Exciton Spin Dynamics in GaAs Heterostructures

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We report the experimental observation of exciton spin relaxation in GaAs quantum wells in moderate magnetic fields. We resolve the electron and hole contributions and discuss the large sensitivity of the spin-relaxation time to exciton localization and quantum well width. We use the long duration of spin orientation to demonstrate deep transient oscillations, resulting from biexcitonic effects.

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The spin-relaxation process in semiconductor heterostructures results in depolarization of the photoluminescence (PL) and of the induced absorption, as well as in dephasing of the electronic wave function. It is believed that this process is substantially modified in two-dimensional systems, especially for holes whose degeneracy at the zone center is removed. While there is a vast literature on the energy relaxation process of electrons and holes in semiconductor quantum wells (QW), there are only a few investigations of carrier spin relaxation. The determination of the dynamics of this process and the understanding of the mechanisms which are involved have been of growing interest in recent years [1–11].

Optical spectroscopy has been extensively implemented for the research of spin-relaxation processes in GaAs QW, mainly by way of measuring the degree of polarization in the PL emitted following cw excitation by polarized light [1,2]. The electron spin-relaxation time, deduced with the assumption of instantaneous hole spin relaxation during thermalization [3], was found to be $\sim$200 ps at 4 K. This is not very different from the spin-relaxation times reported for bulk GaAs and AlGaAs [4]. Recent PL excitation experiments in QW in magnetic fields up to 20 T claimed inhibition of the spin flip of conduction electrons during thermalization [5].

Time-resolved optical spectroscopy allows separation between the initial depolarization, resulting from the thermalization process, and that of low-energy carriers at the bottom of the band. Correlating time-resolved and cw PL spectroscopy, Freeman *et al.* have shown that spin lifetimes cannot reliably be extracted from cw spectra [6]. They have also found that the depolarization rate is sample dependent. Using the same technique and exciting a high-quality QW sample at the excitonic resonance, Damen *et al.* reported an electron spin-relaxation time constant of $\approx$50 ps and instantaneous spin relaxation for the holes [7]. Theoretical studies, however, predict a significant suppression of the spin flip rate for free heavy-hole states near the zone center [8–10]. This apparent disagreement between theory and experiment indicates that the process of spin relaxation of excitons is not well understood and further experimental data are required.

Time-resolved absorption measurements have the potential to discriminate between the relaxation of spins in the conduction and valence bands, and to overcome a basic limitation of ultrafast PL techniques in performing an excitation at the band-gap energy. Tackeuchi *et al.* [11] have performed such measurements at room temperature, and found instantaneous depolarization of the holes and a 30-ps electron spin-relaxation time.

In this paper we report on a time-dependent absorption experiment with several GaAs QW samples at liquid-helium temperature, in magnetic fields up to 4 T. Using circularly polarized pump and probe tuned to the band gap, our measurements resolve for the first time the hole spin-relaxation time and show the relative insensitivity of the spin-relaxation process to a moderate magnetic field applied parallel to the growth axis. We also demonstrate large variations of the hole spin-relaxation time between samples and discuss our findings in the framework of present theories. The preservation of spin orientation and phase coherence for long durations allows the observation of coherent oscillations which accompany the initial rise of the differential absorption signal, for the case of oppositely handed pump and probe polarizations. We attribute these oscillations to the formation of biexcitons, and use their period to obtain the biexciton binding energy.

We used mode-locked pyridine 2 and styryl 8 dye lasers, both with $\approx$1-ps time resolution. The polarization of the pump (σ^+) was fixed during an experiment, while the mounting of the quarter-wave plate in the probe beam allowed reversing of the probe handedness (from σ^+ to σ^-) without affecting the zero time of our setup. The experiment was performed at various pump intensities, from 0.3 to 30 W/cm^2, with the probe intensity being roughly equal to that of the pump (we have verified that the results are independent of the probe intensity).

We have studied three different GaAs/AlGaAs samples: a square multiple quantum well (MQW) sample, a stepped MQW sample, and a superlattice. The square MQW sample has 20 periods of 80-Å GaAs wells separated by 300-Å $Al_{0.3}Ga_{0.7}As$ barriers, with a strong heavy-hole excitonic absorption line at 1.570 eV. The stepped MQW sample has 100 stepped wells, with adjacent layers of 30 Å GaAs and 100 Å $Al_{0.1}Ga_{0.9}As$, separated by 100-Å $Al_{0.3}Ga_{0.7}As$ barriers. The structure is embedded in the intrinsic region of a *p-i-n* structure.

The wave functions associated with the first energy levels of the electron and holes are confined mainly in the 30-Å GaAs layer. The first electron energy level in this structure coincides with the potential step of the well, which makes the structure prone to large potential disorder due to well width and alloy fluctuations. Indeed, the absorption spectrum of that sample shows a wide (≈ 6 meV), inhomogeneously broadened, heavy-hole excitonic peak at 1.617 eV. The superlattice sample consists of 100 periods of alternating 30-Å layers of GaAs and $Al_{0.3}Ga_{0.7}As$, with the heavy-hole excitonic absorption line at 1.683 eV. This structure is also embedded in the intrinsic region of a *p-i-n* junction.

Figure 1 shows the temporal evolution of the signal when the stepped MQW sample is degenerately pumped and probed just below the heavy-hole excitonic absorption peak (1.613 eV). The inset shows the two allowed heavy-hole exciton transitions in GaAs QW, coupled to σ^+ and σ^- polarizations and degenerate at zero magnetic field. Figure 1(a) shows the change of absorption of a σ^+ probe and that of a σ^- probe, following excitation by a σ^+ pump. In Fig. 1(b) we plot the σ^- signal with better definition. The data shown in the figure were taken at zero magnetic field with pump intensity of approximately 30 W/cm^2 (corresponding to exciton density of 1.5×10^{10} cm^{-2}). The first few tens of picoseconds after excitation are characterized by a sharp decrease of the σ^+ signal and a sharp rise of the σ^- signal. The two curves then converge gradually and coincide approximately 350 ps after excitation, indicating that complete spin relaxation has been reached by then. This behavior suggests the existence of two sequential processes. In Fig. 1(c) we plot the logarithm of the difference between the two signals of Fig. 1(a), as a measure of the net relaxation rate of the difference between the σ^+ and σ^- exciton populations. Two time constants, approximately 50 and 120 ps, are clearly observed. We associate the short one with the spin relaxation of the heavy hole, and the long one, after which the two spin populations are equalized, with the electron spin relaxation. Note, however, that the σ^- signal is decaying at long delays rather than increasing with the spin relaxation of the electrons. This point will be addressed in detail later in this paper. The same general behavior, of two time constants and a decay of the σ^- signal at long delays, was observed when the pump intensity was lowered over two decades.

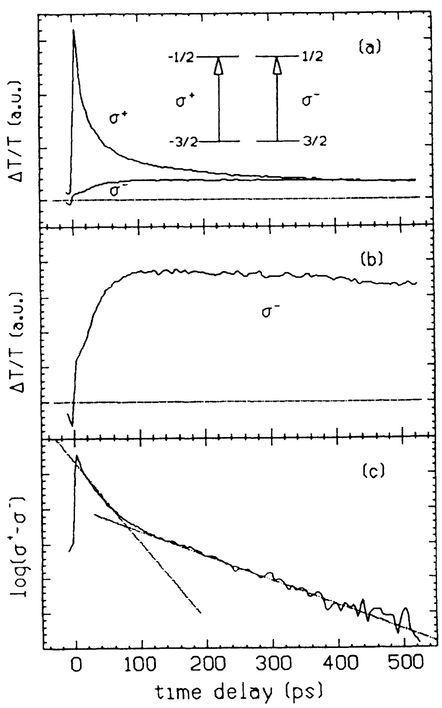

FIG. 1. The differential absorption signal slightly below the heavy-hole exciton of the stepped MQW sample, with σ^+ pump polarization and intensity of 30 W/cm^2. (a) The signals for σ^+ and σ^- probe at $B=0$. (Inset: The allowed optical transitions.) (b) The σ^- signal with better definition. (c) The logarithm of the difference between the σ^+ and σ^-.

The superlattice sample also shows a clear double-exponent behavior, with somewhat different time constants (35 and 250 ps for the holes and electrons, respectively). The square MQW sample, on the other hand, behaves differently: The rise of the σ^- signal is instantaneous and the hole spin relaxation cannot be resolved. The σ^- and σ^+ signals approach the same level after 400 ps. This behavior is similar to that which was observed by Damen *et al.* for a high-quality sample [7]. The difference between the square MQW sample and the two other samples shows up in another form: The pump-probe signal in that sample does not show any Stokes shift relative to the absorption spectrum, contrary to the case of the two other samples. The existence of such a shift between the linear and the nonlinear responses is an indication of the existence of localized excitons in the sample [12]. Furthermore, we have conducted pump-probe measurements with *linear* polarizations on the three samples in a magnetic field. While the stepped MQW and the superlattice samples showed absorption quantum beats between Zeeman-split levels [13], no trace of such beats were observed in the square MQW sample. We have previously shown that these beats are observed due to the slow dephasing of localized excitons.

Present theories for hole spin relaxation [8–10] do not address the excitonic case in general, and the effect of localization in particular. It is thus difficult to perform a direct comparison between our results and the theory. However, it is clear that our measurements and those of Ref. [7] cannot be reconciled with the energy-independent long relaxation time predicted in Ref. [9]. To apply the results which were calculated for free holes in Ref. [10] to the case of excitons one should perform a weighted averaging of the calculated relaxation rates over all k states which contribute to the two-dimensional excitonic wave function. As a zero-order estimate we take the scattering rate at $k \sim 1/a_0$ (where a_0 is the Bohr radius) for the appropriate well widths. This yields a faster relaxation rate than at $k=0$, in better agreement with the experimental results. In addition, we note that the low-energy localized excitons, which contribute to the Stokes-shifted differential absorption signal, have a limited phase space for scattering, and therefore maintain their spin orientation and phase for longer duration. We are thus led to believe that hole spin relaxation in free excitons in wide QW is very fast, and is accompanied by complete dephasing. Holes in localized excitons in narrow QW, on the other hand, take several tens of picoseconds to completely relax their polarization, keeping their phase coherence. A more comprehensive theory is required to describe these effects.

Focusing on the instantaneous rise of the signal, a very striking phenomenon is observed. Figure 2 is a closeup of the first few picoseconds of σ^- signal in the stepped MQW sample, with 3-W/cm^2 pump and probe intensities. The sudden change of absorption is accompanied by deep damped oscillations. Similar oscillations were measured with the superlattice sample, but none were observed with the square MQW sample. Three main features are apparent in Fig. 2: a negative dip followed by oscillations and a final positive signal (decreased absorption). All three features exist throughout the low-energy side of the excitonic absorption line, and their amplitude scales linearly with the intensity of the probe and approximately as the square root of the intensity of the pump, across 3 orders of magnitude. The period of the oscillations is independent of both the intensity and the excitation energy. The oscillation period was measured to be 1.6 ps for the stepped QW sample and 2 ps for the superlattice sample. The oscillation amplitude decreases slightly at 30 K and at 60 K it is completely washed out. The effect of magnetic fields up to 4 T was to suppress the signal, with a gradual small increase of the oscillation period.

We checked the influence of pulse width and pulse shape on the observed signal, by changing the cavity length of the laser. There was no measurable change of the oscillation period or the damping. We also verified that the internal field of the *p-n* junction in both the stepped MQW and superlattice samples is not the common factor behind the oscillatory transient. Applying a +1.5 V voltage to a processed superlattice sample, the measured signal in this flat-band situation was identical to the signal measured with no electrical contacts.

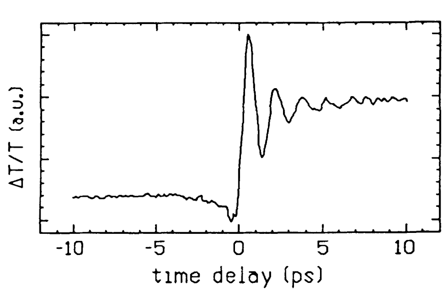

FIG. 2. The transient σ^- signal for the stepped MQW sample.

We examined several possible mechanisms to explain the observed oscillations, which are indicative of the existence of a fundamental energy gap of about 2.5 meV. Removal of spin degeneracy due to spin-orbit coupling can exist in principle in asymmetric structures but the energies of the σ^+ and the σ^- transitions remain degenerate. Moreover, the observation of the oscillations in the symmetric superlattice, under flat-band conditions, contradicts this explanation. In addition, the effect is too small (by orders of magnitude) to explain such a large energy gap. The insensitivity of the oscillation period to the energy and intensity of the excitation tends to reject any explanation which is based on optical nutations [14]. The fact that the oscillations are observed only for the case of pump and probe of opposite circular polarizations raises the possibility that the oscillations are of biexcitonic origin. Excitons created by a σ^- probe at a location where σ^+ excitons were created by the pump would bind with these pump excitons to create a biexciton molecule. The observed oscillations can thus be interpreted as resulting from a renormalization by the pump of the available states for absorption of the probe: As states are eliminated at the exciton energy E_x, other states are created at the lower biexciton energy E_{bx} (the exciton energy minus the biexciton binding energy). This gives rise to a σ^- polarizability which has two terms: a positive one at E_x (decreased absorption) and a negative one at E_{bx} (increased absorption). The result would therefore be a beating in the macroscopic polarizability at the difference frequency, i.e., the biexciton binding energy. The bandwidth of our laser, ~1.5 nm, is large enough to observe such a splitting. Indeed, as the pulse is distorted to get a larger bandwidth, the observed oscillations are deeper. Our results imply that the biexciton binding energy in these samples is 2–2.7 meV. This value is in agreement with recent PL measurements in narrow QW which give 2.8 meV for the biexciton binding energy [15]. It is, however, larger than previously reported values [2] for wide GaAs QW, ~1 meV, and calculations which suggest an upper limit of 2 meV for narrow QW [16].

The dynamics of the spin-relaxation process following the damping of the oscillations, and its dependence on the magnetic-field strength, substantiates this interpretation. Figure 3 shows typical data measured with oppositely handed circular polarizations on the stepped MQW sample, with 3 W/cm^2. The $B=0$ curve shows a large instantaneous rise and a pronounced drop at long delay times. When the magnetic field is applied, however, both features gradually disappear. We observe that the larger the instantaneous rise, the larger the drop at long delays. The spin-relaxation times, however, remain nearly constant. A careful analysis of the data, by subtracting the σ^- signal from the σ^+ signal, shows an increase of no

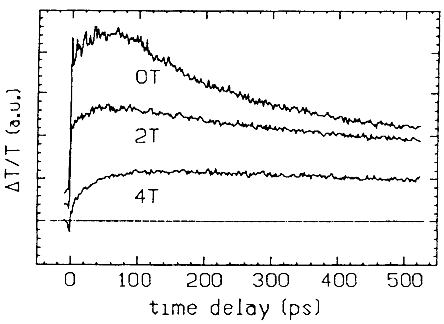

FIG. 3. The differential absorption signal for a σ^- probe at several magnetic fields.

more than 25% in the relaxation times between 0 to 4 T. This behavior can be understood as resulting from the interplay between spin relaxation, biexciton pairing, and phase-space filling. Following the damping of the oscillations, and before spin flip of σ^+ pump excitons occurs, the only contribution to the σ^- signal is of biexcitonic origin. As the population of σ^- pump excitons builds up at the rate of the electron spin relaxation, a spontaneous biexcitonic pairing of pump excitons takes place. A late arriving probe pulse finds less and less free pump excitons to pair with and the biexcitonic contribution to the pump-probe signal decays. The remaining contribution to the signal is due to phase-space filling, which was built up with the spin flip of the holes. This explains the gradual decrease of the signal at long probe delays, and the observation that the net decrease is proportional to the instantaneous rise of the signal. The effect of a magnetic field would then be to suppress exciton pairing due to the removal of the degeneracy in energy (Zeeman splitting), and thereby to reduce the biexcitonic contribution to the signal. This results also in a decrease of the binding energy which is manifested as an increase of the measured oscillation period. A further support to this picture comes from the intensity dependence of the signal. It can be seen that the $B=4$ T curve at 3 W/cm^{-2} (Fig. 3) shows a similar temporal evolution to the $B=0$ T curve at 30 W/cm^{-2} [Fig. 1(b)]. As phase-space filling effects become dominant at high intensities, the relative contribution of biexcitons diminishes.

We also looked at the case of pumping with σ^- polarization and probing with σ^+ polarization, by reversing the direction of the magnetic field; some increase of the spin-relaxation rate was observed, but the general behavior remained unchanged. We note that the Zeeman splitting in this sample in a field of 4 T is approximately 0.4 meV, comparable with $k_B T$ at liquid-helium temperature [13]. Finally, the negative dip measured at early times seems to map the pulse shape. Contrary to the other features of the short-time-scale signal, this part does not saturate at high laser intensities and becomes dominant at pump intensities larger than 30 W/cm^{-2}. It may thus be a redshift contribution from the ac Stark effect of the pump pulse. Indeed, a redshift was predicted for near band-gap pumping, on the grounds of biexcitonic interactions [17].

In conclusion, our measurements show that the role of biexcitonic effects in GaAs QW is more important than was previously believed. We demonstrate the strength of time-resolved measurements which are performed on time scales shorter than the dephasing time of the induced polarizability. They enable the observation of small energy gaps that otherwise would have been hidden by the large inhomogeneous broadening in QW samples.

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[1] C. Weisbuch, R. C. Miller, R. Dingle, A. C. Gossard, and W. Wiegmann, Solid State Commun. **37**, 219 (1981).

[2] R. C. Miller and D. A. Kleinman, J. Lumin. **30**, 520 (1985).

[3] R. C. Miller, D. A. Kleinman, W. A. Nordland, and A. C. Gossard, Phys. Rev. B **22**, 863 (1980).

[4] A. H. Clark, R. D. Burnham, D. J. Chadi, and R. M. White, Phys. Rev. B **12**, 5758 (1975); Solid State Commun. **20**, 385 (1976); G. Fishman and G. Lampel, Phys. Rev. B **16**, 820 (1977); K. Zerrouati, F. Fabre, G. Bacquet, J. Bandet, J. Frandon, G. Lampel, and G. Paget, Phys. Rev. B **37**, 1334 (1988).

[5] M. Potemski, J. C. Maan, A. Fasolino, K. Ploog, and G. Weimann, Phys. Rev. Lett. **63**, 2409 (1989).

[6] M. R. Freeman, D. D. Awschalom, J. M. Hong, and L. L. Chang, in *Proceedings of the Twentieth International Conference on Physics of Semiconductors*, edited by E. M. Anastassakis and J. D. Joannopoulos (World Scientific, Singapore, 1990), p. 1129.

[7] T. C. Damen, Karl Leo, Jagdeep Shah, and J. E. Cunningham, Appl. Phys. Lett. **58**, 1902 (1991).

[8] A. Twardowski and C. Hermann, Phys. Rev. B **35**, 8144 (1987).

[9] T. Uenoyama and L. J. Sham, Phys. Rev. Lett. **64**, 3070 (1990).

[10] R. Ferreira and G. Bastard, Phys. Rev. B **43**, 9687 (1991).

[11] A. Tackeuchi, S. Muto, T. Inata, and T. Fujii, Appl. Phys. Lett. **56**, 2213 (1990).

[12] L. Schultheis, M. D. Sturge, and J. Hegarty, Appl. Phys. Lett. **47**, 995 (1985).

[13] S. Bar-Ad and I. Bar-Joseph, Phys. Rev. Lett. **66**, 2491 (1991).

[14] L. Allen and J. H. Eberly, *Optical Resonance and Two Level Atoms* (Wiley, New York, 1975).

[15] B. Deveaud (private communication).

[16] D. A. Kleinman, Phys. Rev. B **28**, 871 (1983).

[17] M. Combescot and R. Combescot, Phys. Rev. B **40**, 3788 (1989).