Silicon quantum dots: Towards more efficient all-silicon solar cells

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Finding **silicon-based solutions for more efficient conversion of solar energy** is absolutely necessary, if photovoltaics is to become the major source of energy in future. Silicon provides all necessary prerequisites – excellent electronic and material properties, nearly ideal band-gap energy, virtually no toxicity and nearly unlimited, easily accessible material resources. A single junction Si solar cell has conversion efficiency limit of ~ 33% (experimentally ~ 25 % [1] has been reached with crystalline silicon). A possible enhancement could be facilitated by novel forms of silicon that would provide carrier multiplication and/or offer different optical properties for multi-junction architecture. For this purpose, amorphous Si or Si nanostructures are being investigated [1]. In this work we concentrate on relevant properties of Si quantum dots (SiQDs).

SiQDs have many advantageous properties - besides size-tunable band-gap, transition rates are enhanced and slower hot carrier relaxation together with stronger Coulomb interaction might facilitate dramatic enhancement of the **carrier multiplication** efficiency. As we have recently reported, in closely packed SiQD systems, carrier multiplication occurs with nearly 100% efficiency via **space separated quantum cutting** [2-4]. Carrier multiplication and long lifetime of the multiplied carriers have been confirmed from steady-state photoluminescence quantum yield measurements [2,3] and also by ultrafast induced absorption spectroscopy [4]. Very recently, the effect of space separated quantum cutting has been investigated also theoretically [5], confirming its possible occurrence via Auger hot carrier “recycling”. This is an efficient effect, which we have reported in our samples before [6], where it enabled observation of strong emission from the Γ–Γ transition, usually quenched by the hot carrier relaxation on ultrafast time scale. High efficiency of the carrier multiplication in closely packed SiQDs occurs nearly at the ideal limit of twice the band gap energy, shifted only by 300 meV [3, 4]. Thanks to that, the multiplication effect for the larger SiQDs takes place already within the solar spectrum, which together with the microsecond lifetime of the multiplied carriers makes this material relevant for real-life photovoltaic application.

Covalent character of Si and generally stronger influence of surface states on optical and electronic properties of smaller SiQDs, can also lead to essential modifications in electron and hole wavefunctions (see figure below). In our most recent investigations on synthesized SiQDs terminated by organic carbon-linked ligands [7,8], we have found **direct bandgap-like radiative rates** and 10-100 times **enhanced absorption cross section** at the band edge, when compared to hydrogen/oxygen terminated SiQDs. We have demonstrated that the direct bandgap-like **emission is spectrally fully tunable** via size of the SiQDs (see figure below), which is in stark contrast to the limited tunability of oxygen terminated SiQDs and has been previously reported only from chemically unstable hydrogen terminated SiQDs [9]. Concerning rate and external quantum efficiency, this material has similar efficiency of emission as bare CdS. Enhancement of the absorption cross-section at the band-edge is very high, when compared to hydrogen/oxygen terminated SiQDs, but absorption remains lower than in truly direct bandgap materials, due to the low density of the direct bandgap-like states. Here, the true advantage remains in the material itself – silicon - and its ultimate performance.

Both effects – efficient carrier multiplication and direct bandgap-like transformation open new possibilities for photovoltaic applications of silicon for solar spectrum shapers or active QD-solar cell. In addition, spectrally tunable optical bandgap is reported for a chemically stable form of SiQDs and is advantageous for all-Si multi-junction architectures.

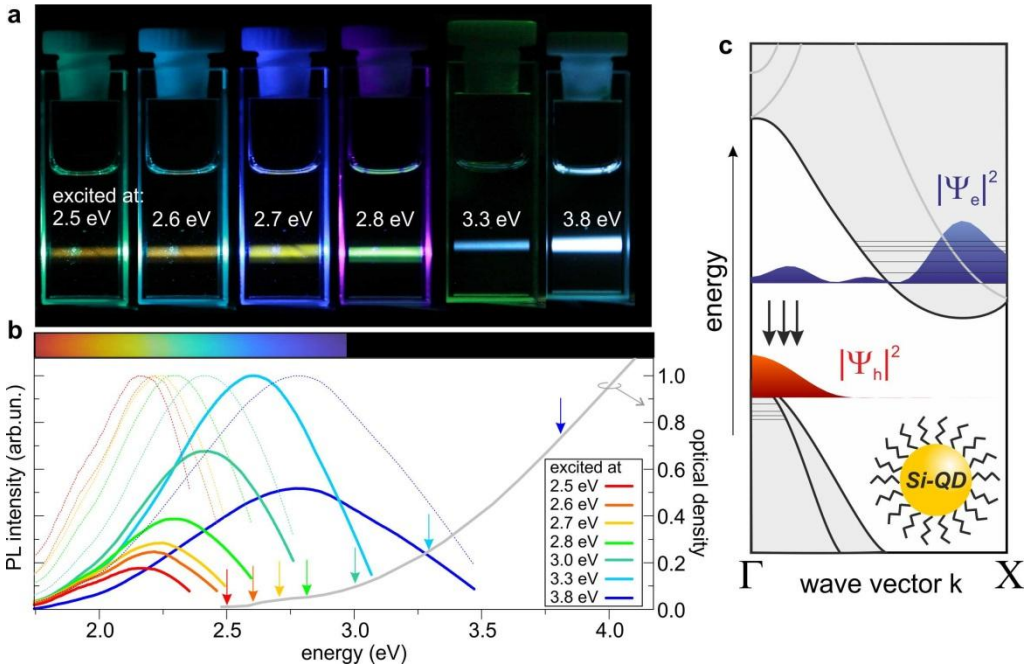

Figure – Radiative recombination in direct bandgap-like SiQDs: (a) True color photo of PL and (b) PL spectra upon various excitation energies. Sample was excited by pulsed laser (Nd:YAG, OPO system, 7 ns, 100 Hz). (c) Sketch of k-space density of electron and hole wavefunctions in the lowest excited state, as calculated by tight binding technique in methyl-capped SiQD.

[1] for review see M. A. Green et al., Prog. Photovolt: Res. Appl. 21 (2013) 1-11
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[3] Timmerman et al., Nature nanotechnology 6 (2011) 710
[4] Trinh et al., Nature Photonics 6 (2012) 316
[5] Govoni et al., Nature photonics 6 (2012) 672
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[8] Dohnalova et al., Light: Science and Applications 2 (2013) e47
[9] e.g. Wolkin et al., Phys. Rev. Lett. 82 (1999) 197