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Magneto-optical spectroscopy of positively charged excitons in GaAs quantum wells

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We report observation of positively charged excitons (X^+) in GaAs quantum wells remotely doped with acceptors. Upon reducing the excess hole density, by photoexciting carriers in the doped barrier layer, we observe the neutral excitonic transition strengthen relative to X^+. Further confirmation of the X^+ assignment is provided by its temperature and magnetic-field dependence. We observe both the antisymmetric (singlet) and symmetric (triplet) X^+ spin states.

Mott-Wannier excitons in semiconductors can be described by the solutions of the hydrogen atom after modeling the crystal by effective electron and hole masses and a dielectric constant. Lampert[1] argued that the existence of the negatively charged hydrogen atom (H^-), as well as the positively charged hydrogen molecule ($H_2{}^+$), suggests that analogous semiconductor complexes should be stable. However, their observation in bulk semiconductors has been hampered, with a few exceptions,[2] by their rather small second carrier binding energies.[3] Calculations[4] have shown that the binding energy is strongly enhanced in two-dimensional structures, even more so than for the neutral exciton due to the trion's larger spatial extent. This has allowed recent observation of negatively charged excitons (X^-) in CdTe (Ref. 5) and GaAs (Refs. 6–9) quantum wells (QW's) remotely doped with donors.

In this work we study GaAs QW's which are remotely doped with acceptors in order to provide an excess hole density in the well. We are able to reduce the hole density using light of energy greater than the band gap of the $Al_{0.33}Ga_{0.67}As$ barriers, since the electrons photoexcited in the barrier are swept by the internal fields of the structure into the QW, where they recombine with the hole gas. Consequently, photoluminescence (PL) spectra taken with a laser energy above the barrier band gap show a doublet structure due to recombination involving neutral (X) and positively charged (X^+) excitons. Consistent with a reduction in the excess hole density, we observe the X PL to strengthen relative to X^+ with the laser intensity. Increasing the sample temperature also causes the X^+ PL to decline relative to X due to its thermal dissociation into a neutral exciton and a free hole. In contrast, for excitation below the barrier band gap, we see a PL band, the width of which is very sensitive to the sample temperature, due to recombination of thermalized, photoexcited electrons with the hole gas. PL and photoreflectance (PR) spectra taken under an applied magnetic field support our assignments of the spectral features.

Our study is conducted on $GaAs/Al_{0.33}Ga_{0.67}As$ QW's, which are remotely doped in their upper barrier layers with acceptors, grown by molecular-beam epitaxy on (311)A-oriented GaAs substrates. The spectra presented here were performed on a sample with a 300-Å GaAs QW, a 600-Å undoped $Al_{0.33}Ga_{0.67}As$ spacer, and 2000-Å Si-doped (1.5×10^{17} cm^{-2}) $Al_{0.33}Ga_{0.67}As$. Si dopants incorporate on As sites on the (311)A surface, thereby forming acceptors. Magnetotransport measurements performed in the dark demonstrated the hole density to be 1.8×10^{11} cm^{-2}, with a mobility of 7.4×10^5 cm^2 V^{-1} s^{-1} at 1.7 K. A second sample with a narrower spacer layer thickness, and hence higher excess hole density in the dark, displayed qualitatively similar spectra.

Figure 1(a) plots PL spectra taken with different laser intensities and a laser energy (E_L) below the band gap of the $Al_{0.33}Ga_{0.67}As$ barriers (E_b). A broad feature from the QW is observed near 1.5165 eV, the line shape of which is essentially insensitive, and the intensity of which is roughly proportional to the laser power density. In contrast, the strength of the lines observed to lower photon energy, which originate from bulk GaAs regions, show a sublinear strengthening with the laser power. We assign the broad QW PL to recombination of thermalized photoexcited electrons with the heavy-hole gas (marked HHG in Fig. 1). Consistent with this interpretation, the high energy side of the QW PL broadens considerably upon raising the sample temperature, as can be

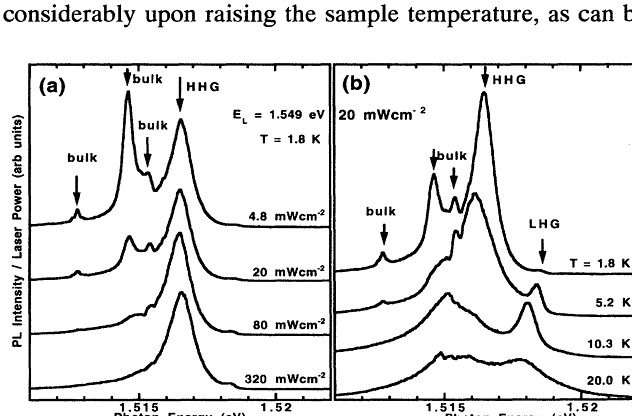

FIG. 1. Laser power density (a) and sample temperature (b) dependence of PL spectra recorded for $E_L \ll E_b$. A broad feature is seen due to recombination of photoexcited electrons with the heavy-hole gas (HHG), whose line shape is insensitive to laser power.

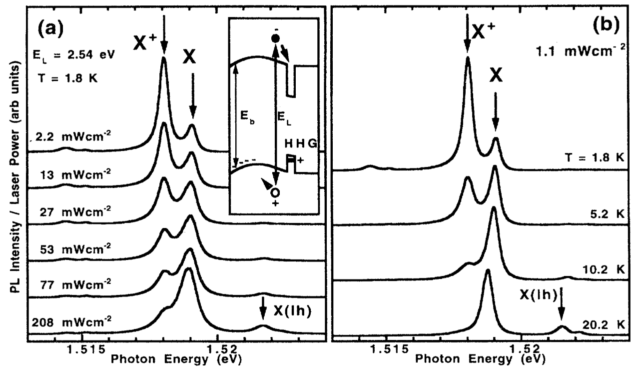

FIG. 2. PL spectra recorded for $E_L \gg E_b$ and different laser power densities (a) and sample temperatures (b). The inset illustrates how electrons photoexcited in the upper barrier layer are swept into the QW, thereby lowering the excess hole density. This explains the strengthening of X relative to X^+ with increasing laser power.

seen in Fig. 1(b), due to thermal population of states above the conduction-band minimum by photoexcited electrons. There is also a strengthening of the light-hole gas feature (LHG) to higher energy due to its population at elevated temperatures. Notice that the LHG peak is stronger relative to the HHG at elevated temperatures than would be expected from the density of states. This may indicate a larger Coulomb enhancement for the less populated light-hole subband.

Remarkably different PL spectra, plotted in Fig. 2, are observed for excitation far above the barrier band gap ($E_L \gg E_b$). For this laser energy, the QW PL is much stronger for the same laser power at $E_L \ll E_b$, and displays a doublet with a splitting of (1.0 ± 0.1) meV. Increasing the laser intensity causes the higher-energy component of this doublet to strengthen at the expense of its lower-energy counterpart.

For $E_L \gg E_b$, most of the light will be absorbed in the upper $Al_{0.33}Ga_{0.67}As$ barrier layer. The electric field created by the acceptors results in photoexcited electrons being swept into the QW, as depicted in the inset of Fig. 2. These photoexcited electrons recombine with the hole gas, producing a strong PL signal and also reducing the excess hole density. Furthermore, the photoexcited holes that collect in the maximum of the valence-band profile of the upper $Al_{0.33}Ga_{0.67}As$ layer, as well as those that relax onto the acceptors, will also tend to reduce the excess hole density in the QW. We have observed a qualitatively similar reduction in the excess electron density of n-type remotely doped QW's upon optical excitation above the barrier band gap.[6] However, the change in carrier density is considerably larger for p-type samples, probably because photoexcited electrons are more efficiently collected in the QW of these structures than photoexcited holes in their n-type counterparts. A similar mechanism has been proposed to explain the observation of negative photoconductivity of two-dimensional (2D) holes in $GaAs/Al_xGa_{1-x}As$ heterojunctions.[10]

We interpret the higher- and lower-energy peaks of the doublet in Fig. 2 as recombination of neutral (X) and positively charged (X^+) excitons, respectively. The latter involves recombination of an electron-hole pair in X^+, leaving a free hole (h^+), i.e., $X^+ \rightarrow h^+ +$photon. Crudely speaking, the X^+ transition energy is shifted below that of X by the binding energy of a free excess hole to a neutral exciton. This assignment for the doublet explains why it is observed for $E_L \gg E_b$ and not for $E_L \ll E_b$, since the excess hole density is smaller in the former case, as discussed above. Another indication of the lower hole density for $E_L \gg E_b$ than $E_L \ll E_b$ is the higher PL energy in Fig. 2(a) than 1(a), produced by the reduction in both band-gap renormalization and the Stark shift induced by the QW charge.[11] Increasing the laser power (for $E_L \gg E_b$) produces more photoexcited electrons in the barrier and thereby further reduces the excess hole density in the QW, lowering the population of X^+ and raising that of X. The probability of recombination in the presence of an excess hole decreases as their average separation increases, explaining the weakening of the X^+ recombination, with concurrent strengthening of X, apparent in Fig. 2(a).

Our interpretation of the doublet observed for $E_L \gg E_b$ is supported by its temperature dependence plotted in Fig. 2(b). With increasing temperature the PL intensity transfers from the lower- to higher-energy peak in the doublet, caused by the thermal dissociation, $X^+ \rightarrow X + h^+$. The light-hole X to higher energy also strengthens with temperature.

The separation of the X and X^+ PL peaks in Fig. 2 implies a second hole binding energy[3] of (1.0 ± 0.1) meV in this 300-Å GaAs QW. As expected, this lies between the 3D and 2D limits calculated by Stébé and Ainane[4] of 0.2 and 2.0 meV, respectively. We deduced these calculated values from Fig. 1 of Ref. 4 by taking the GaAs donor Rydberg as 5.8 meV and the mass ratio to be 0.58, corresponding to in-plane, zone-center effective electron and heavy-hole masses of 0.067 and 0.115,[12] respectively. One would expect the second hole binding energy for X^+ to be greater than the second electron value for X^-, due to the larger hole effective mass. In fact, calculations[4] predict the binding energy to be just 17% larger for X^+ than X^- in the 2D limit. This is roughly consistent with our observation that the X^+ binding energy is quite similar to that we measured for X^- in two 300-Å GaAs QW's of (0.9 ± 0.1) (Ref. 8) and (1.0 ± 0.1) (Ref. 9) meV. X^+ may also be more sensitive than X^- to residual electric fields across the QW, due to the greater electric-field-induced spatial polarization of the hole (than electron) wave function, which will reduce the second carrier binding energy.

Figure 3 plots PL spectra taken with different applied magnetic fields. The spectra were recorded with the incident and emitted light circularly polarized and propagating parallel to the field direction and perpendicular to the QW plane. The laser energy was above the $Al_{0.33}Ga_{0.67}As$ band gap, allowing observation of peaks due to X and X^+ at zero field. Notice that X peak shows a diamagnetic shift to higher energy with field in both polarizations, similar to that observed for neutral excitons in undoped QW's.[13] The X^+ transition also shifts to higher energy with field, but at a shallower rate than X, so that the separation of X and X^+ increases considerably. This indicates a large enhancement in the second hole binding energy due to the extra confinement of the X^+ wave function introduced by the magnetic field.

Notice the PL peak, which emerges in σ^- polarization in Fig. 3(a) just below the X line around 2 T and forms a well-

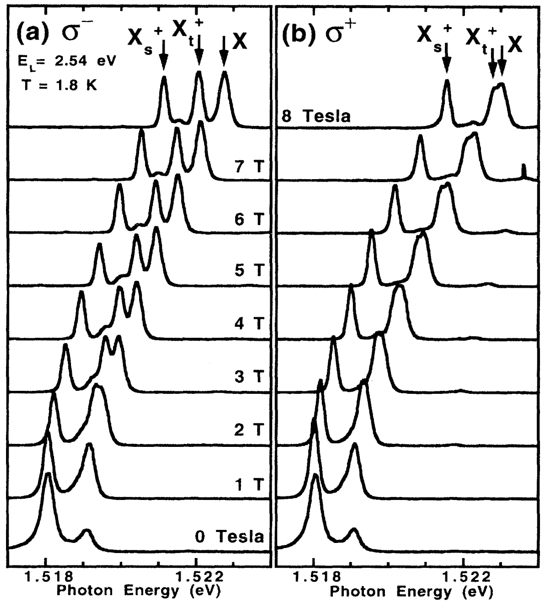

FIG. 3. Magnetic field dependence of PL spectra recorded for $E_L \gg E_b$ and emitted in σ^- (a) and σ^+ (b) circular light polarization.

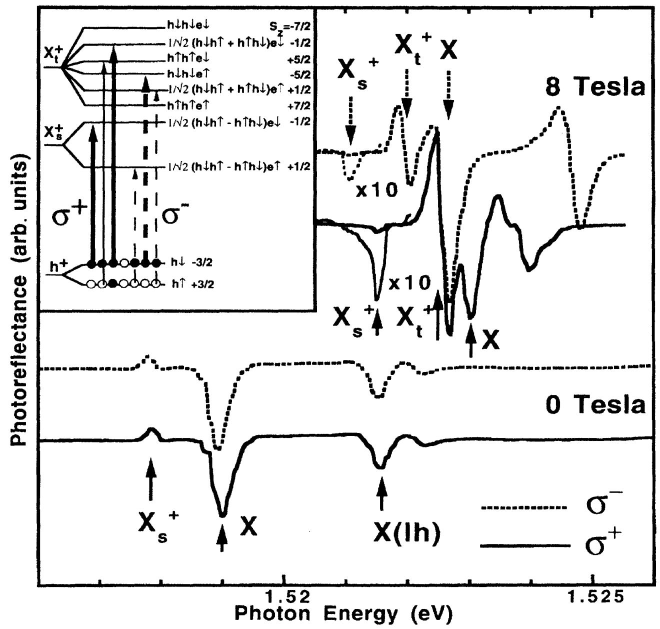

FIG. 4. Polarized PR spectra recorded with applied magnetic fields of 0 and 8 T. The inset schematizes the allowed transitions, $h^+ + \text{photon} \rightarrow X^+$, which can be excited with circularly polarized light. Only transitions where the total z spin (s_z) changes by ± 1 are allowed for $\sigma^\pm$ polarization.

resolved distinct peak at higher fields. We have recently observed a qualitatively similar phenomenon in the magneto-optical spectra of remotely n-type doped QW's containing excess electrons, where we demonstrated the magnetic-field-induced transition to originate from an excited state of the negatively charged exciton with an electron spin wave function that is symmetric upon interchange.[9]

The inset of Fig. 4 schematizes the Zeeman splitting of the spin states of X^+. At zero field the twofold degenerate ground state, which we label by the degeneracy of the two hole spins as spin singlet (X_s^+), has an antisymmetric spin wave function upon interchange of the holes, while it is symmetric in the sixfold degenerate excited state (spin triplet, X_t^+). Calculations for H^- and the semiconductor negative donor center (D^-) have shown that only the spin-singlet is stable at zero field, but that spin-triplet states can also bind in the presence of a magnetic field.[14,15] Optical interband transitions (indicated by the vertical arrows in the inset of Fig. 4) can occur in the presence of a free hole, i.e., $h^+ + \text{photon} \leftrightarrow X^+$. These transitions are allowed if the total z component of the spin changes by $+1$ or -1 for σ^+ and σ^- circular light polarizations, respectively.

We ascribe the magnetic-field-induced transition in Fig. 3(a) (marked X_t^+) to a spin-triplet state of X^+, which, as discussed above, is stable only in the presence of a magnetic field. Its emergence below the X line indicates the binding of this triplet state to occur for a field of around 2 T. Inspection of the inset of Fig. 4 demonstrates that the lowest energy spin-triplet transition is expected in σ^-, consistent with the polarization of the observed transition. Notice too that a spin-triplet transition is also expected in σ^+ polarization, but to higher photon energy than that for σ^-. Evidence for this transition can be seen in Fig. 3(b) where the X line shows a broadening and small splitting at the highest fields.

Further evidence for the assignment of the X^+ transition is provided by the PR spectra plotted in Fig. 4. For this technique we measure the alternating reflectivity, which is induced by a second, mechanically chopped laser beam incident on the sample. The chopped beam was chosen to have a photon energy (2.54 eV) above the barrier band gap, so that, as discussed above, its effect is to modulate the hole density in the QW. Since the hole density recovers only partially during the modulation period, the average density will be relatively small for the PR measurements. Hence PR allows us to measure optical *excitation*, as opposed to emission, due to the excitonic transitions. In comparison PL excitation has the disadvantage that it is difficult to measure the lowest energy X^+ transition which, as will become apparent below, is of most interest in the finite field excitation spectra. The QW transitions tend to be obscured in direct reflectivity spectra by interference oscillations originating from other interfaces in the sample.

The PR spectra taken at zero magnetic field show features due to X and X_s^+, at similar energies as their corresponding PL peaks. Notice that the PR due to the two transitions have opposite sign, consistent with the oscillator strength of X^+ increasing, and X decreasing, with excess hole density. Under applied magnetic field the PR features shift to higher energy tracking their PL peaks. The spin-triplet X_t^+ transitions are also seen to emerge in the PR spectra at finite magnetic field, with the same circular light polarizations as their corresponding PL. These triplet transitions, marked X_t^+, can be clearly resolved in both polarizations in the 8-T spectra of Fig. 4.

Notice in Fig. 4 that the singlet X_s^+ transition is stronger in σ^+ than σ^- at 8 T, while at zero field its intensity is roughly equal in the two polarizations. This circular polarization of the charged exciton transition in excitation spectra was reported as proof for the existence of negatively charged excitons in n-type CdTe QW's,[5] while we have also seen this phenomenon in n-type GaAs QW's.[8,9] The origin of the circular polarization can be readily explained with reference to the inset of Fig. 4. *Excitation* from the higher-energy hole spin state ($h\downarrow$) will be stronger than from the lower-energy one ($h\uparrow$) due to its higher population at low temperature. This explains the observation that the X_s^+ feature is stronger in σ^+ than σ^- polarization in Fig. 4, and provides further confirmation that the transition is due to X_s^+. The degree of circular polarization implies the magnitude of the heavy-hole g factor to be 0.34, smaller than the electron value of 0.42 that we reported from our study of X^-.[8,9] In contrast to X_s^-, since both the σ^- and σ^+ triplet transitions have a strong contribution from the more populated hole state (see inset of Fig. 4), the X_t^+ transition should not show a strong circular polarization. However, the energetic overlap of the features due to X and X_t^+ hinders an analysis of their circular polarization.

In conclusion, we have observed positively charged excitons in GaAs QW's, remotely doped with acceptors to provide an excess hole density. Our assignment of the transition is confirmed by the weakening of X^+ and concurrent strengthening of X with decreasing excess hole density; thermally induced dissociation of X^+ with temperature; the excitonlike diamagnetic shift of X, and increasing separation of X and X_s^+, with an applied magnetic field; and the partial circular polarization of (singlet) X_s^+ in high-field photoreflectance spectra. Consistent with calculations, the second hole binding energy, measured as (1.0 ± 0.1) meV in a 300-Å GaAs QW, is only slightly larger than the corresponding value for X^-. The excess hole density in the QW can be reduced by illumination at a photon energy above the barrier band gap, due to their recombination with electrons photoexcited in the upper barrier that are swept into the QW. Excited states of X^+, where the two-hole spin wave function is symmetric upon interchange (spin triplet), become bound at finite magnetic field, producing new transitions in both emission and excitation spectra.

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[1] M. A. Lampert, Phys. Rev. Lett. **1**, 450 (1958).

[2] See, for instance, B.Stébé *et al.,* Solid State Commun. **26**, 637 (1977); T. Kawabata, K. Muro, and S. Narita, *ibid.* **23**, 267 (1977).

[3] Defined as the energy difference between the charged exciton and a neutral exciton plus a free charge carrier.

[4] B. Stébé and A. Ainane, Superlatt. Microstruct. **5**, 545 (1989).

[5] K. Kheng *et al.,* Phys. Rev. Lett. **71**, 1752 (1993).

[6] A. J. Shields *et al.,* Superlatt. Microstruct. **15**, 355 (1994).

[7] G. Finkelstein *et al.,* Phys. Rev. Lett. **74**, 976 (1995).

[8] A. J. Shields *et al.,* Phys. Rev. B **51**, 17 128 (1995).

[9] A. J. Shields *et al.*, Phys. Rev. B (to be published)

[10] A. S. Chaves and H. Chacham, Appl. Phys. Lett. **66**, 727 (1995); M. J. Chou, D. C. Tsui, and G. Weimann, *ibid.* **47**, 609 (1986).

[11] C. Delalande *et al.,* Phys. Rev. Lett. **34**, 2482 (1987).

[12] R. C. Miller, D. A. Kleinmann, and A. C. Gossard, Phys. Rev. B **29**, 7085 (1985).

[13] W. Ossau *et al.*, in *Properties of Impurity States in Superlattice Semiconductors*, Vol. 183 of *NATO Advanced Study Institute, Series B: Physics*, edited by E. Y. Fong *et al.* (Plenum, New York, 1988), p. 285.

[14] D. M. Larsen, Phys. Rev. B **20**, 5217 (1979).

[15] D. M. Larsen and S. Y. McCann, Phys. Rev. B **45**, 3485 (1992); **46**, 3966 (1992).