PHYSICAL REVIEW B VOLUME 59, NUMBER 16 15 APRIL 1999-II

Spin coherence in semiconductor quantum dots

J. A. Gupta and D. D. Awschalom
Department of Physics, University of California, Santa Barbara, California 93106

X. Peng and A. P. Alivisatos
Department of Chemistry, University of California, Berkeley, California 94720

(Received 24 November 1998)

Femtosecond-resolved Faraday rotation is used to probe spin dynamics in chemically synthesized CdSe quantum dots 22–80 Å in diameter from $T=6-282$ K. The precession of optically injected spins in a transverse magnetic field indicates that the measured relaxation lifetime of the spin polarization is dominated by inhomogeneous dephasing, ranging from ~3 ns at zero field to <100 ps at 4 T. Fourier analysis reveals a multiperiodic Larmor precession, with several distinct g factors ranging from ~1.1 to 1.7. [S0163-1829(99)51316-7]

Research into semiconductor quantum dots (QD's) is driven by their promise in exploring carrier behavior in the mesoscopic regime between bulk and molecular systems, and a variety of technological applications which exploit their size-tunable optical properties.[1,2] Recent interest in manipulating semiconductor spins for applications ranging from spin-polarized magnetoelectronics[3] to quantum computation[4] is based on the ability to control and maintain spin coherence over practical length and time scales. To this end, QD's have been suggested as potential elements for such devices due to control over the structural and electronic environment of localized carriers.[4]

Here we employ all-optical spin resonance methods[5,6] to study spin coherence in a series of CdSe QD's spanning the regime in which carriers are energetically confined to clusters smaller than the exciton Bohr diameter. Time-resolved Faraday rotation (TRFR) is used to monitor the dynamics of optically injected carrier spins as a function of applied magnetic field, temperature, and injection energy. The data indicate nanosecond spin relaxation lifetimes at zero field which are dominated by inhomogeneous dephasing upon the application of a modest transverse field. Fourier analysis of the resultant spin precession reveals distinct g factors that modulate the TRFR decay envelope at the corresponding difference frequencies. Spin precession in QD's is seen to be thermally robust, persisting to $T=282$ K.

Single-crystal CdSe QD's are synthesized by solution-phase pyrolytic reaction of organometallic precursors.[7,8] The wurtzite crystals have mean diameters ranging from 22 to 80 Å with a standard deviation of ~5–10 % and are slightly prolate (with size-dependent aspect ratios). Surface-related trap states and barriers have been studied for their influence on carrier recombination dynamics,[9] Auger-assisted photoionization,[10] and Stark shifting of single dot emission.[11] To identify surface effects in our optical measurements, a second series of QD's was synthesized in which 1–3 ML of higher band-gap CdS shells were epitaxially grown onto the bare CdSe cores.[12] These core/shell QD's show improved photoluminescence (PL) quantum yields and photochemical stability through increased hole localization in the core. Both types of QD's have organic ligands complexed to the surface which provide additional passivation and prevent aggregation during synthesis. Samples are prepared by dissolving the QD's in an organic polymer producing a thin transparent film in which the QD's are randomly oriented.

Optical measurements are performed in a magneto-optical cryostat in magnetic fields up to 7 T and temperatures from ~4 to 300 K. An optical parametric amplifier laser with a 250-kHz repetition rate produces ~150 femtosecond pulses of energy-tunable ($E_{\text{laser}}=1.7-2.6$ eV) and 3.1 eV light, as well as a white light continuum. The continuum and 3.1 eV beams are used for absorption and PL characterization, respectively. The tunable output is adjusted to particular QD energy levels and split into pump and probe beams which are normally incident on the sample and focused to a ~100-μm diameter spot. In the TRFR experiment, a circularly polarized pump pulse excites electron-hole pairs that are spin polarized along the optical path. The number of excited pairs is kept more than an order of magnitude lower than the number of dots sampled ($\sim 10^{10}$) to avoid Auger processes and biexciton effects.[13,14] When an in-plane magnetic field is applied, the pump-injected spins comprise a coherent superposition of states quantized along the field direction and separated in energy by the Zeeman splitting.[5] As the system evolves in time, the energy difference between the spin states produces a quantum beating of spin magnetization along the optical path that results in an oscillatory Faraday rotation of time-delayed linearly polarized probe pulses at the corresponding Larmor frequency, Ω_L. The magnitude of the spin g factor is determined from the oscillation frequency, while the decay envelope gives a spin relaxation lifetime T_2^*, which generally includes both longitudinal and transverse relaxation processes. Typical rotations of ~50 microdegrees are measured using a balanced polarization bridge.[5] By photoelastically alternating the pump helicity and mechanically chopping the probe beam, the signal-to-noise ratio of the bridge difference output is improved with lock-in amplifiers.[15]

Figure 1(a) compares the zero-field TRFR of core and core/shell QD samples at $T=6$ K. Both samples have 40 Å CdSe cores, with the addition of 3 ML CdS for the core/shell sample. The core/shell scan has been normalized to account for a lower number density of dots in the film, and the un-

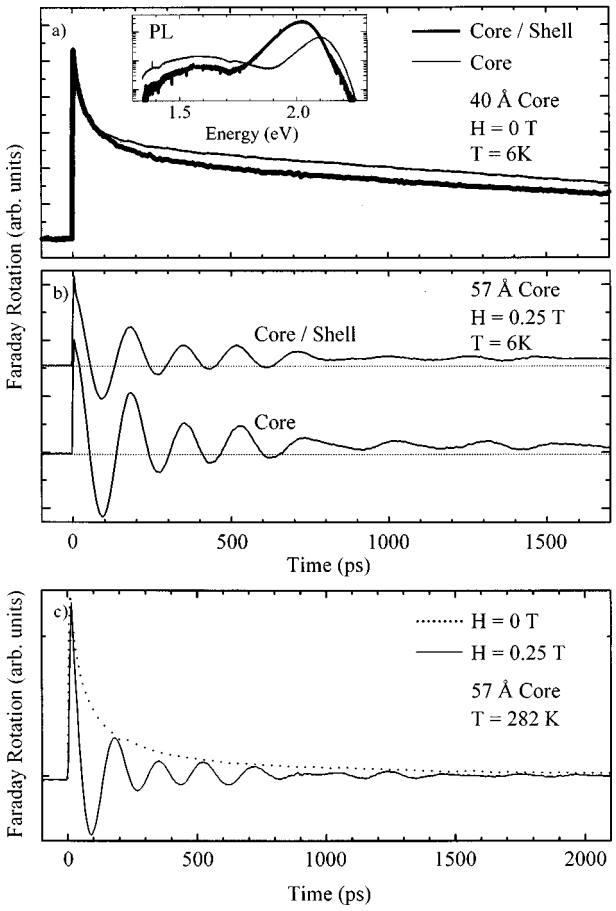

FIG. 1. (a) TRFR of core and core/shell (~3 ML CdS) QD's with 40 Å cores. $E_{laser}=2.16$ eV is tuned near the first QD energy level. Inset: PL spectra (log scale) with excitation at 3.1 eV. The core/shell data are normalized by the estimated number of QD's within the excitation spot. (b) Spin precession at $H=0.25$ T in core and core/shell (~1 ML CdS) QD's with 57 Å cores. $E_{laser}=2.1$ eV is tuned to the second QD energy level. The plots are offset for clarity, with the dotted lines indicating the signal baseline. (c) TRFR at $T=282$ K of the 57 Å QD's with E_{laser} as in (b).

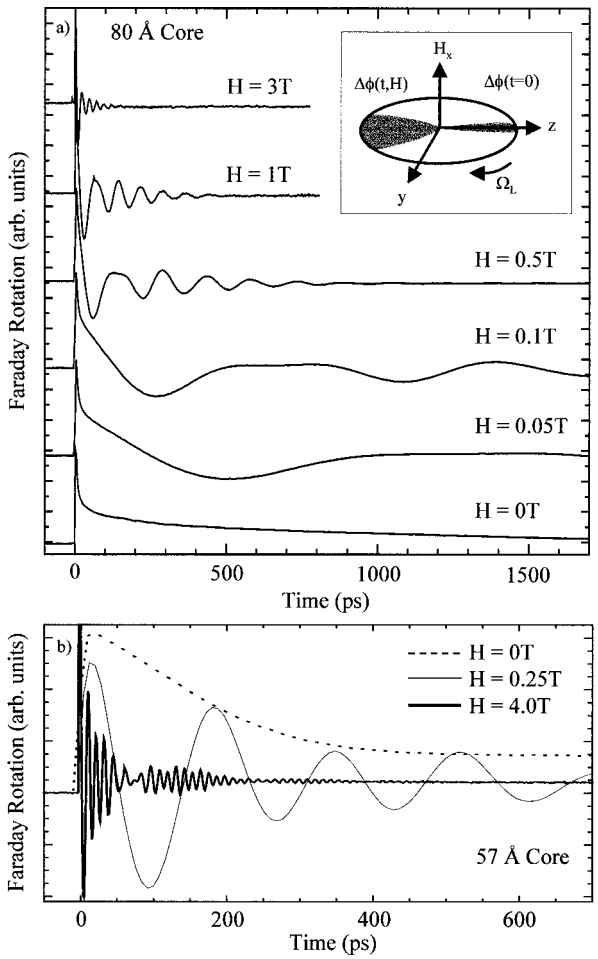

FIG. 2. Field-dependent TRFR at $T=6$ K. (a) $H=0$–3 T scans for 80 Å QD's, with $E_{laser}=2.0$ eV tuned near the first QD energy level. Inset: Illustration of field-dependent angular spreading of the net spin polarization arising from inhomogeneous dephasing. (b) $H=0$–4 T scans for the 57 Å QD's, with E_{laser} as in 1(b).

certainty in this calculation is larger than the apparent signal difference. The TRFR can be fit with a biexponential decay, yielding lifetimes of order 100 ps and 3 ns. The decay lifetimes are generally ~20% shorter for the three core/shell samples studied compared to samples with the same core diameter but without the CdS shell. We see no systematic size dependence of these lifetimes for QD's 22–57 Å in diameter (variations of 100 ± 50 ps and 3 ± 0.5 ns), although shorter lifetimes of 40 ps and 1 ns are observed for 80 Å QD's. It is difficult to separately identify the spin relaxation of electrons and holes because little is currently known about strongly confined carrier spin lifetimes in these QD's. Biexponential decays in time-resolved absorption studies of excitons localized at interface fluctuations in narrow GaAs quantum wells have been attributed to the spin relaxation of holes (~50 ps) and electrons (~150 ps).[16] Shown in the inset is a comparison of the PL from 40 Å core and core/shell QD's taken at $T=6$ K (normalized as above). A log scale is used to contrast the difference in relative intensities between surface trap (1.6 eV) and band-edge (2 eV) emission. The core/shell PL shows weaker surface trap and stronger band-edge emission due to increased hole localization in the CdSe core, as well as a 70-meV PL redshift due to electron delocalization into the CdS shell.[12]

Application of a transverse magnetic field ($H=0.25$ T) allows the comparison of Larmor spin precession between core and core/shell (1 ML CdS) QD's with 57 Å cores, shown in Fig. 1(b). The TRFR of the two samples is qualitatively similar although small differences in oscillation frequency and decay exist which may be due to different effective electronic sizes and/or size distributions whose contributions will be discussed later in the paper. Figure 1(c) demonstrates the persistence of spin precession at $T=282$ K for the 57 Å core QD's. The zero-field decay yields spin relaxation lifetimes of 50 ps and 0.4 ns. Measurements from $T=6$–280 K indicate little change in signal magnitude or decay up to 100 K, and no change in the oscillation frequency over the temperature range studied.

Figure 2(a) shows the evolution of the TRFR as the field is increased from $H=0$–3 T for 80 Å QD's. The oscillation frequency increases with H as expected from Larmor precession. The decay envelopes of the data indicate a ~30-fold increase in the spin relaxation rate as the field is increased from 0 to 3 T. Spin precession becomes unobservable for $t>200$ ps at $H=3$ T, but continues for $t>1.7$ ns (limited by

the mechanical delay line) at low fields. This field dependence suggests that the decay of the measured spin coherence is dominated by inhomogeneous dephasing within the ensemble of QD's. As depicted in the inset, the initial spin polarization (represented by the narrow shaded region) is excited along the z axis at $t=0$ ps. Transverse spin relaxation related to the decoherence of individual spins produces an angular spreading of the initial spin packet as a function of time, $\Delta\phi(t)$. Explicitly field-dependent spreading $\Delta\phi(t,H)=t(\mu_B\Delta gH/\hbar)$ can arise from a distribution of g factors precessing at slightly different rates (the field inhomogeneity is negligible over the laser spot). An inhomogeneous spin relaxation rate $(T_{\rm inh})^{-1}=\Delta g\mu_B H/(\hbar\sqrt{2})+(T_2^*)^{-1}$, which depends linearly on H, is obtained assuming a Gaussian distribution of g factors. Plotting $(T_{\rm inh})^{-1}$ vs H yields an estimate of ~10% for the g factor variance in this sample. Similar inhomogeneous dephasing is seen in 57 Å core QD's, whose TRFR at $H=4$, 0.25, and 0 T is shown in Fig. 2(b). The dephasing rates appear slower in the 57 Å QD's compared to the 80 Å QD's, suggesting an association of the inhomogeneous dephasing with the QD size distribution (~5% and 15%, respectively). This is supported by static circular dichroism measurements on CdSe QD's that have suggested a size dependence of the excitonic g factor.[17]

Examination of the precession at $H=4$ T reveals multiple frequencies resulting from distinct g factors which modulate the decay envelope. This is also observed in the 80 Å QD's as a double ''hump'' at early times [~50 ps in the 0.5 T scan of Fig. 2(a), for example]. High-resolution TEM studies do not indicate any pronounced peaks in the size distribution which would account for the presence of such distinct g factors. We further expect that any crystalline anisotropy due to either the hexagonal lattice or the nonspherical shape is averaged out over the randomly oriented ensemble. However, dichroism experiments suggest that QD energy levels may exhibit different excitonic g factors,[17] and to explore this possibility, the excitation energy is varied to compare the response from different QD states. The inset of Fig. 3(a) shows several QD energy levels that are discernible as peaks in the optical absorption spectrum (solid line) for 57 Å QD's. The dotted lines are three of the Gaussian components whose sum is used to fit the absorption and which give energies and inhomogeneous linewidths of the QD levels that are consistent with previous studies.[2,18] Figure 3(a) shows the TRFR of the 57 Å QD's at $H=4$ T with $E_{\rm laser}$ (whose bandwidth is represented by shaded regions in the inset) tuned to the first and second QD energy levels. The π phase shift in the spin precession as the energy is tuned between the two levels reflects the Faraday rotation's sensitivity to dispersion in the absorption spectrum.[19] Although the TRFR at 2.04 eV could contain contributions from the first and second levels of different QD's in the distribution, this situation would not be expected at 2.1 eV, where there is little overlap of the inhomogeneously broadened energy levels. The similarity of the oscillatory behavior in Fig. 3(a) suggests that the multiperiodicity is not the superposition of spin precession from distinct QD levels. In addition, measurements of subpicosecond energy relaxation[20] between these levels suggest that the nanosecond-scale dynamics are due to ground-state carriers.

A priori, the Faraday rotation should contain signatures of both electron and hole spins, subject to the exchange-

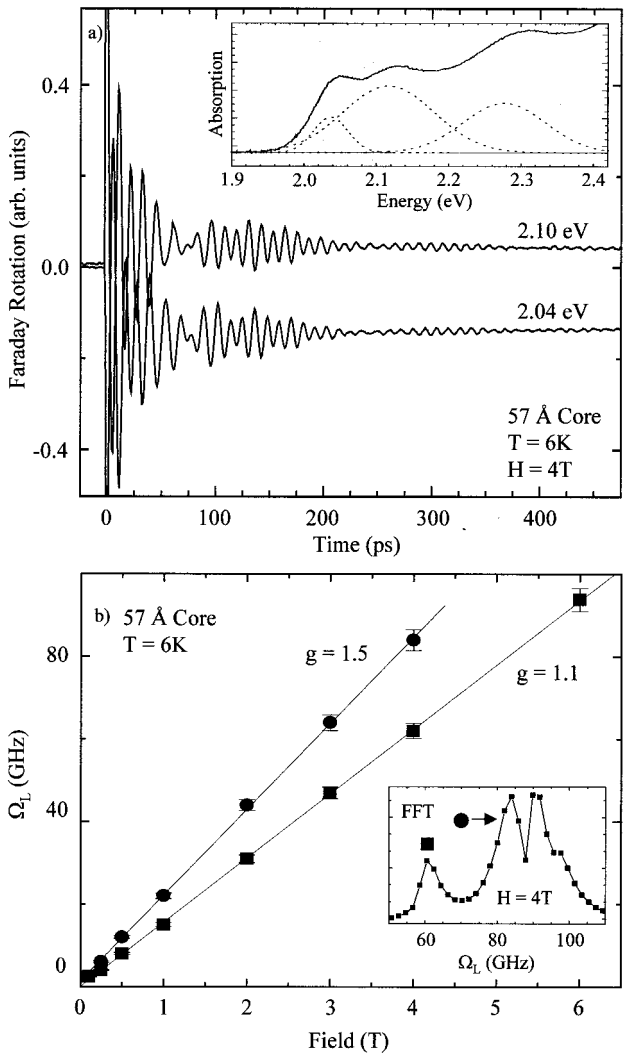

FIG. 3. 57 Å QD's at $T=6$ K. (a) TRFR with the laser tuned to the first (2.04 eV) and second (2.1 eV) QD energy levels. Inset: Associated absorption spectrum. Dotted lines represent Gaussian components whose sum is used to fit the spectrum. Shaded regions indicate the exciting laser's spectral position and bandwidth for the two scans. (b) Larmor frequencies extracted from FFT's of the TRFR with $E_{\rm laser}=2.0$ eV tuned near the first energy level. The solid lines are fits to the data indicating g factors of 1.5 and 1.1. Inset: FFT at $H=4$ T.

mediated coupling between them. Fast-Fourier transforms (FFT) of the multiperiodic TRFR for 57 Å QD's at low fields show distinct frequencies corresponding to g factors with magnitudes of ~1.1 and 1.5. The inset of Fig. 3(b) shows additional frequencies (g~1.6, 1.7) that become resolvable at $H=4$ T and produce lower frequency modulation of the decay envelope. Figure 3(b) shows the two consistently resolvable Larmor frequencies as a function of applied field. Both frequency components are linearly proportional to the field from 0.1–6 T. Although the g factor of ~1.1 is comparable to estimates of hole g factors, the electron g factor in CdSe is expected to be ~0.7.[17,21] Hole precession in semiconductors has not been observed due to rapid hole spin scattering in bulk systems[6] or hole spin pinning along the growth axis in quantum wells.[5] A similar axis exists in these wurtzite QD's, but the strength of any resultant pinning for near-spherical shapes has yet to be investigated.

Accurate comparison of these results with excitonic or free-carrier g factors requires further investigation into the dynamics of strongly exchange-coupled electron and hole spins. Recent theory suggests fine-structure splitting of QD energy levels due to the exchange interaction and crystal asymmetry.[22] It is important to note that in contrast to more traditional time-resolved optical measurements, the Faraday rotation does not explicitly arise from an optically active transition, and therefore may contain signatures of optically passive fine-structure exciton states (dark excitons).

Carrier trapping at surface sites becomes increasingly important as the size of QD's is reduced. The TRFR at low temperature for core and core/shell samples below 40 Å in diameter deteriorates by ~20% over time scales comparable to the scan duration (15 min), which adds uncertainty to the estimated spin relaxation lifetimes discussed above. Seen in PL measurements with nonresonant excitation, light-induced changes of optical properties in QD's have been attributed to mechanisms that depend on surface localization of carriers or photo- ionization.[10,11,13] Although previous studies indicate improved photochemical stability for CdS shell QD's,[12] the high peak intensities of femtosecond lasers may contribute to the observed degradation in signal through Auger-related processes.[11,13] The precession dynamics of surface-localized carriers will generally depend on the nature of the spin-orbit coupling at surface sites. TRFR in an applied field for QD's 40 Å in diameter and smaller is qualitatively different than for larger QD's. We observe a large monotonic decay of the Faraday rotation on which relatively weak oscillations are superimposed (peak to peak amplitude <10% of the total TRFR signal). The magnitude of this monotonic component varies in reproducibility, and has also been sporadically observed in the larger samples [note the small offsets in Fig. 1(b) and in the bottom curve of Fig. 3(a)]. The origin of this behavior is not clear, but the observation of photodegradation and variable reproducibility suggest that carrier trapping at surface sites may play an important role in the spin dynamics in these QD's.

In summary, we have used time-resolved Faraday rotation to monitor coherent carrier spin dynamics in semiconductor QD's, where inhomogeneous dephasing of spins is seen to limit the precession lifetime. The observation of spin precession at room temperature is promising for future coherent device applications. However, the multiperiodic and size-dependent Faraday rotation indicate a need for further understanding of the effects of the QD surface and electron-hole exchange on spin dynamics in these mesoscopic systems.

We acknowledge support from ARO DAAG55-98-1-0366, AFOSR F49620-99-1-0033, ONR N00014-99-1-0077, NSF DME-9871849, and DMR-9701072.

[1] A. P. Alivisatos, Science **271**, 933 (1996).
[2] D. J. Norris and M. G. Bawendi, Phys. Rev. B **53**, 16 338 (1996). The first (2.04 eV) and second (2.12 eV) energy levels in the 57 Å QD absorption spectrum [inset Fig. 3(a)] are consistent with the state assignments $1S_{3/2}1S_e$ and $2S_{3/2}1S_e$, respectively.
[3] G. Prinz, Phys. Today **48** (4), 58 (1995).
[4] D. Loss and D. P. DiVincenzo, Phys. Rev. A **57**, 120 (1998).
[5] S. A. Crooker, D. D. Awschalom, J. J. Baumberg, F. Flack, and N. Samarth, Phys. Rev. B **56**, 7574 (1997).
[6] J. M. Kikkawa and D. D. Awschalom, Phys. Rev. Lett. **80**, 4313 (1998).
[7] C. B. Murray, D. J. Norris, and M. G. Bawendi, J. Am. Chem. Soc. **115**, 8706 (1993).
[8] J. E. Bowen Katari, V. L. Colvin, and A. P. Alivisatos, J. Phys. Chem. **98**, 4109 (1994).
[9] V. Klimov, P. Haring Bolivar, and H. Kurtz, Phys. Rev. B **53**, 1463 (1996).
[10] M. Nirmal *et al.*, Nature (London) **383**, 802 (1996).
[11] S. A. Empedocles and M. G. Bawendi, Science **278**, 2114 (1997).
[12] X. Peng, M. C. Schlamp, A. V. Kadavanich, and A. P. Alivisatos, J. Am. Chem. Soc. **119**, 7019 (1997).
[13] V. Klimov and D. W. McBranch, Phys. Rev. B **55**, 13 173 (1997).
[14] V. Klimov, S. Hunsche, and H. Kurz, Phys. Rev. B **50**, 8110 (1994).
[15] J. M. Kikkawa, I. P. Smorchkova, N. Samarth, and D. D. Awschalom, Science **277**, 1284 (1997).
[16] S. Bar-Ad and I. Bar-Joseph, Phys. Rev. Lett. **68**, 349 (1992).
[17] M. Kuno *et al.*, J. Phys. Chem. **108**, 4242 (1998).
[18] W. Hoheisel, V. L. Colvin, C. S. Johnso, and A. P. Alivisatos, J. Chem. Phys. **101**, 8455 (1994).
[19] S. A. Crooker, D. D. Awschalom, and N. Samarth, IEEE J. Sel. Top. Quantum Electron. **1**, 1082 (1995).
[20] U. Waggon *et al.*, Phys. Rev. B **54**, 17 681 (1996). Time-resolved absorption data at 2.1 eV indicate nanosecond-scale decays of pump-induced transmission, although it is unclear whether this arises from absorption of small QD's in the distribution or state filling effects.
[21] B. L. Gel'mont and M. I. D'yakonov, Fiz. Tekh. Poluprovodn. **7**, 2013 (1973) [Sov. Phys. Semicond. **7**, 1345 (1973)].
[22] Al. L. Efros *et al.*, Phys. Rev. B **54**, 4843 (1996).