Core/shell Colloidal Quantum Dots for Silicon Compatible Lasers

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A light source integrated on silicon is a major missing link in silicon photonics. A new hybrid approach is to use colloidal quantum dots as a gain material. This technique boasts simple production, easy deposition and bright luminescence, tunable between 1000 and 2500nm. Lasing attempts with PbSe nanocrystals have proven difficult, because of the eightfold degeneracy of the first excitonic transition, resulting in a high lasing threshold. We investigate a new quantum dot by adding a CdTe shell around a PbTe quantum dot. This system could result in a type-II band alignment, lifting the degeneracy and resulting in low thresholds.

Introduction

Silicon photonics research tries to integrate optical circuits on a chip for applications in telecommunication and (bio)sensing. It focuses on silicon as a material system to reach these goals. With this choice silicon photonics can build on a vast library of production processes and tools from the CMOS industry. Moreover the high index contrast of the silicon-on-insulator substrates makes them highly suitable for extremely small scale circuits.

Silicon has however one major drawback. Its indirect bandgap makes it hard to include sources. Workarounds focus on crossing the indirect bandgap problem [1] or integrating an active layer on top of the passive silicon layer [2]. Traditionally for this last route III-V chips are made separately and bonded on the silicon substrate. This technique is advanced, but remains expensive and hard to scale up.

We propose colloidal quantum dots as a possible alternative. These quantum dots are made in a wet chemical synthesis and are spherical with diameters ranging from 1 to 10nm, corresponding to emission wavelengths going from 1200nm to 2500nm. Quantum yield is typically very high. Deposition is easy and can be tailored to the application, making this approach cost-effective and simple to scale up.

Core NIR quantum dots

Colloidal quantum dots are made in a wet chemical synthesis. This means we start from atomic precursor solutions of lead and a chalcogenide. We inject one precursor into the other at high temperature, resulting in nucleation of extremely small nanocrystals, followed by a homogeneous growth, until the desired size is reached. In this procedure the nanocrystal surface is capped with an organic fatty acid ligand for stability. The nanocrystals finally are suspended in a nonpolar solvent and stored until use.
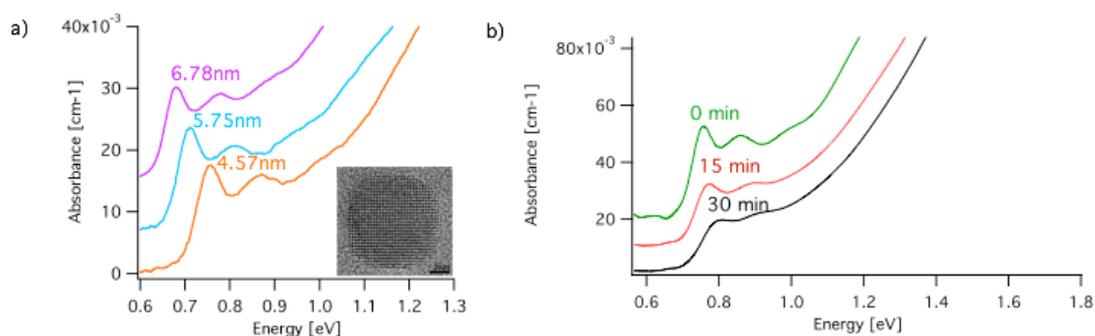
Figure 1: a) Absorption spectra of PbTe nanocrystals with increasing size. b) PbTe nanocrystals oxidize in air in a matter of minutes

Because lead chalcogenides have a large Bohr radius over 10nm, quantum confinement of the carriers splits the bands around the band edge into discrete levels. This quantum confinement effect is clearly visible in the absorption spectra of nanocrystal suspensions of different sizes, where the peak associated with the first excitonic transition clearly redshifts with increasing size (fig. 1.a). Moreover the luminescence from this transition is very efficient with quantum yields as high as 80% for PbSe[3].

These features make lead chalcogenide nanocrystals an interesting gain material for lasers. A first demonstration used PbSe nanocrystals in a glass capillary pumped by a 2ps Ti:Sapphire laser [4]. Lasing however was only observed at low temperatures up to 250K and at increasing threshold pump fluences up to several mJ/cm^2. This corresponds to several hundreds of MW of power to reach the lasing threshold, currently limiting it to pulsed operation. Attempts for lasing on silicon chip with PbSe nanocrystals filling up the holes of a photonic crystal cavity have stranded at the amplified spontaneous emission level, but were performed at room temperature and under CW pumping [5].

Currently there are two problems with these NIR emitting nanocrystals. The first problem is related to the eight-fold degeneracy of the excitonic transition. To reach population inversion for lasing each nanocrystal needs to have four excited electron-hole pairs. This explains the high lasing threshold. On top of that Auger recombination, where the exciton recombines by giving energy to another exciton instead of emitting a photon, becomes very efficient in these small quantum dots, which increases the threshold power and reduces the gain lifetime to a few picoseconds.

Secondly these nanoparticles oxidize in a matter of minutes, days or hours, depending on the material. Oxidation effectively reduces the size of the nanocrystal, blueshifting the spectra, reducing quantum yield and destroying the monodispersity of the nanoparticles (fig. 1.b).

Core/shell NIR quantum dots

For this purpose we are developing core/shell NIR emitting nanoparticles, consisting of a PbX core and a CdX shell (X=Se, Te). The shell is added in a second wet chemical procedure through exchange of lead atoms by cadmium atoms (cationic exchange). The thickness of the shell is tunable by choosing a specific growth time.

CdX (X=S, Se, Te) has a wider bandgap than PbX. At the interface the bands can align

in two ways (fig. 2.a). Type-I alignment resolves the oxidation problem, because the electron hole pair is confined to the core. Type-II alignment however could lift our eight-fold degeneracy. Upon excitation of a first exciton, the hole will be confined in the shell whereas the electron remains in the core. If a second exciton is created, the two holes in the shell and the two electrons in the core feel a coulomb repulsion, splitting the level and lifting the degeneracy. This implies population inversion is now reached upon excitation of just one exciton per nanocrystal, a regime in which Auger recombination is impossible. Hence a type-II core/shell nanocrystal would dramatically reduce the CW lasing threshold.

No data or model currently exists describing band alignments for quantum dots. Based on bulk values, we expect PbTe/CdTe to have the largest chance of having a type-II band alignment as a nanocrystal. Our measurements of the first exciton luminescence lifetime of the PbTe core nanocrystals show a lifetime of $1.4\pm0.1\mu s$ constant over the entire wavelength range and with a clear single exponential decay. PbTe/CdTe core/shell nanocrystals however show a double exponential decay curve (see picture). By fitting these curves we can extract two lifetime constants: one fast component of $1.5\pm0.5\mu s$ and one slow component of $7\pm0.5\mu s$. This result suggests that a second, longer lived decay path becomes available after adding a shell, next to the decay path of the exciton recombination in the core. The second path cannot be explained by a recombination of exciton fully located in the shell, because the bandgap is too wide. The only possible explanation left is a transition with slightly different energy between a core and a shell level. This indirect spatial transition would indeed increase the lifetime, because the overlap of the electron and hole wave function will be reduced. Hence this suggests a type-II alignment of the core/shell nanocrystals.

By deconvolution of the decay curve and integrating each exponential, we can deduct the spectrum of each decay path and determine the contribution of each decay path to the total steady state luminescence. The result is plotted for one nanocrystal suspension (fig. 2.b). We can clearly relate the spectrum of total intensity measured from the pulsed excitation experiments to the steady state data. This shows that for PbTe/CdTe core/shell nanocrystals the slow decay path, associated with an indirect spatial transition between core and shell, dominates the steady state luminescence.

Currently further investigation is ongoing to increase homogeneity of the shell around the core particles.

Towards a silicon compatible laser

For photonic integration a series of deposition methods are available with control over thickness and volume fraction. Dropcasting a pure nanocrystal film has resulted in thick high volume fraction, but inhomogeneous layers with cracks due to the drying procedure. This technique will be improved in the future. The best films were obtained by doping 20% polystyrene in toluene with organic capped nanocrystals and spincoating the polymer. This gives optically high quality films, however with low volume fractions limited to a few percent. Patterning is possible using standard UV contact lithography.

We have designed a CMOS silicon photonic test chip and fabricated it at LETI through the ePIXnet european network of excellence. It comprises of two sets of structures. One structure couples a photonic wire of 220nm height and 400nm width to a broad nanocrystal doped polymer waveguide through an adiabatic inverted taper structure. This converts
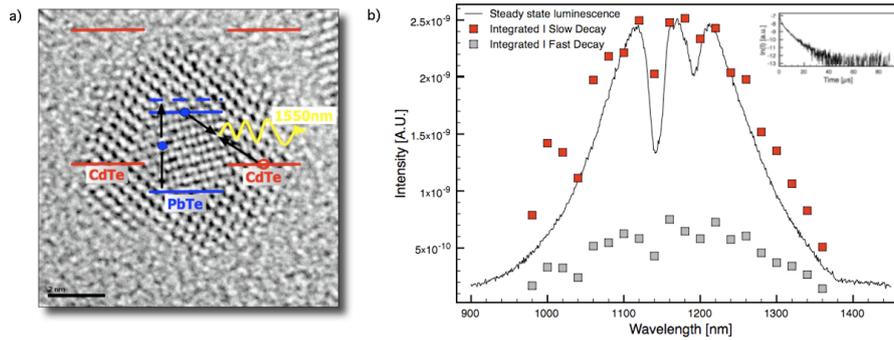
Figure 2: a) Type-II band alignment as opposed to type-I, where both core levels are in the shell bandgap. b) Steady state luminescence [solid line] correlated to amplitude of slow decay path [red squares] and fast decay path [grey squares].

the confined silicon waveguide mode to the broad polymer waveguide mode. The polymer waveguide will be defined later in our cleanroom facilities with nano imprint lithography. With this structure we will characterize the modal gain and optimize the polymer doping with the variable stripe length method. Various lengths of polymer waveguides will be optically pumped. The emitted light will be collected at the silicon waveguide with a grating in the waveguide, which couples light from the waveguide to a fiber. A second structure contains two silicon waveguides and tapers with a polymer waveguide in between and adds reflection gratings in the silicon waveguides, designed to have a broadband reflection of 99%. This Fabry-Perot resonator will be used to start lasing experiments.

Conclusion

We have developed a PbTe/CdTe core/shell wet chemical synthesis to overcome problems of oxidation in air and to lift the 8-fold degeneracy of the first exciton level. Luminescence lifetime studies reveal a second decay path compared to the PbTe core nanoparticles. A silicon photonics chip was designed to characterize these nanoparticles further.

Acknowledgements

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