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FREE TO BOUND EXCITON RELAXATION IN [001] AND [111] GaAs/GaAlAs QUANTUM WELLS

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Abstract—We have investigated the relaxation from free to bound excitons in [001] and [111] $GaAs/Ga_{0.7}Al_{0.3}As$ quantum wells by analyzing the photoluminescence polarization in the presence of a magnetic field applied in the Faraday configuration. The Stokes shifts of our samples, which amount to ~3 meV, indicate that the photoluminescence is due to excitons bound to some kind of defects in the quantum wells. We have obtained a systematic decrease of the degree of polarization with increasing magnetic field for resonant excitation of heavy-hole excitons. We interpret this fact as a manifestation of the decrease of correlation between momenta and spins of the excitons as they decay from free to bound excitons. We obtain an effective out-scattering time due to the processes of energy relaxation from free to bound excitons of the order of 50 fs, which is independent of the crystallographic orientation.

1. INTRODUCTION

The optical properties of excitons in quantum wells (QWs) have been the subject of intense research in recent years for fundamental and applied reasons. A large body of experimental work deals with absorption, or pseudo-absorption, via photoluminescence excitation (PLE) and photoluminescence (PL) spectroscopy, in which excitons play a fundamental role. A usual finding is the shift of the peak of the PL below those of the absorption or PLE spectra. This is the so called "Stokes shift", which is widely used as a negative indicator of sample quality. Bastard *et al.* explained the Stokes shift in terms of exciton trapping at random interfaces defects[1], and obtained that Stokes shifts smaller than ~10 meV could be due to "intrinsic" interface defects of the order of 200 Å. In a more recent work, a linear relation between the line-width of the PLE excitonic peak and the Stokes shift has been found[2]. This behavior can be explained assuming the existence of randomly distributed interface defects and that the well width fluctuations extend over a length scale which is large compared with the size of the excitons[2].

Nowadays, it is generally accepted that good samples can exhibit Stokes shifts of a few meV, and that they are due to the difference in the binding energy between free and bound excitons. As the samples studied here present Stokes shifts of ~3 meV, we believe that their PL is due to bound excitons. In order to study the free to bound exciton relaxation we have used optical orientation methods.

Optical orientation, which allows the excitation of states with a preferential spin orientation, using selective optical excitation with circularly polarized light, is very powerful for investigating electronic properties of semiconductors[3]. The optical orientation manifests itself in a polarization of the PL, which is a consequence of the excitation of states with a preferential spin orientation, and it depends on the ratio between the lifetime and the spin relaxation time of excited states[4]. Usually, the polarization excited by circularly polarized light is quantified by means of the degree of circular polarization, $\mathscr{P}$. For one of the exciting helicities, $\mathscr{P}$ is defined as the fractional difference of the PL intensities of two circular polarizations, σ^+ and σ^-, at a given energy: i.e. for σ^+ excitation, $\mathscr{P} = (I^+ - I^-)(I^+ + I^-)$.

In this work, we investigate the relaxation between free and bound excitons by studying the dependence of $\mathscr{P}$ on magnetic field, under resonant excitation of the heavy-hole exciton and detection at the maximum of the Stokes-shifted PL.

2. EXPERIMENTAL DETAILS

The samples studied here were grown by MBE on [111]B semi-insulating GaAs substrates, with crystal orientation tilted 3° to improve their optical quality, and have been described previously[5]. Four different $GaAs/Ga_{0.7}Al_{0.3}As$ samples with well thicknesses of 60, 75, 100 and 130 Å were investigated. We have also studied a [001]-oriented $GaAs/Ga_{0.7}Al_{0.3}As$ QW of 100 Å for comparison purposes. PL and PLE spectra were obtained, at 2 K, with magnetic fields applied in the Faraday configuration up to 13.5 T. The samples were excited with the light from a LD700 dye laser, a Rhodamine 6G dye laser or a Ti–Zf laser, pumped by ion lasers. The incident light was circularly polarized by means of an achromatic $\lambda/4$ plate. The emitted light was analyzed into its σ^+ and σ^- com-

ponents, and it was detected with photon counting techniques.

3. RESULTS AND DISCUSSION

Figure 1 depicts PLE spectra of a 75-Å [111]-oriented QW at two different magnetic fields; the sample was excited with σ^+ light, and the emission, that was detected at the maximum of the PL, was analyzed into its σ^+ (solid PLE spectra) and σ^- (dashed PLE spectra) components. The upper traces of Fig. 1(a) and (b) correspond to the degree of polarization of the luminescence as a function of the exciting energy.

At zero magnetic field, Fig. 1(a), the pseudo-absorption spectra show two clear peaks, at 1.555 and 1.575 eV, which correspond to the ground state of the heavy-hole ($h_1(1s)$) and light-hole ($l_1(1s)$) excitons. The structure near 1.67 eV is due to the h_2 transition between the second confined electron and hole states. We have assigned the small peak at 1.562 eV in the σ^+-PLE spectrum to a forbidden transition between the second heavy-hole and the first electron subband levels, h_{12}. The degree of polarizations as a function of the exciting energy, Figure 1(a) upper trace, presents three clear structures: two peaks, corresponding to the $h_1(1s)$ and h_{12} excitons, where $\mathscr{P}$ exceeds 50%, and a deep at the $l_1(1s)$ exciton, where $\mathscr{P}$ is slightly negative. These values of $\mathscr{P}$ can be explained in terms of the spin of electrons and holes involved in the different excitonic transitions, considering that the spin-relaxation time of holes is much shorter than that of the electrons, and that the relaxation of holes occurs preferentially with conservation of hole parity[6]. In the case of the h_{12}, the positive value of $\mathscr{P}$ can be understood taking into account valence band-mixing effects.

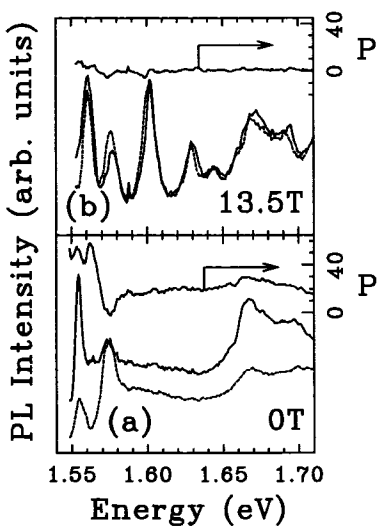

Fig. 1. Intensity (left axis) and degree of polarization (right axis) of the maximum of the photoluminescence as a function of the exciting energy at two different magnetic fields, for a 75-Å [111]-QW: (a) 0 T and (b) 13.5 T. The solid (dashed) PLE spectra were recorded in the $\sigma^+\sigma^+$ ($\sigma^+\sigma^-$) configuration.

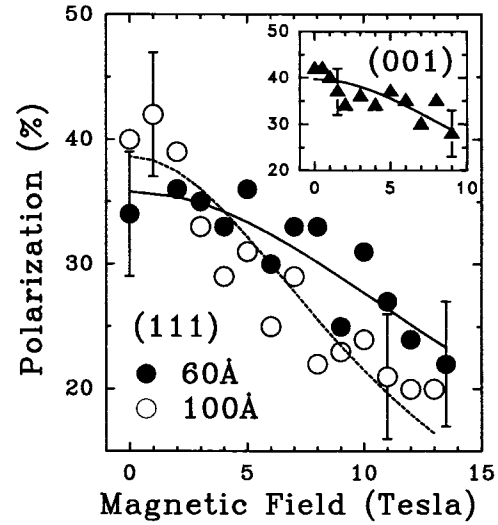

Fig. 2. Degree of polarization vs magnetic field for resonant excitation of the heavy-hole exciton in a 60-Å [111]-oriented QW (●) and in a 100-Å [111]-oriented QW (○). The lines represent the best fit with equation (1). The inset shows the degree of polarization and the best fit for a 100-Å [001]-oriented QW.

Let us consider now the effects of a magnetic field. The PLE spectra recorded at our maximum field—Fig. 1(b)—are much richer than those obtained at zero field. The new structures are due to excited states of excitons, whose observation is favored by the reduction of exciton radii and the increase in binding energies[7]. Conversely, the degree of polarization of the PL at 13.5 T [Fig. 1(b), upper trace] is almost zero for all the exciting energies. This result is in contrast with recent PLE experiments under high magnetic fields, which have shown that the relaxation time of the magnetic moment of electrons is much longer than the recombination time, and that the magnetic moment is conserved in the recombination as well as during the thermalization process from the excited states[8]. Moreover, calculations of the spin relaxation time of QW electrons in a magnetic field have obtained an enhancement of this time, in the $n = 0$ Landau level, amounting to 1.6 when the field is increased from 6 to 15 T[9]. However, our results present a systematic decrease of the degree of polarization with increasing field for the different samples, as it is clearly seen in Fig. 1(b) for the 75 Å QW. Due to the fact that the decrease in $\mathscr{P}$ is observed in the whole spectral range, i.e. for the ground- and excited-excitonic states, we believe that it does not arise during the excited- to ground-state excitonic relaxation, but during the relaxation from free to bound excitons. In order to study this latter relaxation, we will concentrate in the case of resonant excitation of the $h_1(1s)$ exciton state.

Figure 2 shows the degree of polarization of the PL, exciting at the energies of the $h_1(1s)$ excitons

observed in PLE, for the 60-Å (●) and the 100-Å (○) [111]-oriented QWs as a function of the magnetic field. The exciting light was σ^+ polarized; the values of $\mathscr{P}$ were obtained at the maximum of the PL spectra. We also show in the inset of Fig. 2 the magnetic field dependence (up to 9 T) of $\mathscr{P}$ for the 100-Å [001]-oriented QW.

In some cases, it is possible to observe a Zeeman splitting between the σ^+ and σ^- components of the emission at high magnetic fields. For the [111]-oriented QWs, the Zeeman splitting of the PL is negligible, therefore, $\mathscr{P}$ was obtained with the spectrometer set at the same energy for both polarizations. However, in the case of the [001] QW, the presence of a Zeeman splitting for fields higher than 9 T originates a situation in which $\mathscr{P}$ depends markedly on the detection energy. Thus, we have limited our analysis for this sample up to 9 T, since for higher fields it is not possible to observe a clear trend in the behavior of $\mathscr{P}$.

In the situation considered here of resonant creation of excitons, all the intermediate states during the absorption, energy and spin relaxation and emission processes are correlated electron–hole pairs[10]. However, one must consider that the initial and final states are not the same, since we are pumping free excitons, while the PL is due to excitons bound to some genre of defect in the QW. We have obtained that the zero-field degree of polarization, $\mathscr{P}(0)$, is $45 \pm 10\%$ for all the samples, including the [001]-oriented QW, while the drop between 0 and 13.5 T varies from 10% (130-Å QW) to 40% (75-Å QW). The $\mathscr{P}(0)$ value indicates that the spin scattering time is not very short on the scale of the total excitonic lifetime, and the dependence of $\mathscr{P}$ on field denotes that the spin-flip rate of the free exciton during its energy relaxation to bound exciton increases with magnetic field.

An analogous decrease of $\mathscr{P}$ has been reported for the hot luminescence of GaAs when the magnetic field, applied in the Faraday configuration, is increased[11]. This decrease is interpreted as a manifestation of the correlation between momenta and spins of the photoexcited carriers and it is found to follow the Lorentzian expression:

$$\mathscr{P}(H) = \frac{\mathscr{P}(0)}{1 + (\omega_c^r)^2 \tau_1^2}, \qquad (1)$$

where ω_c^r is the reduced cyclotron frequency and τ_1 represents an effective out-scattering time due to any processes of energy relaxation. For two-dimensional systems, Zakharchenya *et al.*[12] have not observed any decrease of circular polarization up to 7 T and therefore they claim that the correlation between momenta and spins is absent in 2D systems. However, our results show a systematic decrease of the excitonic polarization for resonant excitation with increasing magnetic field, and we believe that this is due to the destroying of the aforementioned correlation during the free to bound excitonic relaxation.

Assuming that equation (1) is valid to describe this process for excitons, with the knowledge of ω_c^r ($\omega_c^r = eH/m_r^*$ where m_r^* is the in-plane reduced effective mass of the exciton) it is possible to obtain an indication of the relaxation time from free to bound excitons.

The cyclotron frequency can be easily obtained from an analysis of the magnetooptical data. Figure 3 shows the fan chart of the PLE peaks, exciting with σ^- polarized light, for a [111]-oriented 100-Å QW. Two sets of transitions can be clearly distinguished: the ground and excited states of the heavy-hole exciton, $h_1(ns)$, $n = 1$–3 (●), and the corresponding light-hole excitons, $l_1(ns)$ (○). Fitting the experimental results with a 2D hydrogenic-like excitonic model[13], it is possible to obtain the in-plane effective masses of the excitons. The results of fitting simultaneously the ground and excited states of the heavy- (light-) hole excitons are shown in Fig. 3 solid (dashed) lines.

We have fitted $\mathscr{P}$ as a function of magnetic field with equation (1), using the values of m_r^* which have been reported recently for the same samples[5]. The result of the fits, with $\mathscr{P}(0)$ and τ_1 as adjustable parameters, are shown in Fig. 2 as solid lines for the 60-Å [111]-QW ($\tau_1 = 20 \pm 15$ fs) and for the 100-Å [001]-QW ($\tau_1 = 35 \pm 15$ fs), and as a dashed line for the 100-Å [111]-QW ($\tau_1 = 30 \pm 15$ fs). For the two other samples this effective scattering time is of the same order. The uncertainties in τ_1 are rather large since ω_c^r is also obtained through a fitting procedure. The fact that the scattering times do not show any systematic dependence on QW width is not surprising

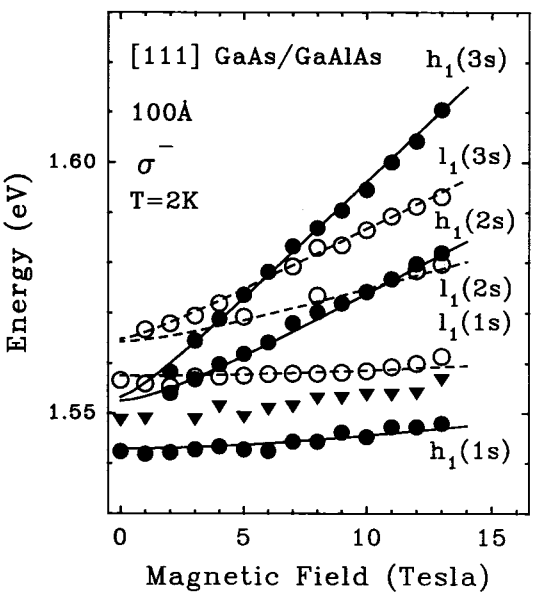

Fig. 3. Energies vs magnetic field for σ^- excitation of the ground and excited state heavy-hole (●) and light-hole (○) excitons for a 100-Å [111]-oriented QW. The triangles depict the forbidden h_{12} exciton. The full (dashed) lines show the result of the fits with a two-dimensional excitonic model for the heavy-hole (light-hole) excitons.

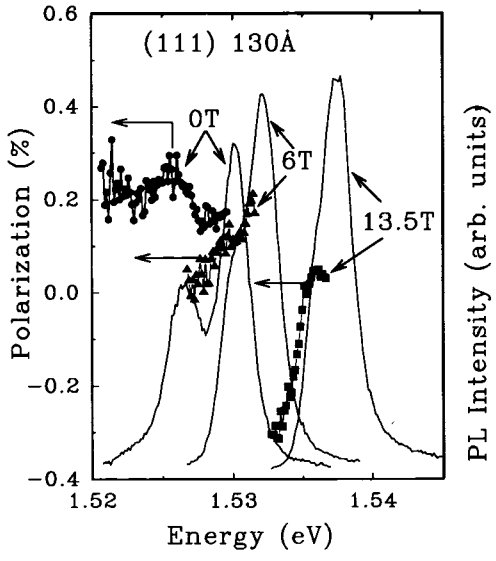

Fig. 4. Degree of polarization of the luminescence, as a function of the detection energy, for resonant excitation of the heavy-hole excitonic-ground state, $h_1(1s)$ (left axis), and photoluminescence spectra exciting at 1.7 eV (right axis) for three different magnetic fields. The sample was grown in the [111] direction with a QW width of 130 Å.

since the defects to which the excitons bound may randomly fluctuate from sample to sample. Similarly, it seems that the process of relaxation from free to bound excitons does not depend strongly on crystallographic orientation.

Figure 4 depicts the spectral dependence of $\mathscr{P}$ for the 130-Å [111]-oriented QW exciting at $h_1(1s)$, for three different fields. The PL spectra, also shown in Fig. 4, were recorded exciting at 1.7 eV with σ^+ light. For this sample, the Stokes shift is negligible. We attribute the high- (low-) energy component of the PL spectra to free- (bound-) exciton recombination. It can be easily seen in Fig. 4 that the blue shift of the PL with increasing field is larger for the bound-exciton component of the PL than for the free-exciton one; in fact, at 13.5 T it is not possible to resolve both components. We believe that this is due to the different effective masses of the free and bound excitons.

The results shown in Fig. 4 yield further evidence of our claim that the decrease of $\mathscr{P}$ with magnetic field is related to the process of free to bound exciton relaxation. Although it is not possible to investigate $\mathscr{P}$, under resonant conditions at the free excitonic peak, we have indications that it does not decrease so markedly with increasing field as it does at the bound exciton emission. Actually, the stronger decrease of $\mathscr{P}$ with increasing field as the detection energy is scanned towards the low energy tail of the PL, where the bound exciton emission dominates the spectra, is apparent in Fig. 4. However, there are two peculiarities in this figure which indicate that further investigations are needed in order to understand the relaxation of excitons in QWs: first, the higher polarization of the bound-exciton component of the PL as compared with that of free excitons at zero magnetic field, and, secondly, the *negative* degree of polarization in the low energy tail of the PL at high fields.

4. SUMMARY

We have investigated the relaxation from free to bound excitons using optical orientation methods in [111]- and [001]-oriented QWs. A systematic decrease of the degree of polarization of the photoluminescence has been found with increasing magnetic field, applied in the Faraday configuration. This behavior has been interpreted as a manifestation of the decrease of correlation between momenta and spins of the excitons as they decay from free to bound excitons. An analysis of the results has obtained an effective out-scattering time due to the processes of energy relaxation from free to bound excitons of the order of 50 fs independently of well width and crystal orientation.

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