Spin precession and the optical Stark effect in a semiconductor-doped glass

J. A. Gupta and D. D. Awschalom
Department of Physics, University of California, Santa Barbara, California 93106
(Received 7 June 2000; revised manuscript received 8 August 2000; published 1 February 2001)

Femtosecond-resolved pump-probe techniques are used to investigate spin-dependent phenomena in a semiconductor-doped glass at temperatures from 6 to 300 K and in magnetic fields from 0 to 2 T. Faraday rotation experiments reveal nanosecond-scale spin lifetimes at zero field that are decreased by an order of magnitude in a transverse field of 2 T. Differential transmission measurements are used to study the optical Stark shift of the absorption edge as the pump energy is tuned below the semiconductor band gap. A pronounced polarization dependence of the Stark shift is observed, yielding 3.8 meV (1.6 meV) shifts for copolarized (cross-polarized) pump and probe beams. These experiments demonstrate a method of polarization-sensitive optical control in semiconductor nanostructures on ~100-fs time scales.

DOI: 10.1103/PhysRevB.63.085303 PACS number(s): 71.35.Ji, 42.50.Md, 42.50.Hz, 78.47.+p

The strong nonlinear optical properties of nanocrystals in semiconductor-doped glasses (SDG) present opportunities to study the effects of quantum confinement on the nonlinear optical susceptibility,[1] and for the use of these materials in fast optoelectronic devices. In addition, there is a rapidly growing interest in the use of carrier spin in semiconductor quantum structures as a medium for the storage of classical and quantum information.[2] Towards this end, semiconductor quantum dots have been proposed as a candidate for solid-state quantum computation,[3] supported by recent measurements of spin coherence in chemically synthesized quantum dots suspended in an organic polymer film.[4] Time-resolved optical studies of carrier energy relaxation in these systems have revealed a dependence of relaxation rates on the degree of surface passivation and the importance of Auger-like relaxation through photoionization into the surrounding matrix.[5,6] Because SDG consist of quantum dots prepared in a glass matrix,[7] measurements of spin coherence in these systems may enable studies of matrix effects on the spin dynamics of localized carriers over a broad range of nanocrystallite sizes.

Here we present pump-probe optical studies that measure spin coherence and spin-dependent nonlinear optical effects in one of a series of commercially available semiconductor-doped glasses (Corning 2-73) consisting of ~6-nm-diameter $CdS_{1-x}Se_x$ ($x \sim 0.5$) quantum dots.[1] Comparable to previous studies in CdSe quantum dots,[4] time-resolved Faraday rotation (TRFR) experiments reveal nanosecond-scale spin coherence lifetimes that are reduced upon application of a transverse magnetic field. However, in contrast to the multiperiodic spin precession observed previously (with g factors ranging from 1.2 to 1.7),[4] the data here are well described by a single g factor of 1.52. Differential transmission (DT) measurements where the pump energy is tuned below the semiconductor band gap show a rigid shift of the SDG absorption edge. This shift is consistent with an optical Stark effect,[8] and is seen to depend strongly on the relative polarizations of the pump and probe, thus demonstrating the ability to perform polarization-sensitive control of optical absorption on 100-fs time scales.

The experiments are performed in a magneto-optical cryostat capable of magnetic fields $H \leqslant 7$ T and temperatures from 2 to 300 K. An optical parametric amplifier operating at 250 kHz is used to produce ~150-fs pump pulses of energy-tunable light ($E_p = 1.7-2.6$ eV, ~10-meV bandwidth) and probe pulses consisting of a white-light continuum. The pump and probe beams are focused to a ~100-μm spot on the sample using an achromatic lens ($f/5$). In time-resolved Faraday rotation, a circularly polarized pump pulse excites electron-hole pairs that are spin-polarized along the optical path. In the presence of a transverse magnetic field, the pump-injected spins comprise a coherent superposition of spin eigenstates that are quantized along the magnetic field axis. Because these states are Zeeman split in energy, the temporal evolution of this superposition results in a quantum beating that corresponds to Larmor spin precession about the magnetic field. The Faraday rotation of linearly polarized probe pulses is proportional to the component of spin along the laser direction, and oscillates at the Larmor frequency, $\nu_L = g\mu_B H/h$, as a function of pump-probe time delay. After passing through the sample, the white-light probe is spectrally resolved using a $\frac{1}{8}$-m spectrometer. The Faraday rotation is then differentially detected using a balanced photodiode bridge.[9] To improve the signal-to-noise ratio, the pump helicity is alternated at 50 kHz using a photoelastic modulator, the probe is mechanically chopped, and the difference signal of the bridge is detected using lock-in amplifier techniques.

In order to monitor pump-induced changes in optical absorption, we measure differential transmission spectra defined as $\mathrm{DTS}(E_d) \equiv [T(E_d) - T_0(E_d)]/T_0(E_d)$, where $T(E_d)$ and $T_0(E_d)$ are the probe transmissions detected at an energy E_d with and without the pump, respectively. These measurements are typically performed with circularly polarized pump and probe pulses whose relative helicity is set by a computer-controlled variable retarder in the probe path. The probe is spectrally resolved after transmission through the sample using a 0.5-m spectrometer equipped with a photomultiplier tube (for single wavelength DTS), and a thermoelectrically cooled dual-channel photodiode array detector (for broad spectral resolution). The effects of laser noise can be reduced when using the diode array by splitting off a portion of the probe before the sample to serve as a reference that is detected by the second channel and to which the trans-

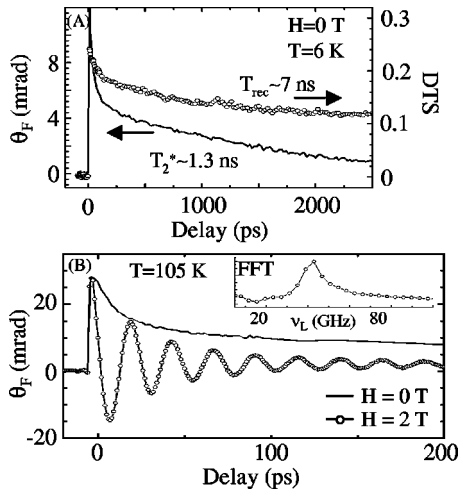

FIG. 1. (A) Comparison of TRFR and DTS at $T=6$ K taken with pump energy $E_p=2.243$ eV (3.5 GW/cm^2), and probe energy $E_d=2.227$ eV. (B) Field-dependent spin lifetimes at $T=105$ K. Data are taken at $H=0$ and 2 T with $E_p=2.236$ eV (0.15 GW/cm^2), and $E_d=2.205$ eV. T_2^* decreases from ~1 ns at zero field to <60 ps at $H=2$ T. Inset: fast Fourier transform of 2-T data.

mitted probe is normalized. Typically, 200 transmission spectra acquired in 20-ms exposures are averaged in order to resolve changes in DTS of $\sim 10^{-3}$. Gray-scale images of DTS are calculated from data sets comprising averaged spectra at each value of pump-probe delay, where T_0 is taken from spectra at negative time delay. Because the white-light continuum exhibits a substantial chirp of ~55 fs/nm, chirp correction of the DTS is performed in software using a calibration function obtained from measurements of two-photon absorption in a GaN epilayer.[10]

A comparison of simultaneously collected Faraday rotation and DTS decays at $T=6$ K is shown in Fig. 1(A). The decay of Faraday rotation yields an effective transverse spin lifetime, T_2^* which can include both longitudinal and transverse spin relaxation processes. For pump energies larger than the semiconductor band gap, the decay of DTS at fixed E_d generally reflects both energy relaxation and recombination processes (with a linearly polarized probe, the contribution from spin relaxation is absent). Energy relaxation in this sample is relatively fast (<1 ps), indicating that slower dynamics reflect a recombination lifetime, $T_{\rm rec}$. Both decays are typically biexponential, with components <100 ps and >1 ns.[11] Because the measured spin lifetimes in undoped samples are convolved with the carrier lifetime, it is useful to compare the decay times from differential transmission spectra and Faraday rotation. In comparing the longer lifetime component, we see that the differential transmission decays more slowly than the Faraday rotation ($T_{\rm rec}\sim 7$ ns versus $T_2^*\sim 1$ ns), indicating that the spin lifetime is not limited by carrier recombination processes. The data at $T=105$ K in Fig. 1(B) shows that in the presence of a transverse magnetic field, spin lifetimes in the SDG are reduced from ~1 ns at zero field to ~60 ps at 2 T. This is similar to previous results in CdSe quantum dots (QDs),[4] where the field-dependent spin lifetimes were attributed to inhomogeneous dephasing effects arising from a distribution of g factors in the sample. The inset to the figure shows a fast Fourier transform of the 2T data that indicates a Larmor frequency of 42.7 GHz, corresponding to a spin g factor of 1.52. This value is close to one of the g factors observed in the CdSe QD's, although it is interesting to note that here we only observe one distinguishable precession frequency. As discussed previously,[4] it is difficult to definitively ascertain the species responsible for spin precession in these systems, given the strongly coupled nature of electrons and holes in nanometer-sized clusters. We also note that spin coherence has been observed in the SDG at $T=290$ K, where the zero-field lifetime is ~360 ps, representing a 60% decrease versus the value at $T=6$ K. We observe no change in g factor over the entire temperature range studied ($T=6-290$ K). During these measurements, care was taken to adjust the pump and probe energies to track the temperature-dependent absorption spectrum that exhibits a redshift of ~100 meV over this range.

The optical Stark effect in semiconductors is manifested as a blueshift of energy levels that is induced by a pump beam tuned below the band gap.[12,13] Excitonic Stark shifts in semiconductors were first described by exploiting the analogy with ''dressed atoms'' where the shift occurs as a result of coupling between virtual excitations and pump photons.[12] Subsequent theories explained Stark shifts in terms of interactions between virtual and real excitons created by the

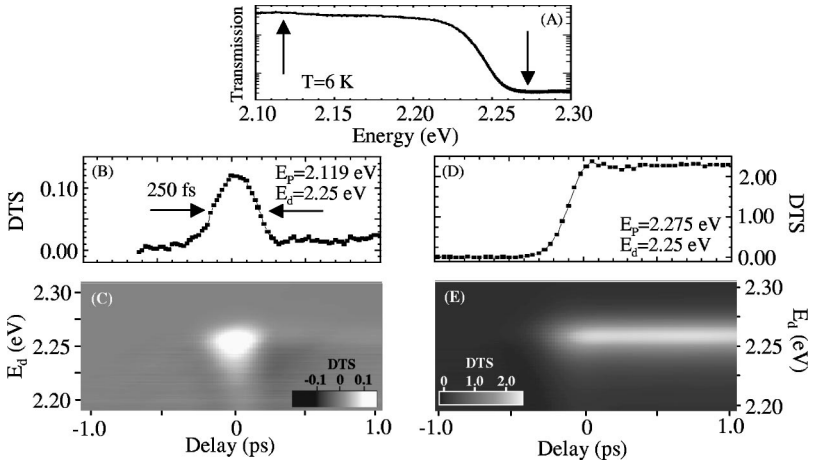

FIG. 2. (A) Linear transmission spectrum. Black arrows indicate pump energies of $E_p=2.119$ eV for (B) and (C) and $E_p=2.275$ eV for (D) and (E). (B)–(E) DTS with a pump intensity of 2.75 GW/cm^2, and co-circular pump/probe. (B) and (D) are linecuts of (C) and (E), respectively, at $E_d=2.25$ eV. All data are taken at $T=6$ K.

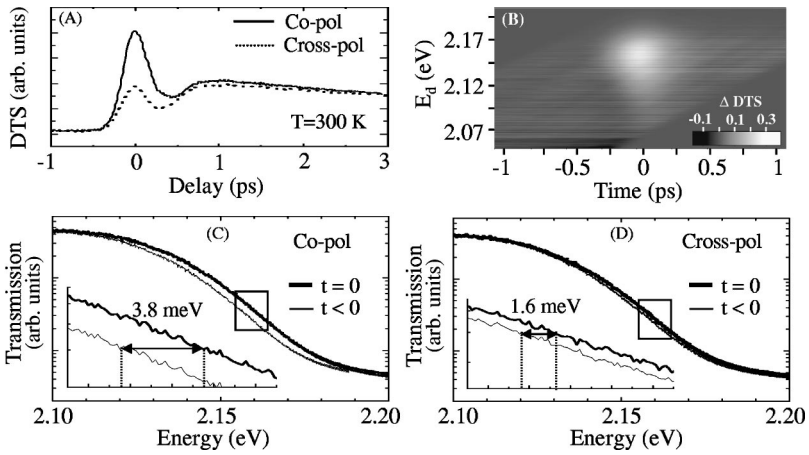

FIG. 3. Variation of DTS with probe helicity at $T=300$ K, $E_p=2.039$ eV. Pump intensity $=4.5$ GW/cm^2 in (A), 10.0 GW/cm^2 in (B)–(D). (A) DTS with $E_d=2.153$ eV. (B) Spectrally resolved difference in DTS of co-polarized and cross-polarized probe beams. (C) and (D) Chirp-corrected transmission data showing a rigid shift of the absorption edge at $t=0$.

pump and probe photons, respectively.[14] In solid-state systems, observation of the Stark shift is made possible by the high peak intensities of order 10^6-10^9 W/cm^2 available from short-pulse lasers. Due to the virtual nature of the excitations, the measured shift only lasts for the pump-probe correlation time (~250 fs), which we obtain from the two-photon absorption experiment in GaN mentioned above. Because the optical Stark effect has been widely studied in atomic systems,[15] quantum dots (with an atomiclike density of states) are a useful arena in which to study similarities and differences of Stark shifts in semiconductor systems. In measurements of DTS, the Stark shift should appear as a peak at zero delay whose amplitude is maximal when the detection energy, E_d, corresponds to an extremum of $d\alpha/dE$, where $\alpha(E)$ is the semiconductor absorption spectrum.[8]

In order to clearly observe the Stark shift, the pump energy and intensity must be adjusted to minimize the generation of real electron-hole pairs. The linear transmission spectrum of the SDG at $T=6$ K in Fig. 2(A) shows that the sample becomes absorptive for energies greater than ~2.22 eV, with maximal absorption reached by 2.26 eV. The data in Figs. 2(D)–2(E) are taken with a pump energy $E_p=2.275$ eV and indicate a strong pump-induced transmission of the probe that persists for nanoseconds [cf. Fig. 1(A)]. The spectral peak of this feature from the data in Fig. 2(E) occurs at $E_d=2.254$ eV, indicating that carriers have energy relaxed ~20 meV within the time resolution of the experiment. The full width at half maximum (FWHM) of this peak is 23 meV and may reflect contributions from an inhomogeneous distribution of ground-state energies in the quantum dots. A linecut of this data at $E_d=2.25$ eV is shown in Fig. 2(D) that is characterized by a 100-fs rise time to a flat plateau. In contrast, long-lived contributions to the DTS are diminished for $E_p=2.119$ eV, leaving a prominent feature at zero delay in Fig. 2(B) whose temporal width of 250 fs matches that of the pump-probe correlation. From Fig. 2(C) we see that this feature peaks at an energy of $E_d=2.247$ eV, which is near to that expected from a calculation of $d\alpha/dE$ using the data in Fig. 2(A). The spectral width of the bright feature from a vertical linecut through the data in Fig. 2(C) at $t=0$ ps is ~30 meV. As expected, this corresponds to the width of the absorption edge since the Stark shift is only measurable in DTS where $d\alpha/dE\neq 0$. The optical Stark effect has been observed in this sample from $T=6-300$ K and is comparable to that obtained in earlier studies.[8]

Polarization resolution of the optical Stark effect has been useful in separately identifying conduction- and valence-band shifts of exciton transitions in GaAs/Al$_x$Ga$_{1-x}$As quantum-well samples.[16] The optical selection rules in zinc-blende semiconductors predict that shifts measured when the pump and probe are cross-polarized solely arise from the conduction band. While this band picture only approximates the situation in these quantum dots, we do observe a significant polarization difference in the optical Stark effect between co-polarized and cross-polarized pump/probe beams. Recent calculations of exciton states in CdSe quantum dots have indicated that state-mixing plays an important role in determining the energy spectrum and optical selection rules,[17] an effect that might set an upper limit on the measured polarization dependence of Stark shifts in this sample. Figure 3(A) shows that at high excitation intensity, the DTS

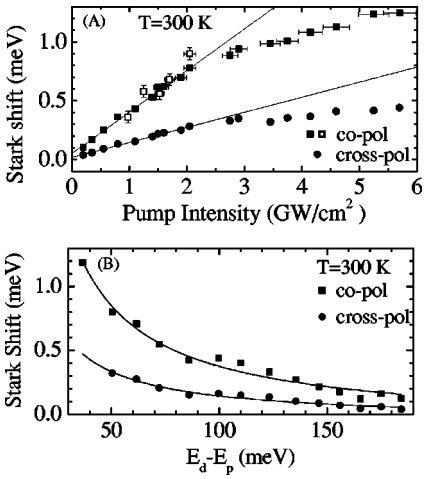

FIG. 4. (A) Stark shift vs pump intensity with $T=300$ K, $E_p=2.033$ eV, and $E_d=2.153$ eV (solid lines are fits to the low-intensity data). (B) Variation of the Stark shift with pump detuning at $T=300$ K with $E_d=2.153$ eV, pump intensity$=0.7$ GW/cm^2. Solid lines are qualitative fits as described in the text. Solid symbols are calculated from DTS taken using the photomultiplier tube, while open squares are obtained from direct measurements of shifts as in Figs. 3(C) and 3(D).

typically contain both the peak due to the Stark shift at zero delay and a longer-lived feature that could be due to two-photon absorption or residual overlap of the pump with the tail of the absorption spectrum. Because two-photon processes excite high-energy carriers given by $E_p+E_d\sim 4$ eV, the relatively slow ~500-fs rise time of this feature could indicate the time for carriers to relax down to E_d, where they contribute to the DTS. The data in Fig. 3(B) are the difference in DTS between co-polarized and cross-polarized probe beams and indicate that little polarization exists after the Stark shift peak, which may reflect concurrent energy and spin relaxation of two-photon generated carriers. There is a significant dependence of this long-lived component on the pump energy, however, that is not expected for two photon processes until $E_p+E_d<E_{\mathrm{gap}}$,[10] which indicates that absorption into low-energy states in the SDG may also contribute. Figures 3(C)–3(D) are taken from linecuts at a fixed time delay of chirp-corrected probe transmission data prior to calculation of the DTS, thus allowing direct observation of the pump-induced shift of the absorption edge. By comparing the transmission spectrum at negative time delay with the spectrum at $t=0$ ps, we are able to measure a blueshift of 3.8 meV for a co-polarized probe, and 1.6 meV for a cross-polarized probe. Because of the high intensities used for these scans, the spectrum does not completely recover for $t>0$ ps (not shown), indicating the inadvertent generation of real carriers. We note that comparable shifts at lower pump energy ($E_p=2.019$ eV) have been observed which show complete recovery of the spectrum for $t>0$ ps.

Calculations of Stark shifts in semiconductors in the perturbative regime (low intensity and large detuning) predict a shift that is proportional to the pump intensity and inversely proportional to the pump detuning.[14] Figure 4(A) shows the dependence of the optical Stark effect on pump intensity for a pump detuning given by $E_d-E_p=120$ meV. We generally observe a departure from linearity (solid lines) as the pump intensity is increased that is consistent with previous studies[8] and has been theoretically described using a many-body treatment.[18] As the pump detuning is increased, the point where the dependence becomes nonlinear shifts toward higher intensities and there is an overall decrease in the Stark shift at fixed pump intensity [Fig. 4(B)].[19] The solid lines in Fig. 4(B) are qualitative fits to the data of the form $a+b/x$, where x is the pump-probe detuning and b is proportional to the pump intensity. While the data are consistent with theoretical expectations, more quantitative analysis is difficult given the unresolved nature of exciton states and the spectrally broad absorption edge that leads to unavoidable generation of real carriers at smaller pump detuning.

In summary, Faraday rotation experiments have revealed nanosecond-scale spin dynamics in a semiconductor-doped glass that persist to room temperature. Femtosecond-resolved differential transmission spectroscopy was used to produce direct measurements of the optical Stark effect and to study its dependence on polarization, pump intensity, and pump detuning. The combination of these techniques may enable optical control of spin coherence by using off-resonant pulses to produce Stark shifts of energy levels during the coherent evolution of spins in a transverse magnetic field.

This work was supported by grants ARO DAAG55-98-1-0366, NSF DMR-9871849 and DMR-0071888, ONR N00014-98-1-0077, and DARPA/ONR N00014-99-1-1096.

[1] G. P. Banfi, V. Degiorgio, and D. Richard, Adv. Phys. **47**, 447 (1998). Estimates of nanocrystal size and composition in the Corning SDG are based on comparisons to the optical absorption spectrum of Schott glass OG-590.

[2] D. D. Awschalom and J. M. Kikkawa, Phys. Today **52(No. 6)**, 33 (1999), and references therein.

[3] D. Loss and D. P. DiVincenzo, Phys. Rev. A **57**, 120 (1998).

[4] J. A. Gupta, D. D. Awschalom, X. Peng, and A. P. Alivisatos, Phys. Rev. B **59**, 10 421 (1999).

[5] V. Klimov, Ch. J. Schwarz, D. W. McBranch, C. A. Leatherdale, M. G. Bawendi, Phys. Rev. B **60**, 2177 (1999).

[6] V. Klimov and D. W. McBranch, Phys. Rev. B **55**, 13 173 (1997).

[7] N. F. Borrelli, D. W. Hall, H. J. Holland, and D. W. Smith, J. Appl. Phys. **61**, 5399 (1987).

[8] S. Tsuda and C. H. Brito Cruz, Appl. Phys. Lett. **68**, 1093 (1996).

[9] S. A. Crooker, D. D. Awschalom, J. J. Baumberg, F. Flack, and N. Samarth, Phys. Rev. B **56**, 7574 (1997).

[10] T. F. Albrecht, K. Seibert, and H. Kurz, Opt. Commun. **84**, 223 (1991).

[11] Further measurements at negative time delays give evidence for microsecond-scale dynamics in both the DTS and TRFR that indicate the presence of a third decay component not resolved in scans of pump-probe time delay on the nanosecond scale.

[12] A. Mysyrowicz, D. Hulin, A. Antonetti, A. Migus, W. T. Masselink, and H. Morkoç, Phys. Rev. Lett. **56**, 2748 (1986).

[13] D. Fröhlich, A. Nöthe, and K. Reimann, Phys. Rev. Lett. **55**, 1335 (1985).

[14] M. Combescot and R. Combescot, Phys. Rev. Lett. **61**, 117 (1988).

[15] C. Cohen-Tannoudji and S. Reynaud, J. Phys. B **10**, 345 (1977).

[16] M. Joffre, D. Hulin, A. Migus, and M. Combescot, Phys. Rev. Lett. **62**, 74 (1989).

[17] Al. L. Efros, M. Rosen, M. Kuno, M. Nirmal, D. J. Norris, and M. G. Bawendi, Phys. Rev. B **54**, 4843 (1996).

[18] C. Ell, J. F. Müller, K. El Sayed, and H. Haug, Phys. Rev. Lett. **62**, 304 (1989).

[19] Stark shifts can be calculated from DTS using the relation $\Delta E=\Delta\alpha(d\alpha/dE)^{-1}$, where $\alpha(E)$ is the absorption spectrum and $\Delta\alpha=-(L)^{-1}[\ln(\mathrm{DTS})+1]$ is the pump-induced change in absorption coefficient (L is the sample thickness).