Direct bandgap silicon quantum dots achieved via capping with electronegative ligands

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Silicon quantum dots (SiQDs) are a material of increasing importance for future technologies - composed of one of the most abundant and non-toxic materials on Earth and have been shown in past decades to offer excellent optical and electronic properties, including positive optical gain. Since bulk silicon is an indirect bandgap semiconductor, its radiative rate is low, compared to direct bandgap materials. This implies poor band-edge absorption and poor emission, both essential for applications in photonics, optoelectronics and photovoltaics.

A partial elevation of the radiative rate is offered by quantum confinement in SiQDs smaller than the excitonic Bohr radius (~4.9 nm). The enhancement, however, is not yet sufficient to make SiQDs competitive with direct bandgap materials. This has been confirmed experimentally for both H- and O-terminated SiQDs. The persistent indirect bandgap character of SiQDs as small as ~2 nm has been recently evidenced also by rigorous DFT simulations [1]. These results suggest that quantum confinement itself is not sufficient to replace the direct bandgap materials, often composed of toxic and/or scarce materials, by silicon. Various other routes towards enhancement of the radiative rate have been employed, including modifications of the optical density of states or via resonant coupling to plasmonic structures.

In our work, we have explored yet another possibility - surface engineering [2]. We have shown that direct bandgap-like states at band edge energies can occur for SiQDs capped with carbon-linked ligands, such as alkyl molecules. Our interpretation builds on the idea that electronegative ligands (carbon) attract the electrons towards the surface of the SiQD, i.e. modify the electronic density in the SiQD in real space. This results also in strong modifications of the electronic density in k-space. For all studied sizes (~2-4 nm), this leads to occurrence of conduction band states that are at the band edge located in the Γ valley, as shown using tight binding simulations coupled with Fourier transformation. The strong radiative rate modification is evidenced from experimental results (absorption, emission) on ensemble and single QD levels.

In this study, we analyze the influence of electronegative capping in general by tuning the valence s/p-orbital energy of the capping element. It is found that lowered p-orbital energy with respect to silicon is beneficial, especially when positioned within the bandgap of the SiQD (see figure). Surprisingly, carbon, one of the common ligands used for SiQDs, is found to offer almost ideal properties to induce enhanced radiative

rate in SiQDs. This is in good agreement with the more rigorous DFT simulation of small SiQDs (up to ~2.5 nm) by another group [3]. Very interestingly, this DFT study has led to yet another possible interpretation of the enhanced rate – direct bandgap-like transitions caused by ligand-induced tensile strain [3]. This could be an additional factor playing role.

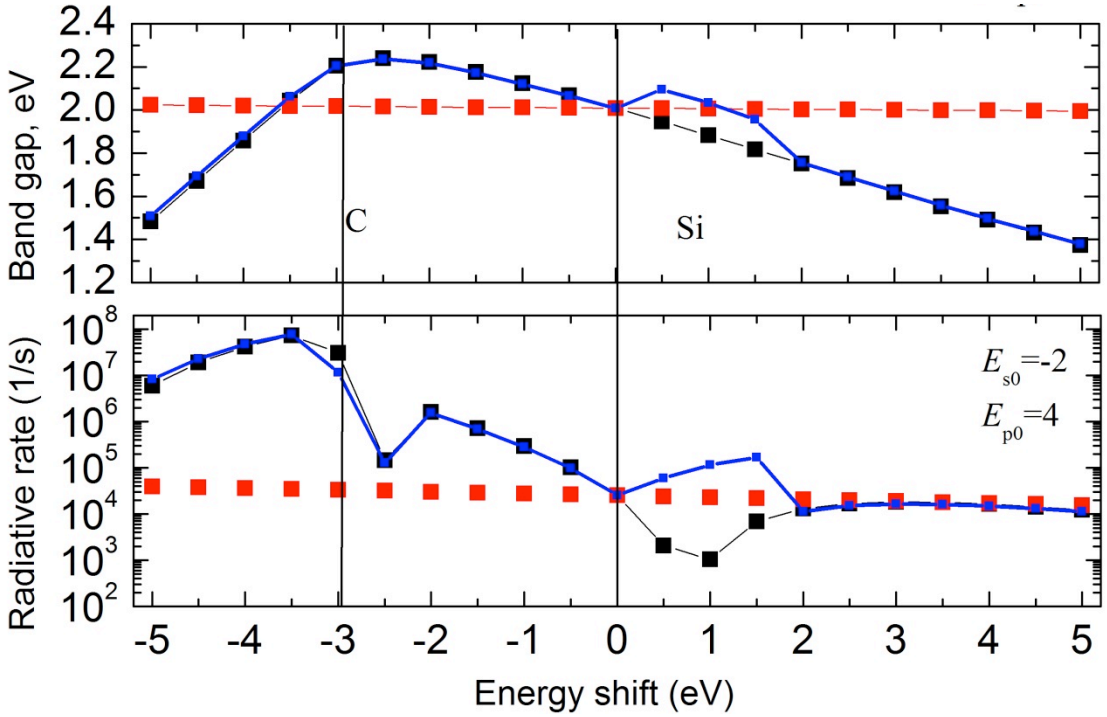

Figure: Shifting s- (red), p- (blue) or s&p- (black) orbital energy in tight binding simulations leads to changes in bandgap energy (top panel) and radiative rate (lower panel).

[1] P. Hapala et al., Phys. Rev. B 87 (2013) 195420.

[2] K. Dohnalova et al., Light: Science and Applications 2 (2013) e47

[3] K. Kusova et al., Adv. Mater. Int., 2014, accepted for publication