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Electron-concentration-dependent quantum-well luminescence: Evidence for a negatively charged exciton

H. Buhmann, L. Mansouri, J. Wang, P. H. Beton, N. Mori, L. Eaves, and M. Henini
Department of Physics, University of Nottingham, Nottingham NG7 2RD, United Kingdom

M. Potemski
Hochfeld-Magnetlabor, Max Planck Institut für Festkörperforschung, and Centre National de la Recherche Scientifique, Boîte Postale 166, 38042 Grenoble, France

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The quantum-well electroluminescence of *p-i-n* GaAs/AlAs double-barrier resonant tunneling diodes has been investigated. The bias-dependent tunability of the resonance conditions for electron and hole tunneling allows for a continuous change of the relative electron and hole concentrations in the quantum well. As the electron concentration is increased, the quantum-well emission line due to heavy-hole free exciton recombination is replaced by a new excitonic line, 2 meV lower in energy. This line is attributed to a negatively charged exciton X^-. The magnetic field and temperature dependence of the quantum-well emission have been used to characterize this transition.

Due to the Coulomb interaction, the low-temperature recombination of free electrons (e) and holes (h) in semiconductors is excitonic in character. In quasi-two-dimensional (2D) structures the excitonic binding energy is up to four times that for the 3D excitons.[1,2] Free excitons may also become bound to impurities or structural defects which further increases the binding energy, i.e., lowers their recombination energy. These changes may be measured using optical spectroscopy.[3,4] In addition, the exciton binding energy is increased in exciton complexes such as excitonic molecules, biexcitons (BX), and trions, i.e., positively (X_2^+) and negatively (X^-) charged excitons. All have been observed in bulk semiconductors[5] while for 2D systems only excitonic molecules have been reported.[4,6] Although an enhanced binding energy of trions in a 2D system has been predicted theoretically,[7] evidence for charged excitons exists only in one case, to our knowledge.[8] For GaAs quantum wells (QW's) the expected binding energy $E_b(X^-)$ of X^- relative to that of the free exciton (X) is between 1 and 2.5 meV, depending on the confinement width[7] and barrier height.[9] Therefore, it should be possible to resolve the X^- recombination line in the QW emission spectrum. The experimental requirement for the formation of negatively charged excitons (X^-) is a system in which free excitons are formed in the presence of free electrons. This can be achieved in photoexcited modulation-doped QW systems[8] and heterojunctions[10] or in *p-i-n* doped double-barrier resonant tunneling diodes (RTD) where, under applied external bias, tunneling electrons and holes recombine radiatively in the QW.[11–14] In the latter case, the relative concentration of electrons and holes in the QW can be varied with applied bias over a wide range, and depends on whether electrons or holes tunnel resonantly.

In this paper we investigate an excitonic recombination line in the electroluminescence (EL) spectra from the QW of GaAs/AlAs RTD's, which appears when electrons become the majority carriers in the QW. We consider the evidence for the association of this line with recombination of negatively charged excitons.

The *p-i-n* devices, grown by molecular-beam epitaxy at 550 °C, incorporate two 6.1-nm AlAs barriers and a 9.1-nm GaAs QW in the undoped intrinsic (i) region. Undoped spacer layers of 20 nm (30 nm) separated the barriers from 2×10^{16}-cm^{-3} n-doped (5×10^{17}-cm^{-3} p-doped) graded contact layers. Optical lithography and wet-etching were used to process square devices with side lengths between 100 and 400 μm^2.

Low-temperature (4.2 K) EL measurements have been performed at various bias voltages in the vicinity of the first electron resonance to investigate the dependence of the QW emission on electron concentration. Figure 1(a) displays a typical current-voltage characteristic $I(V)$ of the used devices. It shows the first light-hole resonance (LH1) at 1.589 V and the first electron resonance ($E1$) at 1.599 V, comparable to other results obtained for *p-i-n* RTD's.[11–14] At LH1 the hole subband of the accumulation layer on the p-doped side is aligned with the lowest light-hole subband of the QW, while at $E1$ the electron subband of the accumulation layer on the n-doped side is aligned with the lowest electron subband of the QW. This results in resonant injection of holes and electrons, respectively, into the confined states of the QW which result in peaks in $I(V)$. The situation for resonant electron tunneling is schematically shown in Fig. 2 (inset). Figure 1(b) displays the observed electroluminescence for five different bias voltages, labeled i–v, in the region of the LH1 and $E1$ resonances. In order to observe an EL signal from the QW, electrons and holes have to be present simultaneously. This is initially the case when the device is biased onto the LH1 resonance. Here, holes tunneling resonantly into the LH1 state thermalize down to the heavy-hole ground state (HH1) and recombine as heavy-hole free excitons with injected electrons at the onset of the $E1$ resonance giving rise to line X. At slightly higher voltage, above the LH1 resonance, the relative electron concentration increases markedly. At this point a new recombination line (Y) approximately 2 meV lower in energy is resolved in the spectra [Fig. 1(b) ii]. It becomes the dominant emission line when

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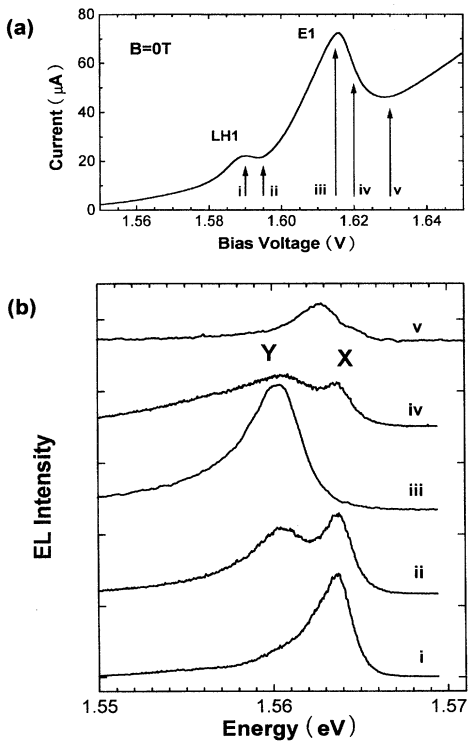

FIG. 1. (a) $I(V)$ characteristic and (b) EL spectra of a 6.1-nm barrier RTD at 4.2 K, active area (200 μm^2). The corresponding bias voltage values for the EL spectra are indicated by arrows i–v in $I(V)$. The zeros are equidistantly displaced.

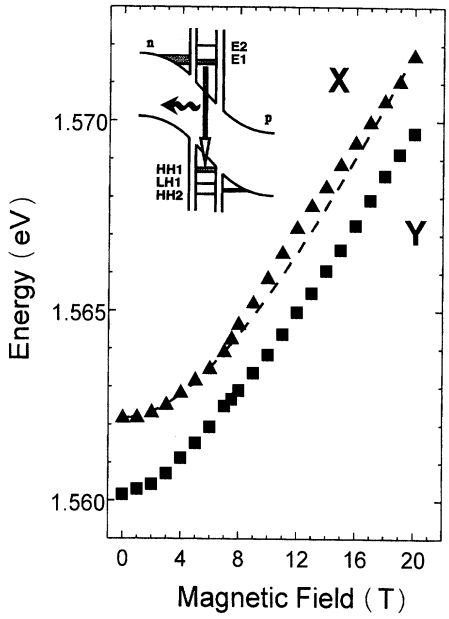

FIG. 2. Magnetic-field dependence of both QW recombination lines X and Y. The dotted line represents a fit of the diamagnetic shift. Inset: Schematic band diagram, showing the situation for the first electron quantum well state being in resonance with the electron accumulation layer.

the tunnel current and electron density in the QW reach maximum values at the peak of $E1$ [Fig. 1(b) (iii)]. At higher bias voltage beyond the $E1$ resonance when the electron density in the QW again decreases, the intensity of Y decreases to zero and X increases in intensity once more. Similar QW photoluminescence (PL) spectra were reported recently for n-i-n RTD's,[15] but the origin of the low-energy line (labeled line B therein) was not explained.

In order to confirm the excitonic nature of the recombination lines we carried out EL measurements in magnetic fields up to 20 T (B parallel to the current). As shown in Fig. 2 both lines X and Y display a clear excitonic behavior with a similar diamagnetic shift. This diamagnetic shift was fitted (Fig. 2, dotted line) with the two-point Padé approximation[16] using the common material parameters for GaAs and the excitonic effective mass as a fit parameter ($=0.044m_e$) in good agreement with the expected heavy-hole exciton mass ($\mu_{hh}=0.042m_e$). Interestingly, the current versus intensity correlation of lines X and Y does not change the field. A series of spectra recorded at a magnetic field of $B=18$ T (Fig. 3) displays the same features as observed at zero magnetic field (Fig. 1), i.e., line Y dominates in the region of the $E1$ resonance. Additionally, in high magnetic field line Y reappears when the electron concentration in the QW increases due to tunneling into the first Landau level[17] of the lowest-energy QW state (labeled vi in Fig. 3).

Temperature-dependence measurements show that heavy-hole free exciton line X recovers in intensity and the intensity of Y decreases when the temperature increases [Fig. 4(b)]. This thermal activation of X points to a new ground state Y for heavy-hole free excitons in the presence of a high electron concentration.

The energy separation between lines X and Y, $\Delta E \approx 2$ meV, is found to be the same for a wide range of p-i-n and n-i-n (Ref. 15) RTD's that we have investigated (same QW width 9.1 nm, but different wafers, different dopings and mesa sizes). The separation is found to be independent of magnetic field and temperature. We now consider various possibilities for the origin of line Y: Its increasing intensity with increasing electron density is inconsistent with excitonic recombination at shallow donors or interface states since in that case a saturation of intensity with increasing injection current would be expected, together with a slight blueshift due to screening of the bound state. We note here that a donor-related recombination line (D^0,h) in the PL spectrum of a n-i-n RTD was recently reported (Ref. 15, labeled line A therein). That line showed the expected saturation and blueshift with increasing electron density and appeared only at low electron densities in the QW, close to the threshold for resonant tunneling. In contrast, line Y appears only well above threshold and at high electron densities.

Biexcitons should have a binding energy of approximately 1 meV in GaAs systems.[4,6] This is much smaller than the observed X-Y splitting. In addition, it is difficult to envisage an increase of the BX intensity with increasing relative electron concentration.

The possibility of a transition from excitonic recombination to free electron–free hole recombination with increasing electron density has recently been proposed theoretically.[18] This transition should occur when the electron density in the QW exceeds a critical value ($n_e > 10^{11}$ cm^{-2}); the exciton

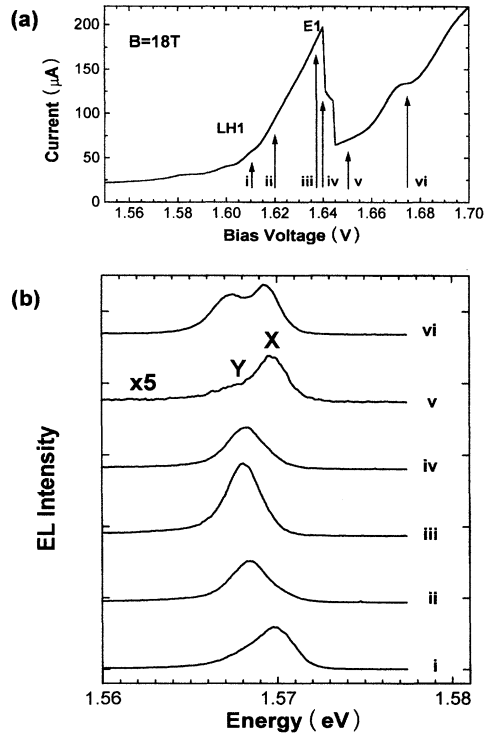

FIG. 3. (a) $I(V)$ characteristic and (b) EL spectra of a 6.1-nm barrier RTD, active area (200 μm^2), at $B=18$ T. The corresponding bias voltage values are indicated by arrows i–v in $I(V)$. The zeros are equidistantly displaced.

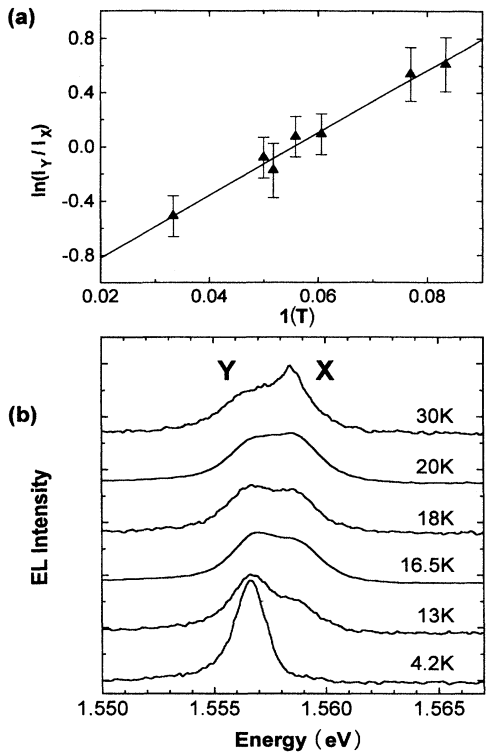

FIG. 4. (a) Temperature variation of the intensity ratio of the QW recombination lines Y and X. (b) Temperature dependence of the EL spectra for a device biased on the $E1$ resonance.

should then become unbound and a free-particle-like transition should occur at about 2–5 meV lower energy. In addition, the free particle transition should recover its excitonic character in high magnetic fields.[18] However, our magneto-EL measurements show clearly that both lines X and Y display excitonic character. Moreover, the features observed for zero magnetic fields do not change even in high magnetic fields (see Figs. 2 and 3) so that an exciton-plasma transition can probably be excluded as an origin for line Y. Therefore, we conclude that the most likely origin of line Y in the QW emission spectra is due to formation of negatively charged excitons in the QW.

Here we note an interesting conclusion which can be drawn from the magneto-EL spectrum. The final state of X^- corresponds to a single electron for which the magnetic-field dependence is the cyclotron confinement energy $\hbar\omega_c/2$, whereas the final state of the exciton has no magnetic-field dependence, since both of the initial particles are annihilated. However, as can be seen from Fig. 2, the magnetic-field dispersion of line Y closely follows that of X. This indicates that we should envisage X^- as an exciton to which the second electron is very weakly bound, consistent with the fact that the X-Y splitting of 2 meV is much smaller than the binding energy of the free exciton in a quantum well [$E_b(X)\sim 12$ meV].

We now analyze the activated behavior of line X. In our experiment an increase of the electron density in the QW increases the density of X^-: $e+X\Leftrightarrow X^-$. Thermal activation pushes this balance to the left (we neglect dissociation of excitons, as their binding energy is large). Assuming that the emission intensities are proportional to the particle densities, the relative intensities of X^- and X will vary as $e^{\{[\mu_e+E_b(X^-)]/kT\}}$, where μ_e is the free electron chemical potential and $E_b(X^-)$ is the X^- binding energy. At low temperatures the electron chemical potential $\mu_e \approx E_F=\pi^2 n_e/m_e^*$. Therefore, Fig. 4(a) can be used to determine the sum of $E_F+E_b(X^-)\equiv\varepsilon$ from a temperature-dependent measurement. Figure 4(b) shows the EL spectra for different temperatures of a typical device biased on the $E1$ resonance to assure a high electron density. At 4.2 K only line Y is visible in the spectrum. As the temperature increases the intensity of Y decreases, while X increases. Figure 4(a), where the intensity ratio is plotted, shows this activated behavior and gives $\varepsilon=2.0\pm0.3$ meV. With $E_b(X^-)=2.0\pm0.2$ meV (observed X-Y line splitting), E_F is not larger than 0.5 meV ($n_e\sim10^{10}$ cm^{-2}). This shows that in our RTD's (6.1-nm AlAs barriers and 9.1-nm well) the QW electron density at the $E1$ resonance is still well below the critical electron density, at which the exciton should become unbound.[10,18]

In conclusion, we have evidence for the formation of negatively charged excitons with a binding energy of $E_b(X^-)=2.0$ meV in a GaAs QW. The binding energy, formation, and recombination of X^- seems to be independent of magnetic field, up to 20 T. We have further demonstrated that RTD's are a useful tool for studying charged excitons since it is possible to change continuously the electron density in the QW by voltage-controlled resonant injection of electrons. Similar devices with an enhanced electron charge buildup in

the QW (Ref. 19) may eventually permit the observation of the expected exciton-plasma transition at sufficiently high electron densities. Enhanced hole charge buildup in appropriately designed RTD's may provide conditions suitable of the positive trion X_2^+.

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