.8–4 nm) “capped” with the virtual element $R^{\delta-}$ simulated as an Si atom with shifted p -orbital energy by Δ_p from the bulk Si value. (a) Band gap energies (HOMO-LUMO transition). (b) Radiative rates. (c) Bulk Si band structure in the Γ -X direction with depicted relative energy position of the p orbitals of various elements with respect to silicon (red). In green are depicted the “ideal” capping elements that might be leading to enhanced radiative rate (gray area). Y axes are linked for all panels.

–2.7 eV (gray shaded area in all panels), present for all the studied SiQD sizes. The highest radiative rates found in Fig. 2(b) correspond to the p -orbital energy shift $\Delta_p = -3.5$ eV, when the p -orbital level is positioned within the Si band gap. This means that the strong modification of the confined carrier states is a result of resonant enhancement of the mixing between the electron states in the X valley and the hole states in the Γ valley. While the valley mixing, including the Γ -X mixing, is well known in semiconductor nanostructures [30–35], in our case the effect is much stronger. The resonant effect for the p orbital might also explain why the radiative rate and band gap energies in Figs. 2(a) and 2(b) are independent of s -orbital energies and only relatively weakly dependent on the Δ_p for p -orbital energy falling into the bulk Si band gap energies.

For SiQDs up to ~ 2.5 nm, the highest radiative rate reaches values of $\sim 10^8$ s $^{-1}$, typical for direct band gap QDs such as CdSe QDs [36]. Fast “direct band-gap-like” radiative rates ($\gtrsim 10^7$ s $^{-1}$) are emphasized by the pink rectangle. This defines the “ideal” range of Δ_p for an enhanced radiative rate, which includes various real elements, such as C, Se, S, Br, N, and Cl. This is shown in Fig. 2(c), where p -orbital energies of various atoms with higher electronegativity than Si are shown, in comparison to bulk Si band structure. Out of all the ideal elements, suggested in Fig. 2(c), a clear link to real systems that have been experimentally investigated is provided by $\Delta_p = -3$ eV, which leads to enhanced radiative rates and well reproduces tight-binding parameters of carbon in literature [37], allowing us to effectively simulate capping by CH $_3$ methyl ligands (C-SiQDs). Organic ligands

FIG. 3. (Color online) Wave-vector-resolved electronic density (“fuzzy band structure”) in H-capped SiQD [(a)–(c)], C-SiQDs ($\Delta_p = -3$ eV) [(d)–(f)] and for H-capped SiQDs immersed in an electronegative field simulated by $U = -3$ eV [(g)–(i)], all simulated for SiQD diameters of 1.8, 2.5, and 3.5 nm. Black dotted lines represent bulk Si band structure. Density of states is normalized to the high density around 3–3.5 eV, i.e., to the density of states of the former bulk Γ_{15} band. Black lines with an arrow indicate phononless radiative recombination between HOMO and LUMO states, with the rate indicated in all panels. The bottom panels show integral wave-vector-resolved electronic density for the HOMO and LUMO states, integrated over the range of 100 meV.

are common in literature, which gives us the advantage to compare our findings with experimental observations.

In Fig. 3 are shown the wave-vector-resolved electronic densities as a function of energy (“fuzzy band structure”) for SiQD of diameters 1.8, 2.5, and 3.5 nm. Panels (a)–(c) depict H-capped SiQD and panels (d)–(f) show C-SiQDs ($\Delta_p = -3$ eV). The integral wave-vector-resolved electronic density, integrated over a range of 100 meV around HOMO and LUMO states, is shown in the bottom panels in Fig. 3. The wave-vector- and real-space-resolved electronic densities are shown separately for HOMO and LUMO states in Fig. 1 for the selected middle sized ~ 2.5 nm SiQD.

For H-capped SiQDs, calculated wave-vector-resolved carrier densities follow the bulk Si dispersion (dashed lines in all panels), in agreement with the density functional theory (DFT) simulations in Ref. [12]. The overlap between electron and hole wave-function densities in both k -space and real space remains low [compare panels (c) and (d) in Fig. 1 and also the bottom panels (a)–(f) in Fig. 3]. Therefore, the phononless radiative recombination rate from the lowest excited state in H-capped SiQDs is very low—of the order of 10^4 s $^{-1}$ —reaching approximately 10^6 s $^{-1}$ for the smallest SiQDs of diameter 1.8 nm. Hence, the optical transitions in H-capped SiQDs of all sizes benefit from the assistance of phonons [38].

In the case of C-capped SiQDs, dramatic modifications are visible for the bottom of the conduction band around the Γ point [compare panels (c) and (d) in Fig. 1 and also the bottom panels (a)–(f) in Fig. 3]. In particular, considerable electronic density occurs for the LUMO state at the Γ point, in strong

contrast to the situation in H-capped SiQDs. Interestingly, also the energy distance between energy levels at the bottom of the conduction band is much smaller for C-SiQDs [note that the two lowest electronic states are separated by ~ 70 meV and hole states ~ 60 meV in the bottom panel of Fig. 1(c), compared to 350 meV for H-SiQD electron states and 140 meV for hole states]. Apart from the new Γ -located electron states, the electronegative capping also changes the structure of the hole eigenstates $|\Psi_h(r)|^2$: In the H-capped QDs the ground hole state wave function is of p -type character. Ligand decreases the energy of the p -type state, and the s -type hole state becomes the ground one. All these changes in both real space [shown previously for 2.5 nm SiQD in Fig. 1(d)] and wave-vector-resolved electronic density lead to dramatically enhanced radiative rates, indicated for the HOMO-LUMO transition in Fig. 3 and in Fig. 2(b).

B. Electronegative environment

Now we will analyze in more detail the effect of the “pull” on the electronic density towards the surface by the effective local electric field.

Panels (g)–(i) in Fig. 3 show the wave-vector-resolved electronic density of states for H-SiQDs of sizes 1.8, 2.5, and 3.5 nm in a field described by $U = -3$ eV. Interestingly, this type of field leads to very different changes in the band structure of SiQDs as compared to panels (d)–(f). A dramatic drop of both the conduction and valence bands and overall shrinkage of band gap is accompanied by modified electronic densities, showing weaker impact on the radiative rates, when

FIG. 4. (Color online) Wave-vector-resolved density of carrier states in 2.5 nm large H-capped SiQD immersed in electronegative environment simulated by gradually lowered p -orbital energy of Si atoms in the SiQD by U . Density of states is normalized to the high density around 3–3.5 eV, i.e., to the density of states of former bulk Γ_{15} band.

compared to covalently bonded ligands. In Fig. 4 is shown separately the effect of various fields U between 0 and -5 eV on SiQD of the size of 2.5 nm. The value $U = 0$ corresponds in such case to the typical H-capped SiQDs and $U = -3$ eV is to be compared with the C-SiQDs, however, unlike for methyl-like capping, the p -orbital shift is not abrupt (i.e., affecting only the surface atom), but rather penetrating the whole SiQDs, gradually lowering the p -orbital levels of all Si atoms inside the SiQD core. The field decay as a result of dielectric shielding effect is simulated by quadratic function. Comparing results of C-SiQDs with the results obtained here, we can see that covalent bonding is more efficient, leading to faster radiative rates. However, the field effect here could be of interest for dramatically lowered band gap energies to the level of bulk silicon and below. The drop in band gap energies for higher fields is in agreement with effects expected from very high electronegativity capping, such as Cl or F.

IV. DISCUSSION

Now we discuss the possible realizations of an “ideal” capping for enhanced radiative transitions and compare our results to available *ab initio* simulations. The available elements with higher electronegativity than silicon are B, As, Te, At, P, Se, C, S, I, Br, Cl, N, O, and F. From this pool, it appears that only few with lower p -orbital energy than Si are beneficial, such as C, Se, S, Br, N, and Cl [gray area in Fig. 2(c)] and the other electronegative elements such as O or F are too far from the interesting interval of Δ_p . There is not much information on Se, but S has been reported by Puzder *et al.* [39],

to lead to formation of deep interband states in a similar way as O [39–41], due to a tendency to form high strain double bonds and bridging bonds. The formation of defect states has also recently been suggested for N [42], another element in our “ideal” capping zone in Fig. 2. For Cl (and F) cappings in ultrasmall Si clusters, DFT calculations [27–29] indicate strong impact on the electronic states for higher than 50% surface coverage. Full coverage of the surface by Cl was shown to lead to the dramatic drop in the valence and conduction band energies with the band gap smaller than in bulk Si [28]. Furthermore, 50% surface coverage enhances the radiative rate ~ 40 times up to $\sim 1.2 \cdot 10^8 \text{ s}^{-1}$ [28], while at larger coverage the rate decreases. The calculations for F have revealed a similar, but less dramatic drop of the valence and conduction band states energy and also a slight increase in the radiative rate in the case of partial surface coverage, followed by a drop for full surface coverage [29]. Simulations by König *et al.* [43] using density functional Hartree-Fock calculations shows a similar drop in HOMO and LUMO energies for small Si clusters, with the drop increasing with the polarity of the capping. Our results indicate that for large SiQDs with $D \gtrsim 4$ nm, covered with F or Cl, one can achieve the band gap smaller than bulk Si and, simultaneously, relatively large radiative rates $\sim 10^7 \text{ s}^{-1}$ [Fig. 2(b)]. However, such material might not be chemically stable. Hence, up until now, C-linked species remain the most beneficial realized ligands for enhanced radiative rate (and enhanced efficiency of emission) of SiQDs. C-linked capping is easily accessible via organic capping with molecules such as alkyl chains, provided by various synthesis techniques. The advantage of C-linked ligands is also that optical band gap was found to remain size tunable in visible spectral range, in

excellent agreement with *ab initio* simulations by Reboredo and Galli [44] for small Si clusters capped with alkyls.

An interesting possibility is also to consider additional effects of possible ligand-induced strain, as discussed in Ref. [21]. An interesting discussion on steric effect is also included in the *ab initio* study by Reboredo and Galli [44], where it is suggested that surfaces with larger bond densities, such as (111) will experience higher strains than, e.g., (100), which could be taken into account in future studies. Unfortunately, it is still unclear whether the strain induced by alkyl capping is enough to induce the observed high radiative rates by itself, which raises a question, whether the roles of ligand-induced strain and electronegativity do not play hand in hand, giving the final direct band-gap-like behavior observed in most organically capped SiQDs.

V. CONCLUSIONS

We conclude that covalently electronegative capping allows one to achieve fast direct radiative transitions as a result of Γ -X valley mixing induced by the covalently bonded ligand. The occurrence of the new Γ -valley levels leads to fast Γ - Γ

phononless radiative recombination with holes, i.e., enhanced radiative rate, observed experimentally (e.g., Refs. [18–20]). As a result, the silicon quantum dots effectively behave as if made from the direct band gap semiconductor. Our tight-binding simulations, despite the inherent limitations stemming from their semiempirical character, provide important insights into the physics behind the radiative rate enhancement and raise the demand for both more advanced simulations and the search for realizations of efficient surface capping by various electronegative chemical elements.

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