RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 51, NUMBER 24 15 JUNE 1995-II

Quenching of excitonic optical transitions by excess electrons in GaAs quantum wells

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(Received 28 October 1994; revised manuscript received 14 April 1995)

We study quenching of neutral excitonic optical transitions in GaAs quantum wells with increasing excess electron density. This occurs abruptly at $\sim 10^{10}$ cm^{-2} with the emergence of the negatively charged exciton at lower transition energy. With further increasing density X^- evolves smoothly into the Fermi-edge singularity. Polarized magneto-optical spectra confirm our assignment.

Excitons, the bound state of the electron-hole Coulombic attraction, dominate the low temperature optical spectra of semiconductors. However, the Coulomb interaction is greatly suppressed by the presence of a dense degenerate electron gas due to phase-space filling. What remains is an enhancement in the oscillator strength of transitions involving electrons near the Fermi energy, referred to as either the *Mahan exciton* or *Fermi-edge singularity*,[1] which has been observed in the emission[2] and excitation[3] spectra of quantum wells (QW's). In this work we report the evolution of the optical properties of QW's between the above extremes of negligible and large electron density. At negligible electron density we observe neutral excitonic transitions in both the emission and excitation spectra. We see a rapid quenching of the excitonic oscillator strength at densities of about 10^{10} cm^{-2}. Concurrently a second transition appears to lower energy, which we ascribe to the negatively charged exciton X^- (i.e., two electrons bound to one hole), recently observed in CdTe QW's.[4] The transition due to X^- evolves smoothly into that due to the weak Fermi-edge singularity seen for dense electron gases.

We studied GaAs/$Al_{0.33}Ga_{0.67}As$ single QW's, remotely doped in their upper barrier layers with donors, grown by molecular-beam epitaxy on (100)-oriented GaAs substrates. Sample 1 consisted of a 220 Å GaAs QW, followed by a 300 Å undoped $Al_{0.33}Ga_{0.67}As$ spacer layer and 400 Å Si doped (10^{18} cm^{-3}) $Al_{0.33}Ga_{0.67}As$, while samples 2 and 3 had a 300 Å QW, a 600 Å spacer, and 2000 Å Si doped (10^{17} cm^{-3}) doped region. Mobilities for the ungated structures at 4 K of between 1.0 and 3.6×10^6 cm^2 V^{-1} s^{-1} and excitonic linewidths as narrow as 0.24 meV indicate high sample quality. The QW electron densities were varied by evaporating Au Schottky gate layers on the sample surfaces and biasing these relative to Ohmic contacts made to the QW's. Electron-density-dependent photoluminescence (PL) and electroreflectance (ER) spectra were recorded at different Schottky biases. For the latter, a small, alternating component was superimposed on the gate voltage.

Figure 1 plots PL and ER spectra measured on a 220 Å QW at 1.7 K with similar illumination intensities and different offset gate biases. A broad PL band can be seen in the +0.8 V spectrum due to recombination of photoexcited holes with the electron gas in the QW. The peak near 1.5055 eV is due to recombination between the lowest electron (e) and heavy-hole (hh) subbands at $k=0$ (labeled $e1$-hh1) and the high-energy shoulder at 1.5285 eV with k-conserving recombination at the Fermi wave vector ($e1_f$-hh1).[5,6] From the separation of these features (Δ) and assuming parabolic electron and heavy-hole bands with effective masses m_e and

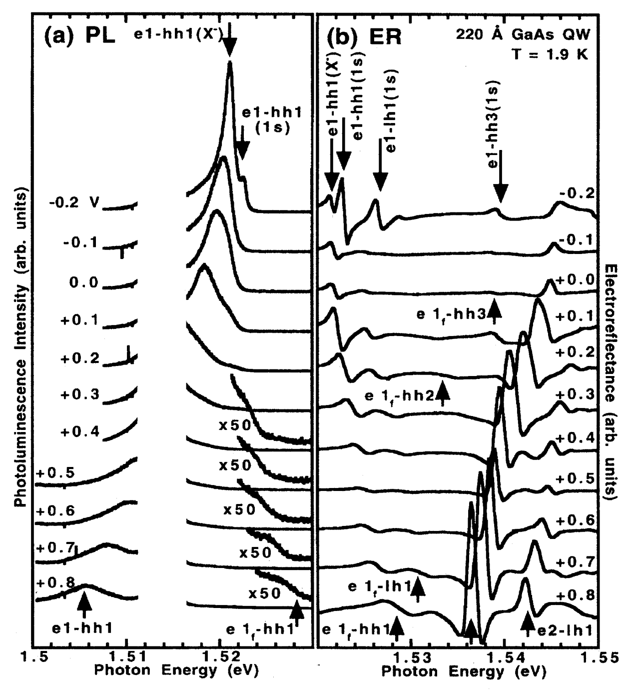

FIG. 1. PL (a) and ER (b) spectra measured on a 220 Å GaAs QW with different offset gate biases as indicated. The electron density increases moving down the figure up to 4.1×10^{11} cm^{-2}. For clarity the bulk GaAs PL is omitted.

m_{hh}, respectively, we estimate the Fermi energy, $E_F = \Delta/(1 + m_e/m_h) = 14.5$ meV, and hence the electron density 4.1×10^{11} cm^{-2}, at this bias. As the gate voltage is decreased, thereby lowering the electron density the $e1$-hh1 peak moves to higher energy, due to reduction of both the band-gap renormalization and the Stark shift in the electric field induced by the charge in the well.[7] Meanwhile the high-energy $e1_f$-hh1 shoulder of the PL band decreases in energy, indicating the reduction in the Fermi energy to be larger than the increase in the gap.

The ER spectra have a complimentary nature to the PL in that only transitions above, rather than below, $e1_f$-hh1 contribute (at low temperature). In the $+0.8$ V spectrum of Fig. 1(b) the lowest-energy QW transition at 1.5285 eV is due to the k-conserving $e1_f$-hh1 transition at the Fermi wave vector. The energy of this transition agrees roughly with the shoulder observed in the PL spectra, demonstrating the recombination to involve free holes, i.e., not strongly localized above the valence band maximum, in contrast to the case for $In_xGa_{1-x}As$ QW's.[2] The strong features near 1.5365 and 1.5422 eV are due to transitions from the second (unoccupied) electron and the first heavy- and light-hole subbands, $e2$-hh1 and $e2$-lh1, respectively.[6] With decreasing electron density the $e1_f$-hh1 transition observed in ER shifts to lower energy, following the shoulder observed in the PL. On the other hand, the transitions involving the second (and third) electron subband move to higher energy with decreasing electron density, due to (as for $e1$-hh1) the reduction in both band-gap renormalization and the Stark shift and in good agreement with calculations.[6]

We now concentrate on the behavior at the lowest electron densities, which is the primary focus of the present work. As the gate bias is decreased, the separation of the maximum and high-energy shoulder of the PL band decreases, due to the reduction in Fermi energy, until eventually only a single peak is observed. It can be seen in Fig. 1(a) that at -0.2 V a second PL peak appears about 1.1 meV to higher energy. The fact that two corresponding features are observed in the ER spectrum taken at -0.2 V demonstrates that both these PL peaks have an intrinsic origin, i.e., neither derives from an impurity or defect (etc.) bound exciton.

A 300 Å GaAs QW (sample 2) shows qualitatively similar behavior. PL spectra taken at gate biases corresponding to a lower range of electron densities ($< 8 \times 10^{10}$ cm^{-2}) are plotted in Fig. 2(a). At gate biases $\geqslant -0.9$ V, a broad band with a high-energy shoulder is again observed, which narrows with decreasing electron density to a single peak at -1.10 V. At -1.16 V, we find again that a new transition emerges on the high-energy side of the PL. Upon decreasing the density further, this higher-energy feature strengthens very sharply and seemingly at the expense of its lower-energy companion. Notice that two weaker, higher-energy lines also emerge in the spectra around -1.16 V.

The three PL transitions observed at the lowest electron densities are also present in ER spectra taken in this bias range, see Fig. 2(b). As the electron density is increased, the ER spectra evolve in a similar fashion to the PL, with these three transitions redshifting before being dramatically quenched near -1.20 V, and replaced by a feature to lower energy. The fact that this lower-energy transition is observed

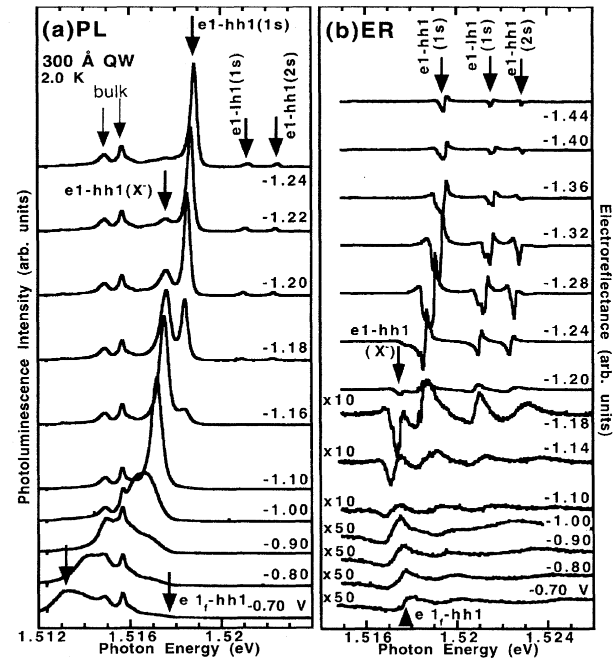

FIG. 2. PL (a) and ER (b) spectra measured on a 300 Å QW with different gate biases corresponding to electron densities less than 8×10^{10} cm^{-2}. Notice that with increasing electron density the neutral excitonic transitions are sharply quenched around -1.18 V and replaced by X^- to lower energy.

in the ER, as well as the PL, spectra, again rules out the possibility that it could be due to a defect or impurity bound exciton.

We ascribe the features which emerge at the lowest electron densities to (neutral) excitonic transitions (X), which are well known to dominate the spectra of undoped QW's. For the 220 Å QW in Fig. 1, the marked features lie close to the expected energies of the $1s$ excitons formed the lowest electron and heavy (light) -hole subbands, $e1$-$h(l)h1(1s)$. Similarly, the transitions observed in the low density limit for the 300 Å QW are due to the neutral excitons, $e1$-hh1$(1s)$, $e1$-lh1$(1s)$, and $e1$-hh1$(2s)$. The feature seen in both Figs. 1 and 2 at energies below $e1$-hh1$(1s)$, *which is induced by adding excess electrons*, we ascribe to a *negatively charged exciton*, labeled $e1$-hh1(X^-), which is created (or annihilated) when a photon is absorbed (or emitted) in the vicinity of an excess electron.

The spectral separation of X^- from X implies a binding energy for the second electron of (1.1 ± 0.1) and (0.9 ± 0.1) meV in the 220 and 300 Å GaAs QW's, respectively. This increase in the binding energy with reduction in the well width can be expected, due the enhanced Coulomb interaction induced by the confinement.[8,9] To compare the measured binding energies to calculations, we express them as a fraction of the three-dimensional (3D) neutral donor binding energy (5.8 meV), obtaining 0.19 and 0.16, respectively. As expected, these lie between the 3D and 2D limits calculated by Stébé and Ainane[8] for $m_e/m_h = 0.6$ of 0.03 and 0.29, respectively. They are also consistent with 0.23 calculated by Louie and Pang[9] for a negative donor center in a 200 Å GaAs QW, bearing in mind that the fixed positive charge of

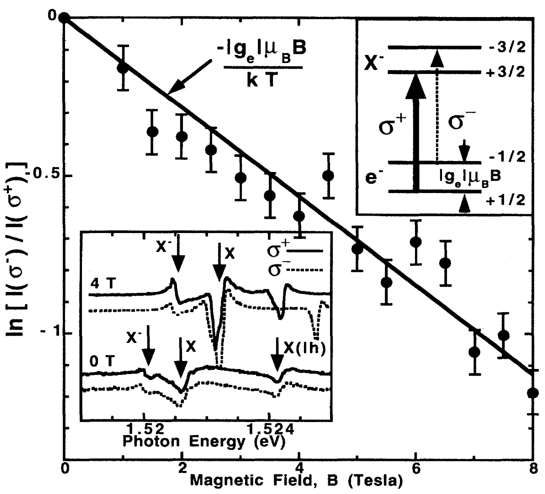

FIG. 3. Magnetic field dependence of the X^- transition in ER spectra taken on a 300 Å QW at 2.0 K with circularly polarized light. Main: Natural log of the ratio of the intensity of X^- in σ^- polarization to that in σ^+ polarization vs field. Lower inset: ER spectra taken at 0 and 4 T. Upper inset: Schematic of Zeeman splitting of X^- transition in field. The higher occupancy of the $+1/2$ initial state explains the observed strengthening of the X^- transition in σ^+ polarization relative to σ^-.

the donor will enhance its binding. There is also rough agreement with the range of values 0.20–0.27 reported by Kheng *et al.*[4] for CdTe QW's.

To verify that the observed transition is due to X^-, we studied excitation spectra taken in a magnetic field with circularly polarized light, as utilized by Kheng *et al.*[4] for CdTe QW's. In a magnetic field, both the initial (i.e., a free electron) and final (X^-) states of the X^- transition undergo a Zeeman splitting, as depicted in the upper inset of Fig. 3. Circularly polarized light causes transitions where the total z component of the spin changes by $+1$ (for σ^+ sense) or -1 (σ^-). Since at low temperature the free electron initial state with z spin $+1/2$ will have lower energy, and therefore higher population, than that with $-1/2$, we can expect the X^- transition to be stronger in σ^+ than σ^- polarization. This is evidenced by ER spectra taken with a magnetic field applied perpendicular to a 300 Å GaAs QW (sample 3) at $T=2.0$ K, which show X^- to be weaker in σ^- than σ^+ polarization (see lower inset to Fig. 3). In the main part of Fig. 3 we plot the log of the ratio of the ER intensity of the X^- transition (I) in σ^- polarization, relative to σ^+, as a function of the magnetic field (B). The straight line through the experimental points demonstrates the expected variation, $I(\sigma^-)/I(\sigma^+)=\exp(-|g_e|\mu_B B/kT)$, with a best fit value for $|g_e|=0.42\pm0.02$. This value is very close to the g factor of bulk GaAs of 0.44 (Ref. 10) and is powerful confirmation that the ground state for the optical transition is an electron, and hence the final state two electrons and one hole, i.e., X^-. We observe the partial circular polarization of the X^- ER transition at 8 T to be destroyed by raising the temperature to 20 K, as predicted by the above relation. A detailed account of the magnetic field dependence will be presented elsewhere.

The dramatic quenching of the neutral excitonic transitions with excess electron density, with accompanying strengthening of X^-, is illustrated by Fig. 4, plotting the integrated areas of the PL peaks in Fig. 2(a) as a function of the gate bias. Also plotted is the electron density determined from the separation of the PL peak and its high-energy shoulder due to the k-conserving transition at the Fermi wave vector, as described in Refs. 5 and 6. As apparent in Fig. 2(a) this high-energy shoulder is only resolved for gate biases larger than -0.9 V, however, interpolation of the determined points shows that the dramatic quenching of X occurs at biases where the electron density is around 10^{10} cm^{-2}. This is also close to the bias where the conductivity measured along the QW drops sharply, confirming the electron density to be small.

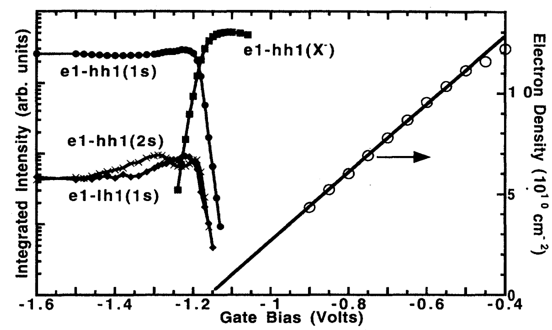

FIG. 4. The gate bias dependence of the integrated PL intensity of the excitonic transitions in Fig. 2(a) (solid symbols) and the electron density determined from PL spectra (open circles).

Theories[11–14] of the electron density dependence of QW optical transitions appear to overlook the formation of a bound X^- state. However, we can discuss our results in terms of filling of real and k space by the excess electrons.[11,12] X will be quenched at electron densities where there is approximately one electron in the vicinity of each absorbed (or emitted) photon. This can be estimated to occur at the density given by $N_{x^-}=[\pi\ a_{x^-}^2]^{-1}$, where a_{x^-} is half the mean spatial extent of X^-. Taking a_{x^-} to be twice the bulk neutral exciton Bohr radius, which is a reasonable approximation for these relatively wide QW's, yields $N_{x^-}\sim3\times10^{10}$ cm^{-2}. Despite the crudity of this analysis, it demonstrates that the experimentally determined electron density required to quench X is roughly consistent with real-space filling arguments. Localization of the electrons in lower-energy regions caused by spatial inhomogeneities would result in X^- appearing at smaller N_{x^-}. However, the fact that we observe X^- in the excitation, as well as emission, spectra indicates that the excess electrons occupy a significant area of the QW and not just small localized pockets. Furthermore, the narrow X PL linewidth of just 0.24 meV observed for the 300 Å QW suggest that inhomogeneities are small.

As the excess electron density is increased further, the Coulomb interaction is weakened by screening and, more significantly, phase-space filling.[11,12] Phase-space filling by the excess electrons results in the removal of the low **k**-vector components of the exciton wave function due to the exclusion principle and causes their eventual unbinding.[11,12] However, some enhancement in the oscillator strength will persist due to multiple electron-hole scattering near the

Fermi energy, giving rise to Fermi-edge singularity. This electron-hole scattering is suppressed at smaller k vectors where the conduction band is degenerate.

Since it seems very unlikely that a bound state involving more than two electrons and one hole would be stable, one would expect a smooth evolution from X^- to Fermi-edge singularity with increasing electron density. Indeed, in contrast to the evolution of X to X^- at lower densities, the X^- ER features in Figs. 1(b) and 2(b) move continuously with increasing electron density to $e1_f$-hh1 at high electron density. The ER feature marked $e1_f$-hh1 is clearly associated with the Fermi-edge singularity, because it tracks the high-energy side of the PL band, as discussed earlier. (Although we refer to the Fermi-edge *singularity*, the excitonic enhancement may be weak for high electron densities in these QW's where the holes are not strongly localized.[13])

In contrast to $e1$, the higher-energy, unoccupied electron subbands, which are unaffected by phase-space filling, can be expected to support bound excitons at all densities. This may explain why sharp, excitoniclike features are observed for the $e2$-hh1 and $e2$-lh1 transitions in the ER spectra in Fig. 1(b), even at electron densities as high as 4×10^{11} cm^{-2}.

In conclusion, we have studied the effect of increasing excess electron density on the excitonic transitions of GaAs QW's. At densities of about 10^{10} cm^{-2}, which are roughly consistent with real-space filling arguments, the excitons capture an extra electron and the neutral exciton is quenched to be replaced by a negatively charged one. The assignment of this excess-electron-induced feature to X^- is confirmed by its partial circular polarization in ER spectra taken in a magnetic field. We measure binding energies of 1.1 and 0.9 meV for this extra electron in 220 Å and 300 Å QW's, respectively. As the conduction band is filled further, the X^- transition evolves smoothly into the Fermi-edge singularity.

We thank L. Wang, M. Tribble, and J. Burroughes for sample preparation. Part of this research (at Cavendish) was funded by EPSRC, UK.

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