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Optically detected magnetic resonance of semiconductor quantum dots

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Abstract. Semiconductor quantum dots have attracted large scientific and technological interests in the last decade. This document describes our attempts to characterize the localization of carriers in CdSe and CdS quantum dots, utilizing optically detected spin and orbit magnetic resonance spectroscopy. The spin resonance resembled a typical magnetic resonance spectrum and has been analyzed in a similar manner. For example, spin Hamiltonian simulation of the paramagnetic spin interactions enabled the chemical identification of carrier's trapping sites (e.g., core, surface or interface). On the other hand, the precession motion around the direction of the external magnetic field was restricted by the so-called magnetic length $\lambda_m = \sqrt{\hbar/eB}$. Still, theoretical consideration associated either with ballistic motion of carriers against the boundary, or orbital motion should enable the determination of the effective mass of an electron, hole and additional charged specie (presumably a charged exciton).

Introduction

Nearly two-decades of research have explored the benefits in the optical and opto-electronic properties of semiconductor quantum dots (QDs) [1]. These materials exhibit unique chemical and physical properties, differing substantially from those of the corresponding bulk solids. Evidently, these differences are associated with quantum-sized effect and the relatively large number of atoms at the QD's surface.

The quantum size effect had been studied extensively in II–VI, III–V, IV–VI and I–VII (e.g., CuCl) randomly dispersed or as single QDs [2]. These studies showed that the aforementioned materials offer the opportunity to tune the electronic and optical properties, with variation in the QD's size. However, the influence of surface/interface at the current time is not well understood. The quality of the surface becomes important in determining electron and hole trapping together with the chemical reactivity. Trapping of charge carriers may influence the observed emission properties to a large extent. For example, the photoluminescence (PL) of QDs occasionally present red-shifted luminescence band associated with surface recombination [3] or surface states mixing with the band edge [4]. Trapped carriers at the surface may polarize the core exciton, leading to a delayed fluorescence and multi-exponential decay process (in combination with the influence of dark states) [5]. It was shown that light emission from a single QD, under continuous excitation, turns on and off intermittently with a characteristic time-scale of seconds [2]. This phenomenon can be due to trapping or to an Auger process at the surface. Thus, the ultimate goal of the described research is concerned with the identification of the surface/interface sites, and trapping and de-trapping processes of photo-generated carriers at those sites. Furthermore, the influence of the aforementioned issues on the recombination processes is mainly emphasized.

Currently there are three main methods for the fabrication of QDs: (1) Chemical, Electrochemical and Epitaxial deposition of a QD's compound on top of a substrate with a different lattice constant leads to strain induced three dimensional islands, known as Stranski–Krastanow (SK) QDs [6–9]; (2) Colloidal chemistry techniques, which enable the growth of QDs with diameters of <10 nm, size distribution of <10%, strain-free dots and the termination of surfaces with organic or inorganic capping [1, 2]; (3) In situ growth of QDs during the preparation of glass or polymer media [10].

The present document discusses the study of representative CdS and CdSe QDs samples, prepared in either one of the synthetic methods discussed above. Optically detected magnetic resonance (ODMR) spectroscopy was used for the study of the localization properties of photo-generated carriers in the studied materials. This method provides the means to chemically identify core or surface/interface states, and correlate them with specific optical transition.

Experimental

Colloidal CdSe QDs, capped either with tri-octy-phosphine-oxide [TOPO] or epitaxial layer of CdS were prepared according to the procedure described in [11]. Then these colloidal QDs were embedded in a transparent polymer film [12] for the convenience of the optical measurements. Strain grown chemical deposited QDs were prepared according to the procedure given in Ref. [13], while CdSe and CdS QDs grown in glass media were prepared by the procedure given in [14].

The ODMR spectra were recorded by placing the sample on a special sample probe at the center of a High-Q resonance cavity, coupled to a microwave (mw) source (~10 GHz), and surrounded by a superconducting magnet. These spectra were obtained by measuring the change in luminescence intensity induced either by a spin or orbit magnetic resonance event at the excited state. This change was plotted versus the strength of the external magnetic field, **B**.

Results and discussion

Representative ODMR spectra of colloidal CdSe (capped with CdS monolayer), CdSe deposited on glass, and CdS grown in a phosphate glass, are shown in Fig. 1. Each spectrum consists of two resonance signals (narrow and wide), ranging between 2000–5000 Gauss, super-imposing on a wide background. Recording of the ODMR spectra at various experimental conditions, by varying the modulation frequency of the mw or

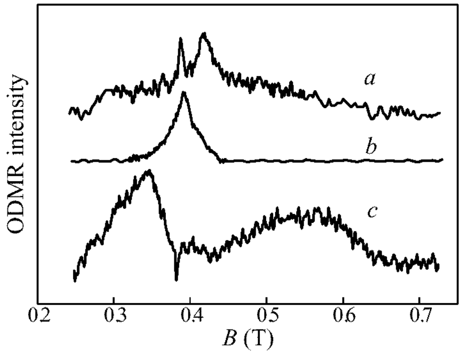

Fig. 1. Spin ODMR spectra of following samples: (a) Colloidal CdSe QDs, capped with epitaxial layer of CdS, (b) Chemical deposited CdSe QDs and (c) CdS QDs grown in phosphate glass medium.

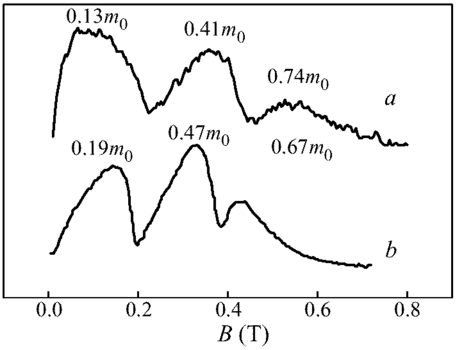

Fig. 2. Representative resonance background of (a) Colloidal CdSe QDs, capped with epitaxial layer of CdS and (b) CdS_xSe_{1-x} QDs grown in phosphate glass.

laser excitation power, showed in all cases that the distinct resonance signals have different response from that of the background (not shown). In addition, the narrow and wide signals also differ from each other. This suggests that the spectra consist of several resonance events, associated with different chemical sites. Theoretical considerations (e.g., treatment of the external magnetic field as a perturbation of the electron motion in confined dots) may suggest that the background is associated either with an orbit or cyclotron motion of the carriers, while the distinct narrow and wide band, correspond to their spin motion. The latter were simulated by the use of the following phenomenological spin Hamiltonian:

$$H_s = \beta S_e g_e \mathbf{B} + \beta S_h g_h \mathbf{B} + S_e D S_h + J S_e S_h \qquad (1)$$

The first two terms correspond to the effective Zeeman interaction of an electron and hole, the third term corresponds to the zero field splitting (may be overlapped by an anisotropic exchange interaction), while the last term, to the isotropic electron–hole (e–h) exchange interactions. The spin Hamiltonian simulation suggests the trapping of a hole within the core of the QD and trapping of an electron at the surface. Twin boundary or edge dislocations were identified as the carrier's trapping sites.

The resonance background, ranging between 0–8000 Gauss (after the subtraction of the spin resonance contribution) is plotted in Fig. 2. Theoretical considerations published elsewhere [12] suggest the correlation between the peak maxima and the effective mass parameters. The represented curves consist of three signals with corresponding effective masses, as indicated in the figure. The 0.13m_0 is identical with the bulk electron effective mass, while the 0.41m_0 is close to the hole effective mass of bulk CdSe. The third resonance has an effective mass of 0.74m_0, presumably corresponding to a three-body complex, composed of one hole bounded to two electrons (e.g., charged exciton). This charged exciton is found in various quantum structures recently, while never been discussed before in semiconductor QDs.

References

[1] (a) A. Eychmuller, A. Hasselbarth, L. Katsikas and H. Weller, *Ber. Bunsen. Phys. Chem.* **95** (1), 79 (1991);
(b) L. E. Brus, *J. Phys. Chem.* **90**, 2555 (1986).

[2] (a) S. A. Empedocles, D. J. Norris and M. G. Bawendi, *Phys. Rev. Lett.* **77**, 3873 (1996);
(b) J. Tittel, A. Mews, H. Weller, A. Eychmuller *et al.*, *Ber. Bunsen. Phys. Chem.* **101**, 1626 (1997).

[3] M. O'Neil, J. Marohn and G.J. Mclendon, *J. Phys. Chem.* **94**, 8585 (1990).

[4] M. G. Bawendi, L. Wilson, L. Rothberg, P. J. Carroll, T. M. Jedju, M. L. Steigerwald and L. E. Brus, *Phys. Rev. Lett.* **65**, 1623 (1990).

[5] A. Eychmuller, A. Hasselbarth, L. Katsikas and H. Weller, *Angew. Chemie* **105**, 43 (1993).

[6] K. Schmidt, P. Petroff *et al.*, *Phys. Rev. B* **54**, 11346 (1996).

[7] B. J. Spencer and J. Tersoff, *Phys. Rev. Lett.* **79**, 4858 (1997).

[8] (a) M. Grundmann, O. Stier and D. Bimberg, *Phys. Rev. B* **52**, 11969 (1995);
(b) M. Grundmann, N. N. Ledentsov, D. Bimberg, P. S. Kop'ev *et al.*, *Phys, Rev. Lett.* **74**, 4043 (1995).

[9] L. W. Wang, J. Kim and A. Zunger, *Phys. Rev. B* **59**, 5678 (1999).

[10] A. I. Ekimov, *J. Lumin.* **70**, 1 (1996) and references wherein.

[11] X. Peng, M. C. Schlamp, A. V. Kadavanich and A. P. Alivisatos, *J. Am. Chem. Soc.* **119**, 7019 (1997).

[12] A. Glozman, E. Lifshitz, M. C. Schlamp and P. Alivisatos, *to be submitted.*

[13] S. Gorer and G. Hodes, *J. Phys. Chem.* **98**, 5338 (1994).

[14] E. V. Kolobkova, A. A. Lipovskii, N. V. Nikonorov, V. D. Petrikov, A. A. Sitnikova and I. E. Jakovlev, *J. Non-Crystalline Solids* **221**, 18-26 (1997).