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Muonium in nano-crystalline II–VI semiconductors

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ABSTRACT

The effect of quantum confinement on shallow-donor muonium states and their ionization in nanocrystalline colloidal II–VI semiconductors was studied by the transverse- and longitudinal-field μ SR techniques. Evidence is found for the formation of surface muon states on nanocrystalline ZnO with hydrogen passivated surfaces. On nanocrystalline CdSe capped with organic molecules the muons probably form states at the surface or substitute for hydrogen in the organic materials. The results obtained so far on nc-CdTe are suggestive of formation of a muonium state inside the nanocrystals, but further studies are needed to find a definitive proof.

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1. Introduction

Quantum confinement in colloidal semiconductor nanocrystals (ncs) results in a set of discrete valence hole and conduction electron energy levels, instead of bands. As a consequence, the optical and electrical properties of such systems depend strongly on the nanocrystal size, leading to extensive research [1,2]. A compelling question that has received a lot of interest recently is whether small nanocrystals can be doped with donor (acceptor) atoms, permitting wide applications of nanocrystal materials in electronic functional devices [3]. The incorporation of hydrogen into ZnO nanocrystals has been hypothesized to be important for the transport properties of ZnO nanocrystal assemblies [4,5].

μ SR is a powerful method to study the isolated hydrogen (muonium) states in semiconductors. In particular, the formation and ionisation of a muonium shallow-donor state in some II–VI semiconductors in the bulk has been extensively studied [6–9].

In this work we present the first results of a μ SR survey of muonium states in nanocrystalline (nc) II–VI semiconductors, focusing on those where the shallow muonium is formed in the bulk. By using the transverse- and longitudinal-field techniques we searched for signs of the different states that might be forming inside, on the surface, or in the space between the nanocrystal cores. The temperature dependences of the signals are compared with that observed in bulk samples for the ionisation of the shallow muonium state.

2. Experimental details

Colloidal CdSe and CdTe nanocrystals used for these experiments were prepared by high-temperature organometallic synthesis. CdSe nanocrystals were prepared following de Mello Donega et al. [10], while CdTe particles were synthesized following the recipe of Wuister et al. [11]. The syntheses and subsequent steps are carried out in the inert atmosphere of an argon-purged glove box. This procedure yields small (≈ 3 nm in diameter) particles with a narrow size distribution ($<10\%$ standard deviation). To obtain larger particles, appropriate amounts of $\text{Cd}(\text{CH}_3)_2$ and $\text{Se}(\text{Te})$ dissolved in trioctyl phosphate (TOP) are added dropwise to the solution with the smaller particles at 240°C . With this method, nc-CdTe samples were synthesized with average diameters of 2.6, 4.7 and 6.4 nm, and nc-CdSe with average diameters of 3.3 and 5.0 nm. The nc solutions were cleaned by adding a small amount of anhydrous methanol, which caused the nanocrystals to precipitate.

The CdSe ncs have a mixed organic capping layer of tri-octyl phosphine oxide (TOPO) and hexadecylamine (HDA). The original dodecylamine (DDA) capping of the CdTe nanocrystals was replaced by either propanethiol (C3) or octadecanethiol (C18) by addition of a large excess of thiol followed by precipitation and redispersion of the particles. This procedure was repeated twice. The octadecanethiol capping results in a much larger separation between the nanocrystals (≈ 4 nm) than in the case of the propanethiol capping (≈ 1 nm).

The ZnO nanocrystals were prepared via the synthesis described by Meulenkamp [12]. The particles were precipitated by the addition of cold hexane, the precipitate was collected,

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redispersed in ethanol and washed once more with hexane and once with acetone. The final nc-ZnO samples are dry powders. The particle surface is passivated by hydrogen, forming a zinc hydroxide outer layer. Four nc-ZnO samples exhibiting quantum-confinement were prepared, with average particle diameters of 2.8 (two samples at different occasions), 3.4 and 4.4 nm. An additional nc-ZnO sample with average nc diameter >26 nm was also prepared as a standard for a system with no confinement effect.

Time-differential μ SR measurements were performed on the EMU instrument of the ISIS Pulsed Muon Facility, using a closed cycle refrigerator and the fly-past set-up to minimize the background signal from sample holders, given the small size of the samples [13]. Transverse-field (TF) measurements were performed on all prepared samples at temperatures from 5 K to room temperature, and at a field of 100 G, already in the high-field limit for the extremely low-hyperfine interaction of the shallow-donor muonium states [6–8]. Longitudinal-field (LF) repolarisation measurements (from 0 to 4500 G) were performed at low and room temperature on some of the samples. The raw data were analysed by using the WiMDA programme by Pratt [14]. The Fourier analysis of the TF time spectra was performed with a maximum entropy (ME) method.

3. Results

The low-temperature TF spectra have the same general traits for all samples studied, with a broad component and a central line, not well separated in most cases, as seen in Fig. 1 for the case of nc-CdTe.

Fig. 2 shows plots of the temperature variation of the parameters characterising the line shape of the spectra obtained

for nc-CdTe and nc-ZnO. A single component was used for the fits to the nc-ZnO data and two component fits were used for nc-CdTe. These simple models do not reproduce the line shapes well, but basic distinctive features are observed on these plots for all samples exhibiting the quantum confinement effect. The broad component vanishes at much higher temperatures than those typical of the ionisation of shallow-donors in the bulk materials, as would be expected of inter-grain diffusion of a conduction electron.

In contrast, the nc-ZnO sample with grain sizes above the confinement threshold shows the shallow state behaviour, proving its presence in this sample.

The collapse of the characteristic satellite lines into a broad line is known to happen when a small concentration of impurities or defects is present in the samples [15], which could be the case here. Another hypothesis to explain the broadened line shapes seen on the ncs in the confinement regime would be a distribution of hyperfine parameters of the interaction between the muon inside the nanocrystal and a bound electron in a confined orbital. The broadening would then result from a dispersion of the muon position within the nanocrystal and (to a lesser extent) the size distribution of the nanocrystals. Simulations based on a finite barrier effective mass approximation, taking into account these two types of dispersion, show a good similarity with the measured spectra. An additional feature pointing to the formation of a paramagnetic state within the ncs on nc-CdTe is that the line shape and temperature behaviour of the sample with longer capping (C18) are very similar to those of the C3 capped sample with the same grain sizes (Fig. 2a).

Different hypotheses have, however, to be considered, as both the broad line and its temperature behaviour could be explained by a dipolar interaction with nearby nuclei with non-zero spin, such as protons or nitrogen on the capping materials, or protons

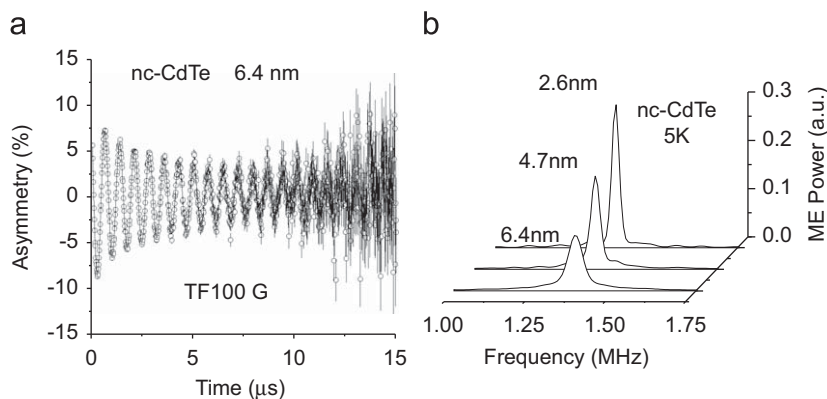


Fig. 1. Representative TF time spectrum (a) and ME distributions (b) on nc-CdTe at low temperature.

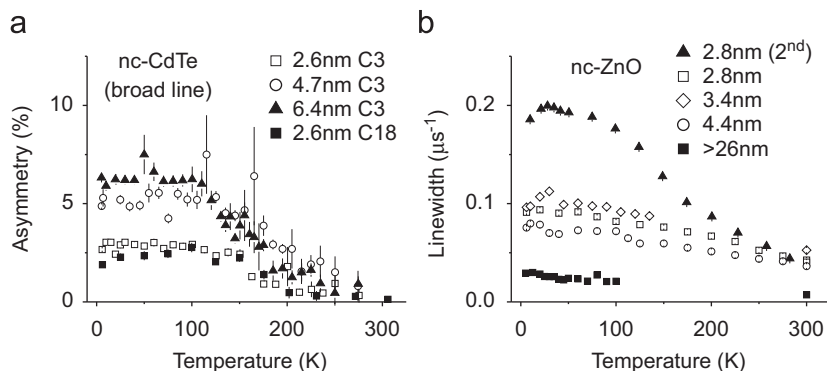


Fig. 2. Temperature variation of parameters fitted to the TF spectra on nc-CdTe (a) and nc-ZnO (b).

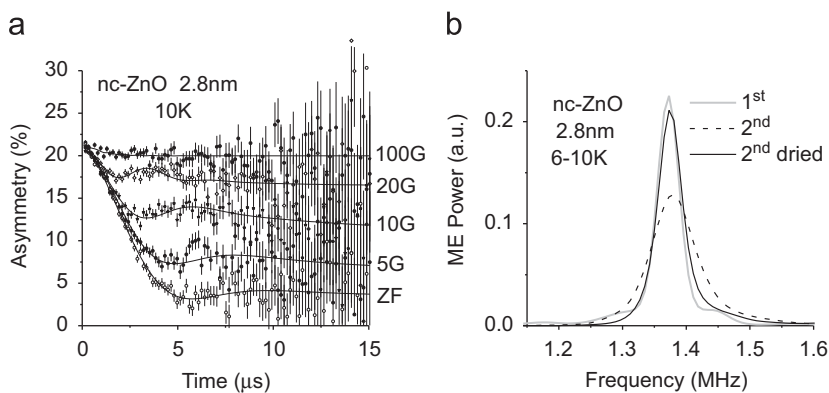


Fig. 3. LF low-field time spectra (a) and TF line shapes for the 2.8 nm nc-ZnO samples (b).

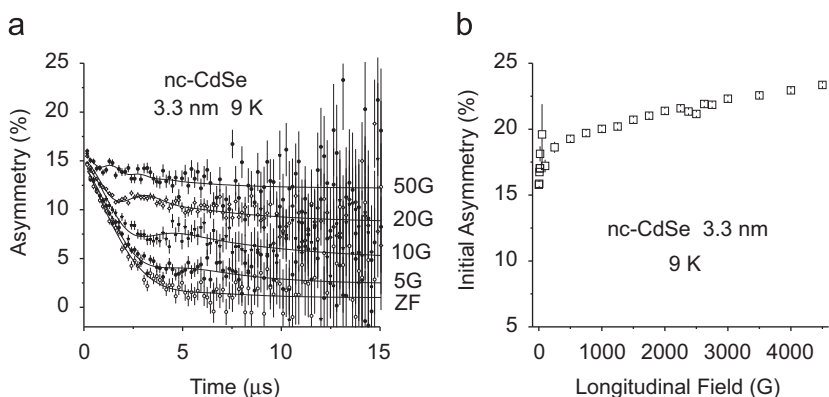


Fig. 4. LF low-field time spectra (a) and LF repolarisation for the 3.3 nm nc-CdSe sample (b).

on the surface of nc-ZnO. The temperature behaviour would be caused by motional narrowing as the muon diffuses through different possible sites.

A TF temperature scan on a mixture of the capping and solvent materials used for the preparation of nc-CdSe does show exactly that although with a significantly larger width for the line shape at low temperature ($0.34\mu\text{s}^{-1}$) and an onset of motional narrowing at temperatures lower than those seen for the semiconductor samples.

LF measurements performed on a second nc-ZnO sample of average particle diameter of 2.8 nm show strong signs of dipolar interaction as seen on fits to the low-field time spectra with a static Kubo–Toyabe function (Fig. 3a) with $\Delta = 0.347(7)$ MHz. The corresponding LF repolarisation shows a constant initial asymmetry up to 4500 G, indicating that no deep states are formed. These results, together with the non-variance of the TF signal with particle size (Fig. 2b), are good indications that the muon stabilises as diamagnetic surface states on nc-ZnO in the confinement regime. Additional strong evidence of dipolar interaction with hydrogen in this system is the observation of a considerable decrease in the linewidth of the low-temperature TF spectrum on this second sample as it was subjected to a drying process (Fig. 3b), without changing the particle size. Note additionally in Fig. 2b the initially larger linewidth for this second 2.8 nm sample at low temperatures.

The nc-CdSe samples, capped with a mixture of TOPO and HDA, show at low temperature and LF low fields a rather strong dipolar interaction, presumably with nearby N nuclei at the surface (Fig. 4a). The fitted $\Delta = 0.512(33)$ MHz is similar to the value obtained for the capping mixture alone ($\Delta = 0.552(32)$ MHz). The TF broad line shape at low temperature is

also compatible with such a dipolar interaction. A compact state is also formed in nc-CdSe, seen as a slow increase of polarization with field in the low-temperature LF repolarization in Fig. 4b. Compact muonium states do not form in bulk CdSe, but again the capping mixture shows a very similar repolarisation.

There are no N atoms in the capping of nc-CdTe; therefore we cannot compare the results of LF measurements on these ncs with those obtained for nc-CdSe and for the CdSe capping materials. LF measurements on nc-CdTe, both the low fields and the full repolarization, show results that are not incompatible with what is observed in the bulk, with a larger distribution of dipolar interaction parameters. This dipolar nuclear interaction is caused by the 25% abundant Cd nuclei with non-zero spin.

4. Conclusions

We have observed strong evidence in nc-ZnO of formation of surface states with dipolar interaction with nearby protons passivating dangling bonds. The plausibility of formation of states inside the nanocrystals is very low in the studied samples.

The data obtained for nc-CdSe also show strong evidence of dipolar interaction, presumably with N atoms of the HDA capping at the surface of the nanocrystals. A deep muonium state is formed, as expected for a substitution of hydrogen in the capping molecules. If any fraction of muonium forms inside the nc-CdSe particles, its signal is hidden within the broad line shape of the dipolar interaction.

The particle size dependence of the TF signal in nc-CdTe and its independence of the size of the capping molecules are good indications of the formation of a large fraction of a muonium state inside the nanocrystals of CdTe in the confinement regime.

Further studies with RF double resonance are under way to check whether an electron is indeed bound to the muon and to measure its g-factor.

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