# Femtosecond Spin-Polarization Spectroscopy in Diluted-Magnetic-Semiconductor Quantum Wells

M. R. Freeman, D. D. Awschalom, J. M. Hong, and L. L. Chang
*IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598*
(Received 14 November 1989)

Charge-carrier spin scattering in diluted-magnetic-semiconductor multiple quantum wells is directly observed through the circular polarization of luminescence in a femtosecond time-resolved measurement. This represents a new short-time regime for direct spin-relaxation studies. Separate observations of electron and hole relaxation are accomplished by varying the applied magnetic field. Surprisingly, the spin-flip scattering rates in these systems appear to be independent of the extremely strong spin-spin–exchange interaction between the charge carriers and the magnetic ions.

PACS numbers: 73.20.Dx, 75.50.Pp, 75.50.Rr, 78.47.+p

Advances in experimental methods and in materials engineering continue to drive progress in the understanding of electronic and magnetic behavior in low-dimensional systems. Currently there is a great deal of interest in spin-dependent effects for quantum-confined electrons[1] and in the magnetic properties[2] of quasi-two-dimensional systems. Epitaxially grown artificial structures of diluted-magnetic-semiconductor (DMS) materials[3] provide unique opportunities for the study of such phenomena, allowing one to control not only the confinement of charge carriers but also the specific spatial regions in which the carriers and magnetic material may interact. DMS materials hold a distinct advantage over other (for example, metallic) magnetic hosts for the investigation of fast phenomena such as carrier spin scattering, in that they can be probed using transient carrier populations generated by optical pulses. The high strength of spin-spin exchange between charge carriers and the localized magnetic ions leads to predictions of carrier spin scattering times in the picosecond regime for these compounds. This paper presents femtosecond time-resolved luminescence measurements which, through their circular polarization,[4] record in real time the spin scattering of optically excited charge carriers in magnetic and nonmagnetic quantum-well structures. The results demonstrate *direct* spin-relaxation measurements in the subpicosecond time regime, and indicate that quantum confinement, in addition to the electron-Mn exchange interaction, plays an important role in relaxing nonequilibrium carrier spin distributions in DMS quantum wells.

The structures used for these experiments are composed of $Cd_{1-x}Mn_xTe$, a zinc-blende crystal with the same direct-gap band structure as GaAs. The low-temperature band gap as a function of Mn concentration interpolates between the 1.605-eV value of pure CdTe and the hypothetical 3.201-eV gap of zinc-blende MnTe. The quantum wells are grown by molecular-beam epitaxy (MBE) on GaAs(100) substrates, and are oriented with the (111) axis perpendicular to the plane of the layers.[5] A 150-nm CdTe buffer layer beneath the quantum wells relaxes the lattice mismatch between the substrate and the deposited material. The crystal quality is monitored during growth by reflection high-energy electron diffraction, while the completed samples are characterized through x-ray-diffraction and low-temperature photoluminescence measurements. A collection of samples, having Mn concentrations in the wells of 0, 6.5%, and 13% and in the barriers between 15% and 38%, are used in these experiments. The well and barrier thicknesses span the range between 18 and 160 Å. A magneto-optical cryostat establishes the environment in which temperature and magnetic field, respectively, are variable from 1.6 to 300 K and 0 to 5 T. The field and the optical axis for luminescence collection are parallel, and this direction and the excitation beam are both oriented within 10° of normal to the layer planes of the sample.

Time resolution on the order of the laser pulse width is obtained through the sum-frequency-generation technique.[6] In this method, a time-delayed probe pulse interrogates a time slice of the luminescence signal as the two pass coincidently through a thin nonlinear crystal, in this case lithium iodate. A small number of sum-frequency photons are generated for those luminescence wavelengths which, along with the probe beam, satisfy the phase-matching condition of the crystal. An angle-tuned crystal is used in order that the detected photon energy may be changed without altering the laser wavelength, simply by rotating the crystal. Actual signal sizes are of order 100 counts per second for quantum structures with high intrinsic luminescence intensity relative to the corresponding bulk material. The sample excitation and probe beams are from a tunable two-jet dye laser synchronously pumped by a frequency-doubled Nd-doped yttrium-aluminum-garnet source mode locked at 76 MHz. The dye laser is cavity dumped at 3.8 MHz in order to obtain high pulse energies, desirable for increasing the efficiency of sum-frequency generation, while maintaining modest average power (typically 1 mW on a 100-$\mu$m-diam focus spot). Experiments are carried out with fiber-prism compressed pulses as short as 60 fs in duration, or, for higher carrier concentrations, pulses directly from the dye laser (as short as 0.7 ps full width at half maximum). The time zero position and the

 

resolution of the measurement are determined by cross correlation of the probe pulse with pump light scattered from the surface of the sample. With the compressed pulses we find that the temporal resolution is limited in the present configuration to 150 fs by dispersion in the optics.

In Fig. 1, initially non-spin-polarized carriers generated by a linearly polarized excitation acquire a net polarization in the presence of a finite magnetic field. The relationship between optical polarization and charge-carrier spin alignment is determined in both excitation and recombination by the relative strengths of the selection-rule-allowed transitions and by the populations of the participating states.[4] The time dependences of the left- and right-circularly polarized components of luminescence are shown for a sample with 86-Å-wide $Cd_{0.87}Mn_{0.13}Te$ quantum wells separated by 86-Å-wide $Cd_{0.62}Mn_{0.38}Te$ barriers. The excitation energy is 200 meV above the energy of the peak of the dc luminescence line (inset), which is where the luminescence is detected. The modest magnetic field (0.75 T) at $T=4$ K in Fig. 1 is sufficient to fully polarize the luminescence, as seen in dc measurements,[7] because of the very high effective $g$ factors ($\sim 1000$) of the carriers due to spin-spin exchange with the Mn ions leading to a band splitting of $\sim 10$ meV. The time-resolved measurement addresses the question of what spin-flip scattering mechanism determines the relaxation of the carrier spins from the initially unpolarized state into the equilibrium orientation in the field. Unpolarized carriers would emit luminescence of equal intensity in both circular polarizations. Since the $\sigma^-$ component in the experiment is absent down to the shortest observation time, the onset time of the *net polarization*, $(\sigma^+ - \sigma^-)/(\sigma^+ + \sigma^-)$, is essentially zero on the scale of the measurement. This indicates very rapid scattering of the holes, because the fully circularly polarized luminescence seen in Fig. 1 from recombination between an $s$-type conduction band and a $p$-like valence band occurs only with polarized holes. This is consistent with the belief that hole "spin" scattering is virtually instantaneous due to very strong spin-orbit effects in the valence band,[4,8] and we find that this rapid hole scattering occurs even when a magnetic field has broken the degeneracy. The rise time of the observed luminescence intensity is slow relative to bulk LO phonon-scattering times ($\sim 100$ fs) because of a carrier cooling bottleneck in quantum wells,[7] and is the limiting factor in our ability to time resolve the polarization.

In Fig. 2 we illustrate the emergence of electron-spin dynamics in the observations at lower magnetic fields which are insufficient to fully polarize the holes for this lower Mn concentration. The strong electron-energy dependence of the spin-relaxation rate is seen by comparing the results for two very different luminescence *detection* energies. The lower detection energy (1.73 eV) is close to the ground state and is therefore indica-

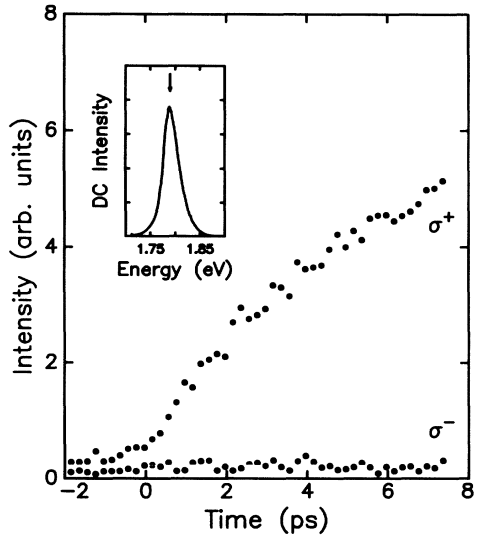


FIG. 1. The time dependence of the left- and right-circularly polarized luminescence components from fifty 86-Å-wide, 13%-Mn containing quantum wells separated by 86-Å-wide, 38%-Mn barriers in 0.75 T at 4 K. The zero-time position is obtained from autocorrelation of the pulse using light reflected from the sample surface. Inset: The dc luminescence line, with the arrow marking the detection energy for the time-resolved measurement.

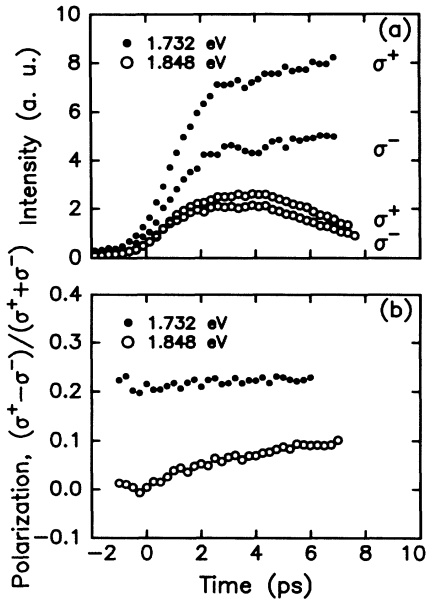


FIG. 2. (a) The time-dependent intensity for left- and right-circularly polarized components of luminescence from 86-Å-wide, 7%-Mn quantum wells separated by 86-Å, 38%-Mn barriers in 0.5 T at 4 K. Results are shown for two detection energies (near the peak, and on the high-energy side of the dc luminescence line). The excitation energy is 1.99 eV. (b) The time-dependent degree of circular polarization represented by the curves in (a).

tive of the behavior of bound excitons, whereas the higher energy (1.85 eV) is several luminescence linewidths above the ground state and corresponds to recombination in the initial nonequilibrium population of free electrons and holes. The data of Fig. 2(a) clearly show the shorter luminescence decay time at higher detection energies due to the steep energy-loss cascade of optically excited carriers on these time scales. This rapid relaxation is to be compared with the several hundred picosecond time constant typical of the energy-integrated luminescence decay which reflects the total carrier lifetime.

Time dependence of the polarization is plotted in Fig. 2(b). For low detection energies, the response is virtually instantaneous and time independent, indicating very rapid electron-spin relaxation. At higher detection energies, the spin dynamics are slower and we clearly observe the spin-lattice relaxation of the electrons as they settle into Zeeman-split levels. The more rapid spin relaxation at lower detection energies is characteristic of all of the quantum wells that we have studied. It is in conflict with a qualitative picture in which electron-spin orientation is erased by spin scattering processes that become slower with decreasing carrier energy (such as spin-spin exchange with the Mn ions), while most of the energy-loss scattering (optical-phonon emission) is spin conserving. Such a model has been invoked, for example, in attempts to quantitatively explain the energy dependence and magnitude of the optically induced magnetization in bulk DMS.[8]

The limiting values of the polarization in Fig. 2 are determined by the applied field and temperature, and are different for the two energies because the centers of the left- and right-circularly polarized luminescence lines are shifted with respect to one another by the Zeeman splitting. Noncompressed laser pulses are used here in order to generate a higher carrier density, on the order of $10^{11}$ electrons/cm$^{-2}$ in each quantum well. With increasing excitation intensity, we observe a strong increase of luminescence intensity at short times on the high-energy side of the luminescence line relative to that of the low-energy side, a consequence of populating the bottom of the conduction band. This is a small effect after time integration, and the shape of the dc luminescence line does not change appreciably over the range of intensities used.

Most theoretical treatments of the carrier spin scattering problem in semiconductors focus on conduction electrons. The calculation of spin-flip times for conduction electrons interacting with magnetic moments in these DMS quantum wells differs from the theoretical description for bulk systems in two substantial respects.[9] The scattering rates appropriate to well and barrier material must be weighted according to the probability given by the wave function for finding the carrier in the well relative to in the barrier. Secondly, the quasi-two-dimensional density of states leads to the weak (steplike) energy dependence of the scattering time in the quantum-confined case. Some of the excitation energies used in these experiments are below the $n=2$ level, and the corresponding scattering time prediction is energy independent. The scattering times decrease as more channels open up at higher carrier energies, and so the fact that shorter times are found at lower detection energies suggests that the theoretical picture should be expanded to include excitonic effects. For excitation above the $n=2$ level (1.85 eV) of the structure of Fig. 2, the sum of calculated intraband and interband electron-Mn scattering rates[9] result in a spin-relaxation time of 5 ps, in good agreement with observation. Such an estimate is indicative only of the order of magnitude, however, and so it is important to perform systematic checks as a function of Mn concentration and quantum-well size. Despite the large carrier-Mn spin-spin–exchange interaction, we find the relaxation times to be *independent* of the Mn concentration $x$ in the well over the range $x=0$–$0.13$, including relatively wide (86 Å) nonmagnetic well samples in which the confined carriers are isolated to a large degree from the magnetic material.[7] These surprising results indicate the presence of fast spin-relaxation processes on nonmagnetic origin in these heterostructures.

To further demonstrate quantum-confinement effects on spin relaxation, we compare dc optical pumping measurements for two structures having very different degrees of quantum confinement; a set of magnetic quantum wells in which the electronic wave functions are well localized by large barriers, and a superlattice character-

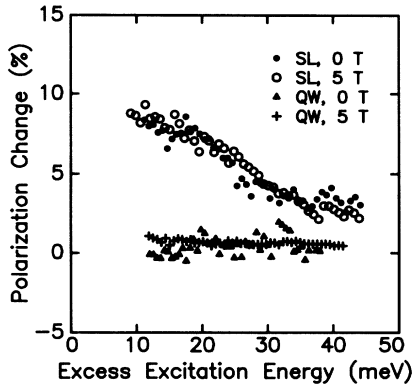


FIG. 3. The luminescence polarization change induced by dc optical pumping for two structures, a set of independent 86-Å-wide, 7%-Mn quantum wells (QW) separated by 86-Å, 38%-Mn barriers, and a superlattice (SL) consisting of 18-Å-wide, 15%-Mn barriers in CdTe, spaced with a 90-Å periodicity. The excitation energy is with respect to the detection point (about 5 meV above the luminescence peak energy). The 5-T data plotted are the polarization as measured with a circularly polarized excitation of helicity opposite to that selected by the field, subtracted from the polarization measured with a linearly polarized excitation.

ized by extended electronic wave functions arising with small barriers, which should exhibit bulklike properties. The time-integrated luminescence polarization indicates the orientation decay time of initially spin-polarized carriers relative to the carrier lifetime. In Fig. 3 we plot the excitation energy dependence of this polarization. The luminescence is detected near the peak of the dc line. The increase in polarization (reflecting an increase in spin-flip time) seen at the lowest excitation energies for the superlattice is similar to the behavior seen in bulk crystals.[10] In marked contrast, the quantum wells display no net polarization regardless of excitation energy, suggesting that an additional relaxation mechanism acts on the confined carriers. Also shown in Fig. 3 are measurements taken in 5 T, for which we plot the polarization *change* induced by creating spins polarized in the orientation *opposite* to that preferred by the field. Application of a field large enough to saturate the Mn magnetization has little effect on the optically induced change in polarization, and provides another indication that the Mn ions are playing a limited role in the spin scattering.

A number of mechanisms may be invoked in order to explain these systematic studies. The most plausible possibility is an enhanced electron-hole exchange strength (and hence electron-spin-relaxation rate, because of the "instantaneous" hole spin scattering) due to the quasi-2D confinement. The large binding energies and oscillator strengths of excitons in quantum wells are well known, and the significance of electron-hole exchange also grows with increasing confinement. Enhancements of the electron-hole exchange energy by roughly 1 order of magnitude[11] relative to the bulk value enable spin-relaxation times of order 1 ps, consistent with our observations. We have also found extremely fast carrier spin relaxation in GaAs/GaAlAs multiple quantum wells, suggesting that the effect is not due to some imperfection of the CdTe/CdMnTe heterostructures.

In summary, we have presented ultrafast time-domain measurements of charge-carrier spin scattering in diluted-magnetic-semiconductor quantum wells, where separate observations of electron and hole scattering are possible in different magnetic fields. The technique has yielded the fastest direct observations of spin relaxation to date. The most striking features of the results are the unexpectedly fast scattering times and the dramatic effect of confinement on spin relaxation observable even in dc measurements. The data do not follow the qualitative trends expected for electron-spin scattering dominated by the strong spin-spin–exchange interaction with the magnetic ions. We attribute the relaxation to a consequence of quantum confinement, and the enhanced electron-hole correlations in a two-dimensional system.

We gratefully acknowledge useful conversations with G. Bastard, additional MBE growth by C. Hsu, and discussions of the manuscript with J. Warnock.

[1]M. Potemski *et al.*, Phys. Rev. Lett. **63**, 2409 (1989); X. Liu *et al.*, *ibid.* **63**, 2280 (1989).

[2]D. D. Awschalom *et al.*, Phys. Rev. Lett. **59**, 1733 (1987); S. J. Allen, Jr., *et al.*, *ibid.* **62**, 2309 (1989).

[3]R. N. Bicknell *et al.*, J. Vac. Sci. Technol. B **3**, 709 (1985); L. A. Kolodziejski *et al.*, *ibid.* **3**, 714 (1985).

[4]See, for example, M. I. Dyakonov and V. I. Perel, in *Optical Orientation,* edited by F. Meier and B. P. Zakharchenya (Elsevier, Amsterdam, 1984).

[5]J. M. Hong, D. D. Awschalom, L. L. Chang, and Armin Segmüller, J. Appl. Phys. **63**, 3285 (1988).

[6]H. Mahr and M. D. Hirsch, Opt. Commun. **13**, 96 (1975); J. Shah, IEEE J. Quantum Electron. **24**, 276 (1988).

[7]M. R. Freeman and D. D. Awschalom, in Proceedings of the Thirty-Fourth Annual Conference on Magnetism and Magnetic Materials [J. Appl. Phys. (to be published)].

[8]H. Krenn *et al.*, Phys. Rev. B **39**, 10918 (1989).

[9]G. Bastard and L. L. Chang (to be published).

[10]J. Warnock *et al.*, Solid State Commun. **54**, 215 (1985).

[11]Y. Chen *et al.*, in *Excitons in Confined Systems,* edited by R. Del Sole, A. D'Andrea, and A. Lapiccirella (Springer-Verlag, Berlin, 1988).