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Can silicon ever be a true direct bandgap semiconductor?

The first observation of a new short-lived photoluminescence band from silicon nanocrystals offers fresh hope.

Silicon is ubiquitous in the electronics industry but is unsuitable for optoelectronic applications because it has an indirect bandgap. In other words, the minimum of the conduction band and the maximum of the valence band have different momenta, so electrons in the conduction band can only annihilate holes in the valence band with the help of phonons. However, the probability of electrons and phonons (vibrations of the crystal lattice) interacting in silicon is low, and so this widely used material is actually a very inefficient light emitter. Many methods have been developed that can improve the light emitting properties of silicon and quantum-confinement effects have been found to be particularly effective. Consequently, two optical emission bands from silicon nanostructures have been identified: a slow 'red' band that is assigned to excitons (bound states of electrons and holes) confined in silicon nanocrystals, and a fast 'blue' band that is usually assigned to defect sites at the interface between the nanocrystal and the surrounding silica matrix, or to defects in the matrix itself. Writing in *Nature Nanotechnology*, Tom Gregorkiewicz and colleagues at the University of Amsterdam and the Ioffe Institute in St Petersburg report that nanoscale silicon has a third fundamental emission band with properties that are significantly different from those of the 'red' and 'blue' bands¹.

As the size of a silicon particle is reduced, two fundamental quantum effects should occur: the bandgap should increase (the 'particle in a box' problem) and conservation of momentum should breakdown (because the localisation of charge carriers in space leads to their delocalisation in momentum space). Consequently, silicon nanocrystals can have emission properties that depend on their size, and nanoscale silicon will behave as a quasi-direct bandgap semiconductor because phonons are not needed to conserve momentum during the "recombination" of the electrons and holes. In 1990 it was demonstrated that porous silicon can efficiently emit light at visible and near-infrared wavelengths due to quantum confinement effects², and

since then researchers have developed various silicon nanostructures with similar light emission properties^{3,4}.

According to the quantum confinement model, as the size of the silicon nanocrystals is reduced, the optical emissions, which are related to fundamental band gap transitions, should move to higher energies (a blue shift). This phenomenon has been confirmed by numerous research groups and is observed in the slow 'red' emission from different modifications of nanosilicon. On the other hand the defect-related 'blue' emission is independent of nanocrystal size. In contrast, the new fast emission band discovered by Gregorkiewicz and colleagues shifts to lower energies (a red shift), as well as increasing in intensity, for smaller nanocrystals (Figure 1). This visible band in the photoluminescence spectrum was measured using time-resolved optical spectroscopy, and the team attribute it to the direct recombination of non-equilibrium (or 'hot') electron-hole pairs in a process that does not involve phonons.

The Amsterdam-St Petersburg team was able to identify the new emission band by considering the fact that silicon also has a direct bandgap at the centre of the Brillouin zone (the Γ -point). However, this bandgap is about 3.3 eV, whereas the indirect bandgap is just 1.1 eV, so direct optical transitions have a negligible (and until now neglected) role in the emission properties of bulk silicon. Moreover, quantum confinement is expected to make this direct bandgap smaller, resulting in a red shift (whereas confinement makes indirect bandgaps bigger).

The emission band has a lifetime in the range of 10-100 picoseconds, and the energy of photo-excited carriers is far above the direct bandgap of bulk silicon. Therefore, at these timescales two fundamental electronic processes – hot carrier energy relaxation and Auger recombination – can influence the emission of light. The first process implies emission of optical phonons and has a characteristic time of 1-10 picoseconds. In the second process, the energy of an annihilated pair is transferred to an electron (or hole), which keeps the electron-hole bath 'hot' for a longer time. To clarify the origin of the new emission band, Gregorkiewicz and co-workers explored two excitation limits. At low excitation levels, statistically only one exciton per nanocrystal is generated and only the first process is possible. At high excitation levels, on the other hand, multiple exciton generation becomes possible and Auger recombination should govern the recombination dynamics. And these two distinct regimes were indeed observed experimentally.

Hot carrier emission has been previously observed in direct bandgap semiconductors such as GaAs (ref. 5), but it was 10^8 - 10^9 times less efficient than emission from fundamental direct bandgap transitions. Gregorkiewicz and colleagues estimate that hot emission represents a significant fraction of the overall emission from silicon nanocrystals (being about 1000 times less efficient than the emission from indirect transitions). Although we cannot say that silicon nanocrystals are true direct bandgap materials – the oscillator strength of the direct transition is three orders of magnitude lower than that of direct bandgap semiconductors – it may be possible to increase the oscillator strength further due to “true” direct band gap transitions by, for example, modifying the interface between the silicon nanocrystals and the surrounding matrix.

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References

1. de Boer, W. D. A. M. *et al. Nature Nanotech.* X, XXX–XXX (2010).
2. Canham, L. T. *Appl. Phys. Lett.* 57, 1046–1048 (1990).
3. Cullis, A. G., Canham, L.T. & Calcott, P. D J. *J. Appl. Phys.* 82, 909–965 (1997).
4. Bisi, O., Ossicini, S. & Pavesi, L. *Surf. Sci. Rep.* 38, 1–126 (2000).
5. Meier, F. & Zakharchenya, B. P. (eds), *Optical Orientation, Modern Problems in Condensed Matter Sciences*, North-Holland Publ. Co., Amsterdam 1984.

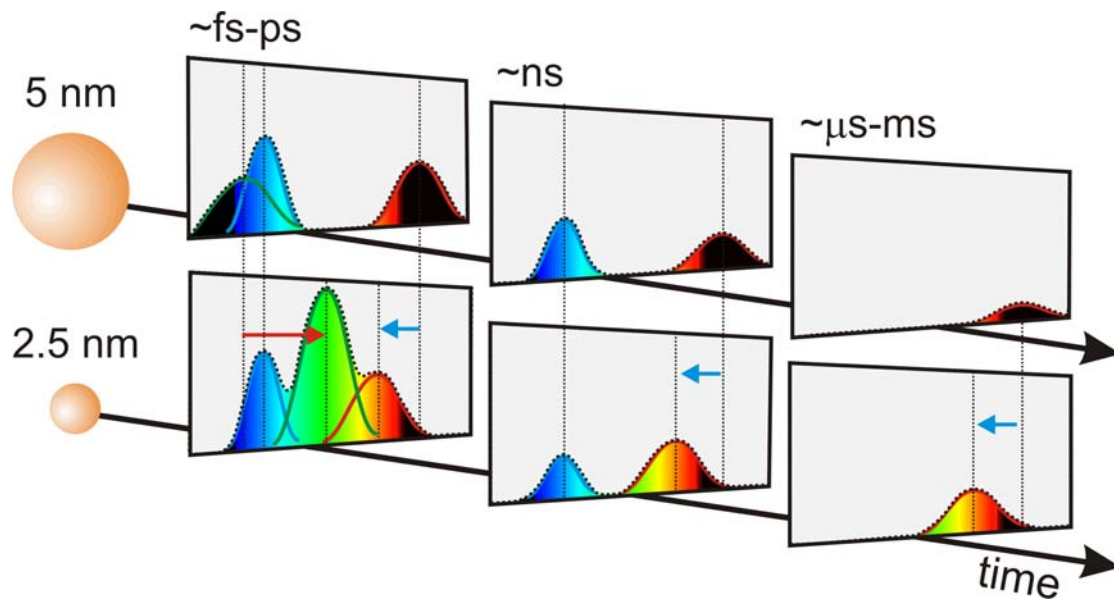


Figure 1. Time evolution of the three fundamental emission bands from silicon nanocrystals. The slow 'red' emission band, decaying in microsecond range and blue-shifting with the reduction the nanocrystal size is shown in red. The fast 'blue' emission band, decaying in nanosecond range and being independent of nanocrystal size is shown in blue. The ultrafast 'hot' emission band, decaying within 10-100 picoseconds and red-shifting with the reduction of the silicon nanocrystal size is shown in green. The black colour corresponds to the invisible optical range.