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Spin-relaxation processes in ZnSe-based spin superlattices: A photoluminescence study

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We have studied the spin-relaxation process in spin superlattice structures, both at zero field (no confining potential) and as a function of applied field (variable confining potential). Evidence of an unexpectedly long hole spin-relaxation time associated with the strain splitting of the valence band has been found. In addition, excitonic spin-relaxation times which are unaffected by the strength of the spin-dependent confining potential were observed. We demonstrate that for excitons, spin flip via the magnetic ion-carrier exchange interaction is not the dominant spin-relaxation mechanism, although it may play a more important role in the case of energetic hot carriers.

The term spin superlattice was introduced by von Ortenberg[1] to describe diluted-magnetic-semiconductor (DMS) based quantum well structures in which the magnetic and nonmagnetic layers have approximately the same band gap at zero magnetic field. In such structures the magnetic field induces a spin-dependent superlattice potential which can be tuned by varying the field strength. Electrons and holes with one spin state are confined in the magnetic layers while those with opposite spin reside in the nonmagnetic layers. The interband transitions in both magnetic and nonmagnetic layers are type I, i.e., spatially direct. These phenomena were observed recently in two similar systems, ZnSe/ZnFeSe (Ref. 2) and ZnSe/ZnMnSe (Ref. 3) quantum wells. The spin dynamics of such a system might be expected to exhibit some interesting pecularities, since the spatial part of the carrier wave function may be substantially different for each spin state. Spin flip processes would then invoke or require a corresponding change in carrier localization.

In this work we have carried out photoluminescence (PL) and reflectivity experiments on a number of different spin superlattices and DMS layers. In addition we have performed a series of dc optical pumping and magnetic-field-dependent PL polarization measurements in order to probe the spin dynamics in this system. Although not as powerful as the time-resolved PL polarization techniques which have previously been used to study conventional type-I DMS-based heterostructures,[4] it is still possible to use these dc techniques to obtain comparative information on the spin relaxation processes. In the optical pumping experiment, the degree of luminescence polarization on excitation with circularly polarized light can provide information on the zero field (no confining potential) carrier spin relaxation, where the system evolves from an initially spin-ordered configuration (produced by the polarized optical pumping) to a random spin orientation as the system relaxes. In this case the degree of PL polarization is determined primarily by the longer of the two carrier spin relaxation times τ_e or τ_h (i.e., electron or hole), assuming the samples are undoped. The complementary experiment is to use standard linearly polarized incident light to look at spin relaxation in a magnetic field (spin-dependent confining potential). Here the carriers relax from an initially random spin orientation (produced by linearly polarized light) to a spin-aligned configuration produced by the spin dependent confining potential. At low and intermediate fields, where the conduction-band spin splitting is of the order of kT or less but the valence-band splitting is much larger than kT, the PL intensity from the upper spin component $(+1/2, +3/2)$ is most sensitive to the hole spin relaxation time, since after the holes spin relax, there is not enough thermal energy to repopulate the upper spin state, whereas both spin states in the conduction band will be populated independent of the electron spin relaxation time. Experimental observation of luminescence from the upper-energy heavy-hole exciton spin component at intermediate fields is then evidence for a long spin relaxation time for holes. At high field (i.e., spin splitting of valence and conduction bands both much larger than kT), PL intensity from the higher-energy spin component will be limited by the shorter of either τ_e or τ_h. With a long hole spin relaxation time the high-field PL intensity from the upper energy component provides a measure of the electron spin-relaxation time.

A total of seven samples were used in this study (Table I). Four samples are spin superlattices; superlattices 1, 2, and 6 are Fe-based, while sample 3 is Mn-based. In addition, three DMS epilayers were studied (samples 4, 5, and 7) for comparison. The thickness of samples 1 to 5 is below the critical limit for strain relaxation to occur and therefore their in-plane lattice constant is commensurate with that of the GaAs substrate. As a result the heavy- and light-hole states are well separated by the in-plane compressive strain. On the other hand, in the thicker

TABLE I. Sample parameters.

Sample	Magnetic ion concentration	ZnSe layer thickness (A)	DMS layer thickness (A)	Number of periods	
1	0.01 (Fe)	100	100	5	
2	0.02 (Fe)	150	100	4	
3	0.02 (Mn)	92	92	4	Thin layers (strained)
4	0.01 (Fe)	. . .	872	Epilayer	
5	0.02 (Mn)	. . .	951	Epilayer	
6	0.01 (Fe)	100	100	50	
7	0.01 (Fe)	. . .	8709	Epilayer	Thick layers (unstrained)

samples 6 and 7 the strain is relaxed and light- and heavy-hole states are degenerate. Details on growth[2] and the experimental techniques[5] were described elsewhere.

Luminescence, polarization, and reflectivity studies were carried out on all samples. The zero field PL spectrum of sample 1 is shown in Fig. 1(a). Two features marked X (at 2.807 eV) and I (at 2.801 eV) are identified as the heavy-hole exciton and an impurity bound exciton, respectively. The rest of the discussion will focus solely on the free exciton line, since qualitatively the two features exhibit the same field-dependent behavior. In the presence of a magnetic field, the excitonic feature is split into two components. The upper transition $X_-(+1/2$ to $+3/2)$ has a predominantly σ_- polarization, while the lower transition $X_+(-1/2$ to $-3/2)$ is polarized mainly as σ_+. This is shown in Figs. 1(b) and 1(c). The energy of these components is plotted as a function of magnetic field in Fig. 2, showing the strongly asymmetric spin splitting typical of a spin superlattice.[2,3] Interestingly, the higher-energy X_- luminescence component is observed even at high fields where the spin splitting is much larger (e.g., 12 meV at 5 T) than kT, the thermal energy. This is indeed surprising, and immediately indicates that the carrier *spin* lifetime is comparable to the radiative recombination time τ_r.

These observations are summarized in Fig. 3, showing the PL intensity ratio $r(-/+)$ of the X_- and X_+ heavy-hole exciton components versus spin excitonic splitting for samples 1, 2, 3, and 4. The fact that the circular polarizations are imperfectly resolved in this experiment does not affect the values of $r(-/+)$. For each sample, the X_- component exhibits substantial intensity up to spin splittings of 10 meV. For all the samples in this study the strength of the X_+ and X_- transitions measured from the

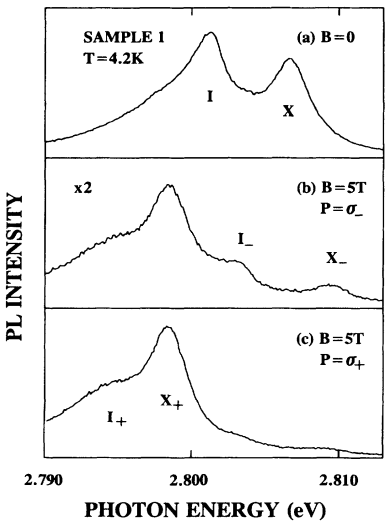

FIG. 1. Photoluminescence spectra from sample 1 at $T=4.2$ K, excited using the 4067-Å line from a Krypton ion laser; (a) $B=0$, (b) $B=5$ T, luminescence analyzed as σ_-, (c) $B=5$ T, luminescence analyzed as σ_+.

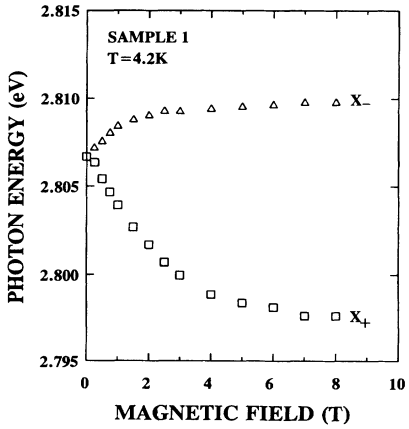

FIG. 2. Energy of the heavy-hole exciton luminescence components vs magnetic field for sample 1. Triangles, $(+1/2, +3/2)$ X_- transitions; squares, $(-1/2, -3/2)$ X_+ transitions.

reflectivity spectra are approximately equal as expected for a spin superlattice.[2] PL intensity ratios and band splittings were found to be independent of the incident laser power (power was varied by one order of magnitude with no effect seen), thus ruling out any spurious effects due to laser heating of the sample.

The above observations imply a spin relaxation time (either τ_e, τ_h, or both) comparable to the radiative recombination lifetime τ_r. To determine the ratios τ_e/τ_r and τ_h/τ_r from the available data, we note that for the heavy-hole excitons, there are four possible spin states with steady state populations of $n{+}{+}$, $n{+}{-}$, $n{-}{+}$, and $n{-}{-}$, where the first subscript refers to the electron spin (i.e., $m_j = \pm 1/2$) and the second to the hole spin (i.e., $m_j = \pm 3/2$). The four heavy-hole excitons are shown in the inset of Fig. 3. Radiative recombination is allowed for the (++) and (− −) transitions while the other two are forbidden. The steady state rate equations (for undoped samples) are of the form

$$\frac{dn_{++}}{dt} = g_{++} - \frac{n_{++}}{2\tau_e} - \frac{n_{++}}{2\tau_h} - \frac{n_{++}}{\tau_r} + \frac{n_{+-}e^{-\Delta E_{VB}/kT}}{2\tau_h} + \frac{n_{-+}e^{-\Delta E_{CB}/kT}}{2\tau_e} = 0 \qquad (1)$$

where ΔE_{CB} and ΔE_{VB} are the spin splittings in the conduction and valence band, respectively, and g_{++} is the generation rate for the (+1/2, +3/2) exciton. For all four states, the rate equations in matrix form are

$$\begin{bmatrix} g_{++} \\ g_{+-} \\ g_{-+} \\ g_{--} \end{bmatrix} = \begin{bmatrix} \left(\frac{1}{2\tau_e}+\frac{1}{2\tau_h}+\frac{1}{\tau_r}\right) & \frac{-B_h}{2\tau_h} & \frac{-B_e}{2\tau_e} & 0 \\ -\frac{1}{2\tau_h} & \left(\frac{1}{2\tau_e}+\frac{B_h}{2\tau_h}\right) & 0 & \frac{-B_e}{2\tau_e} \\ -\frac{1}{2\tau_e} & 0 & \left(\frac{B_e}{2\tau_e}+\frac{1}{2\tau_h}\right) & \frac{-B_h}{2\tau_h} \\ 0 & -\frac{1}{2\tau_e} & -\frac{1}{2\tau_h} & \left(\frac{B_e}{2\tau_e}+\frac{B_h}{2\tau_h}+\frac{1}{\tau_r}\right) \end{bmatrix} \begin{bmatrix} n_{++} \\ n_{+-} \\ n_{-+} \\ n_{--} \end{bmatrix} \qquad (2)$$

where $B_e = \exp(-\Delta E_{CB}/kT)$ and $B_h = \exp(-\Delta E_{VB}/kT)$. The constants g_{ij} describe the net generation rate of excitons at the band edge and are assumed to be equal since the incident linearly polarized light creates equal numbers of $m_j = \pm 1/2$ electrons and $m_j = \pm 3/2$ heavy holes. The intensity ratio $r(-/+)$ will not depend on the absolute magnitude of the generation rates because the equations involved are linear. The two curves in Fig. 3 are obtained from the solution of these equations, assuming $\Delta E_{CB}/\Delta E_{VB} \approx \alpha N_0/\beta N_0$ and two different sets of values for τ_h/τ_r and τ_e/τ_r. As a function of applied magnetic field, the intensity ratio drops rapidly at first, reflecting the large spin splitting in the valence band. For the case where τ_h is long (solid line in Fig. 3), a kink (at $\Delta E \sim 1$ meV) appears at the point where the valence-band splitting is of the order of kT. Beyond this point, the increasing valence-band splitting has no effect on the hole spin populations. The intensity ratio then decreases more gradually, reflecting the smaller field dependence of the conduction band splitting. The solid curve fits the data rather well with the ratio $\tau_h/\tau_r = 4$. As discussed before, the intensity ratio at high field values reflects the electron spin relaxation rate, from which we find the ratio $\tau_e/\tau_r \approx 0.04$. The dashed curve in Fig. 3 shows a situation where τ_e is long and τ_h is short ($\tau_e/\tau_r = 1.0$, $\tau_h/\tau_r = 0.04$) and does not agree with the experimental results. From the above discussion it is evident that it is the holes which relax slowly in this system, with a relaxation time longer than the radiative recombination time.

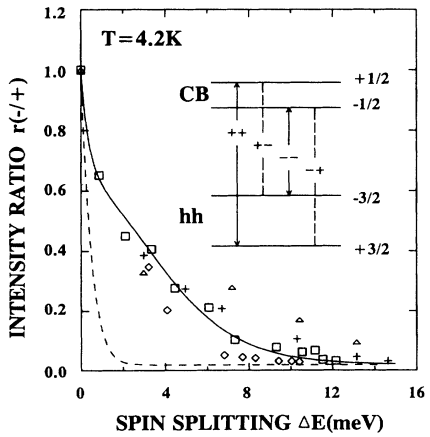

FIG. 3. PL intensity ratios of the heavy-hole exciton components vs exciton spin splitting. Squares, sample 1; rhombuses, sample 2; crosses, sample 3; triangles, sample 4. The solid and dashed lines represent theoretical calculations discussed in the text. The inset indicates the four heavy-hole excitons. Solid lines indicate allowed transitions while the dashed lines denote forbidden ones.

It is interesting to note that there is no obvious dependence of the relaxation time on the degree of carrier confinement; the results are adequately described by a constant τ_e and τ_h. In fact sample 4 which is a thin epilayer (no quantum wells or confining potential) shows the same characteristic behavior. This would not be the case if spin-flip exchange with the magnetic ions were the dominant spin relaxation mechanism.[6,7] Also, manganese-based samples (Mn^{2+} ground spin state $S = 5/2$) exhibit

spin relaxation times similar to those with Fe (Fe^{2+} ground spin state $S=0$) in spite of totally different spin state of these two ions. Thus we conclude that spin-flip exchange scattering of the carriers with the magnetic ions is not the dominant excitonic spin relaxation mechanism, at least not for magnetic ion concentrations used in this study.

To explain the anomalously long hole spin relaxation time, we note that both samples 6 and 7 in which the light- and heavy-hole excitons are degenerate show spin relaxation times which are too fast to measure in the present experiment, and the upper energy luminescence component is not observed. This implies that the strain-induced valence-band splitting is directly responsible for the slow hole spin relaxation as has been observed in III-V bulk materials.[8] This is also consistent with the observation of the upper heavy hole exciton luminescence component in bulk CdFeSe samples which have the wurtzite crystal structure,[9] in which the heavy-light hole degeneracy is lifted by the uniaxial crystal field.

Finally, we discuss the results of the zero field polarization measurement under optical pumping, summarized in Table II. In this configuration, spin polarized carriers are created by pumping with circularly polarized light, and the resulting PL polarization provides a measure of the spin relaxation rate relative to the recombination time. The spin polarizations can be analyzed using the equations developed before with the appropriate values of the generation rate constants. Qualitatively the results are consistent with the field-dependent measurements, with significant polarizations observed in the strained samples (1 to 5) and essentially no polarization in the strain-relaxed samples (6 and 7). However, the signals are considerably smaller than would be expected from the long hole relaxation time obtained in the field-dependent measurements. Using the parameters derived from the field-dependent measurements, we would expect a polarization of about 50%. Also the signal shows some dependence on magnetic species and concentration.

The important difference between the zero field optical pumping experiment and the field-dependent intensity ratio measurements is that the optical pumping signal may be affected by fast spin relaxation processes of the initially energetic carriers, while the field dependent measurements are a direct probe of the "cool" excitonic spin relaxation time. As the hole energy and momentum relaxation takes place, spin relaxation will occur through the mixing of spin components in the different hole states, whereas at the top of the valence band relaxation may become very slow.[7,10] In this respect the strain splitting in the valence band has a similar effect to the confinement-induced or crystal-field-induced band splitting. The combined zero field and field-dependent data bear out these theoretical predictions and indicate that these effects play a significant role in the hole spin relaxation in these systems. Also, spin-flip exchange scattering may be important for energetic carriers even though it is not a factor in the relaxation of cool excitons. This would be consistent with calculations of spin flip exchange scattering rates which predict a strong momentum dependence.[7] Time dependent polarized luminescence experiments would be needed to clearly separate the different spin flip rates in this case.

TABLE II. Zero field PL polarization under optical pumping.

Sample	Polarization (%)	
1	7.5	
2	9	Thin
3	8	layers
4	9	(strained)
5	4	
6	<1	Thick
7	<1	layers (unstrained)

In summary, we have studied the spin relaxation process in DMS layers and ZnSe-based spin superlattice structures, both at zero field (no confining potential) and as a function of applied field (variable confining potential). We observe an anomalously long hole spin relaxation time associated with the strain splitting of the valence band. For excitons, we also conclude that spin flip via the magnetic ion-carrier exchange interaction is not the dominant spin relaxation mechanism, although it may play a more important role in the case of energetic hot carriers. Thus excitonic spin relaxation times were found to be independent of the confining potential within the resolution of the experiment. The long spin relaxation times observed in these systems should make them easily amenable to higher resolution time dependent experiments where the spin dynamics can be probed in detail as a function of the magnetic-field induced spin dependent confining potential.

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