Colloidal semiconductor quantum dots: From synthesis to photonic applications

I. Moreels[1], P. Kockaert[2], B. De Geyter[3], D. Van Thourhout[3], and Z. Hens[1]

[1] Physics and Chemistry of Nanostructures, Ghent University, Krijgslaan 281 S12, B-9000 Ghent, Belgium

[2] Optics and Acoustics Department, Université libre de Bruxelles, Av. Adolphe Buyl 87 B-1050 Brussels, Belgium

[3] Department of Information Technology, Ghent University - IMEC, Sint-Pietersnieuwstraat 41, B-9000 Ghent, Belgium

Interest in semiconductor colloidal nanocrystals has grown considerably due to the many advantages they offer. In this paper, we focus on the nonlinear refractive index n_2 and nonlinear absorption α_{NL} of near-infrared PbS and PbSe nanocrystals (Q-PbS(e)), and their interaction with Silicon-on-Insulator (SOI) ring resonators. We first demonstrate that Q-PbS(e) have a negative n_2, in combination with absorption saturation. We then show that by depositing these nanocrystals as a thin film on SOI rings, the ring resonances can be strongly influenced by the nanocrystals. Both results hold considerable promise for the further investigation of hybrid SOI devices.

Introduction

Semiconductor colloidal nanocrystals are synthesized using wet chemical methods.[1] As the nanocrystal diameter typically varies between 1 and 15 nm, quantum confinement effects strongly influence the optical properties. Essentially, bulk semiconductor bands are transformed into discrete energy levels and the band gap becomes size-dependent. Most colloidal nanocrystals also show a strong band-edge luminescence, opening pathways for lasing applications in a wide spectral range, from near-UV to mid-infrared.[2]
In this paper we will focus on yet another promising property of these quantum dots: the nonlinear refractive index n_2 is expected to be enhanced with respect to the bulk material,[3] and the existence of discrete energy levels leads to absorption saturation. Combined with the facile nanocrystal processing in for instance polymer thin films, a variety of all-optical applications on a silicon platform might eventually be realized.

Optical properties of NIR nanocrystals

For applications in the near-infrared (NIR), PbS and PbSe nanocrystals (Q-PbS and Q-PbSe) are excellent candidates. Optical properties can be tuned from 1 µm to beyond 2 µm, covering the entire telecom spectral range (figure 1). The bulk exciton Bohr radius of PbS and PbSe is much larger than the typical nanocrystal size, leading to strong quantum confinement and the appearance of sharp peaks in the absorption spectrum. These are the result of transitions between the quantum dot's discrete energy levels.

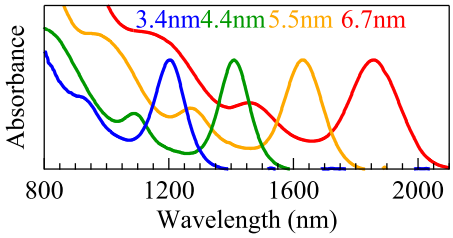

Figure 1: Absorbance spectra of different Q-PbSe suspensions. A blue shift of the transitions with decreasing Q-PbSe size is observed.

The nonlinear refractive index

We have studied the nonlinear refractive index n_2 of Q-PbSe and Q-PbS suspensions with the Z-scan technique.[4, 5] This technique is well suited to determine both the sign and magnitude of n_2, given that the laser beam intensity I_0 is known. Figure 2(a) shows a typical n_2-spectrum for a ca. 1 µM Q-PbSe suspension ($I_0 = 12\,\mathrm{MW/cm^2}$). A strong resonance in n_2 occurs in the vicinity of the absorption peaks, indicating that it originates from electronic transitions within the nanocrystal. Further evidence follows from the change in refractive index $\delta n = n_2.I_0$ (figure 2(b)). At high I_0, saturation is observed, which can be explained by the existence of discrete energy levels. As I_0 increases, more electrons will be promoted to the first excited state, until this level is completely filled. Further increasing I_0 will then no longer promote more electrons, leading to a saturation in δn. Similar results are obtained for Q-PbS nanocrystals.

Absorption saturation

The Z-scan technique has a major drawback. We studied n_2 at energies around the band gap, using high repetition rate lasers (10–82 MHz). Consequently, thermal nonlinearities are unavoidable and they hamper the determination of the electronic n_2. A measurement of the nonlinear absorption coefficient α_{NL} is not influenced by thermal effects. Figure 2(c) shows the absorbance spectrum of the Q-PbS suspension used. We measured α_{NL} at 1.55 µm, using a 57.5 µm wide Gaussian beam. In figure 2(d), we show that α_{NL} decreases with increasing optical power. The bleaching can again be explained by state filling of the quantum dot's energy levels at high optical intensities, confirming the electronic origin of the nonlinear optical properties.

Hybrid nanocrystal - SOI ring resonators

Following these promising results, the interaction of Q-PbS and Q-PbSe with the evanescent wave of a Silicon-on-Insulator (SOI) notch filter (figure 3(a)) was studied. First, a 1 µm photoresist layer was spincoated on top of the entire structure, after which optical lithography was used to selectively remove the resist from the SOI ring. Next, a nanocrystal suspension was mixed with a polymer (polystyrene) and spincoated on top of the photoresist layer. The patterned resist ensures that direct contact between the doped polystyrene layer and the SOI structures is avoided, except for the ring resonator.

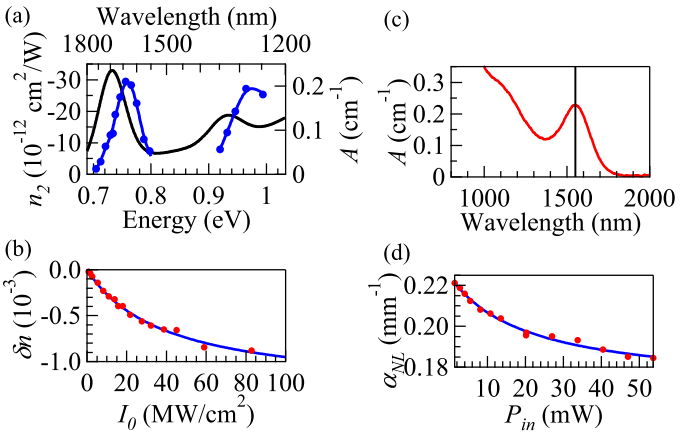

Figure 2: (a) n_2-spectrum (blue) compared to the absorbance spectrum (black). (b) Intensity dependence of δn. A clear saturation is observed. (c) Q-PbS Absorbance spectrum of particles with a peak absorption at 1.55 µm. (d) The nonlinear absorption coefficient α_{NL} at 1.55 µm decreases with increasing optical intensity.

Figure 3(b) shows a typical transmission spectrum of a coated notch filter with length $L = 39.4$ µm and group index $n_g = 4.16$. To gain insight in the interaction between the Q-PbSe doped thin film and the SOI ring, the loss per circulation a of the ring and transmission t of the coupling section were calculated from the resonance linewidth F and depth D:[6]

$$F = \frac{(1-at)\lambda_0^2}{\pi L n_g \sqrt{at}}, \quad D = \frac{(a-t)^2}{(1-at)^2} \tag{1}$$

-2log(a) then represents the absorption coefficient of the ring. It is compared to the Q-PbSe absorbance spectrum in figure 3(c). The excellent agreement confirms a strong coupling of the light in the ring resonator to the Q-PbSe doped thin film.
In a second example, the volume fraction of Q-PbS nanocrystals in the polystyrene layer was varied between 0.75 and 6.6. Figure 3(c) shows that the ring resonances shift toward higher wavelengths as f increases. This is due to the increase in the refractive index of the doped polymer cladding, which in turn increases the effective refractive index of the ring. Also, the Q-factor decreases strongly (figure 3(d), black dots). Calculation of a and t shows that the decrease in Q-factor is mainly due to the strong decrease of a (blue dots). t remains fairly constant (red dots). This again demonstrates that the transmission spectrum of the notch filter is strongly influenced by the nanocrystal absorption.

Conclusions

Q-PbS and Q-PbSe show strong NIR, size-dependent absorption peaks. A negative n_2 is observed and the electronic origin is established by the saturation of α_{NL} and δn. After depositing a nanocrystal doped polymer on a SOI notch filter, the transmission spectrum can be efficiently tuned by the quantum dot absorption. These results hold considerable

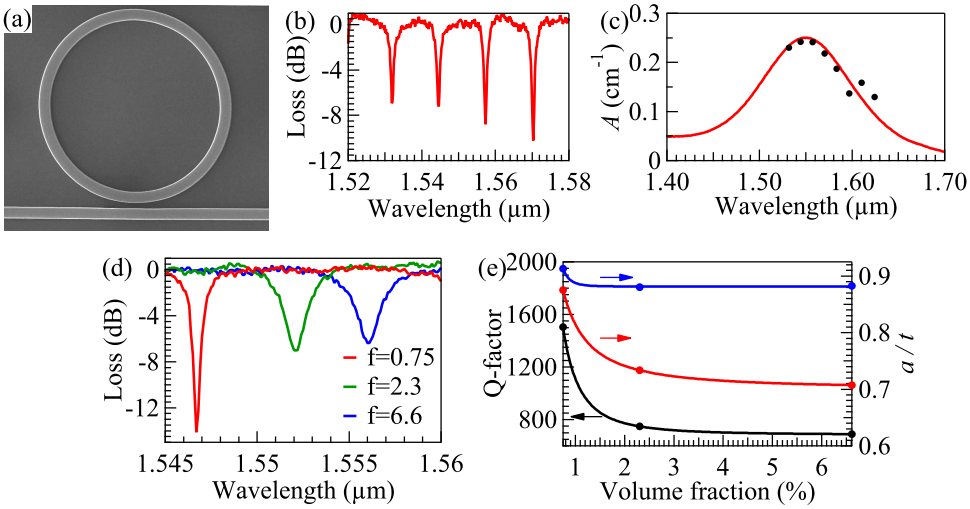

Figure 3: (a) SEM image of a SOI notch filter. (b) Transmission spectrum for a Q-PbSe coated ring. (c) Comparison of the absorption coefficient of the ring (-2log$a$) with the Q-PbSe absorption coefficient. (d) Transmission spectra for Q-PbS coated rings with varying Q-PbS volume fraction f. A shift to higher wavelengths is observed with increasing f due to the increase in the effective refractive index. (e) The Q-factor decreases with increasing f (black dots). This is due to an decrease in a (blue), as t remains fairly constant (red).

promise for further investigations of the nonlinear optical properties of hybrid SOI devices.

Acknowledgments

The authors acknowledge IWT-Vlaanderen for a scholarship. This work is also funded by the Belgian Science Policy Office (IAP VI-10).

References

[1] C. B. Murray, S. H. Sun, W. Gaschler, H. Doyle, T. A. Betley, and C. R. Kagan, "Colloidal synthesis of nanocrystals and nanocrystal superlattices," *Ibm Journal of Research and Development*, vol. 45, no. 1, pp. 47–56, 2001.

[2] A. L. Rogach, A. Eychmuller, S. G. Hickey, and S. V. Kershaw, "Infrared-emitting colloidal nanocrystals: Synthesis, assembly, spectroscopy, and applications," *Small*, vol. 3, no. 4, pp. 536–557, 2007.

[3] E. Hanamura, "Very large optical nonlinearity of semiconductor microcrystallites," *Physical Review B*, vol. 37, no. 3, pp. 1273–1279, 1988.

[4] M. Sheikbahae, A. A. Said, T. H. Wei, D. J. Hagan, and E. W. Vanstryland, "Sensitive measurement of optical nonlinearities using a single beam," *Ieee Journal of Quantum Electronics*, vol. 26, no. 4, pp. 760–769, 1990.

[5] I. Moreels, Z. Hens, P. Kockaert, J. Loicq, and D. Van Thourhout, "Spectroscopy of the nonlinear refractive index of colloidal PbSe nanocrystals," *Applied Physics Letters*, vol. 89, no. 19, p. 193106, 2006.

[6] A. Yariv, "Universal relations for coupling of optical power between microresonators and dielectric waveguides," *Electronics Letters*, vol. 36, no. 4, pp. 321–322, 2000.