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Trion formation in narrow GaAs quantum well structures

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We study the optical and electrical properties of *n-i-n* GaAs/AlAs double-barrier resonant tunneling diodes. Under illumination, new resonances appear in the current-voltage curves due to tunneling of photoexcited holes. By tuning the bias and the intensity of illumination, we can control independently the number of electrons and holes tunneling into the quantum well. This allows us to create charge conditions in the well that favor the formation of either positively charged, neutral, or negatively charged excitons. Our measured value of the binding energy of the second electron in the negative trion is significantly larger than that of the second hole in the positive trion.

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Many-particle systems are characterized by complexity and self-organization arising from simple physical laws. For instance, the long-range Coulomb interaction between electrical charges is responsible for the bound states of matter. In atomic and semiconductor physics, the simplest case is a bound pair formed by two opposite charges, of which the hydrogen atom and the exciton are representative examples. The role of particle mass on the formation of the bound complex becomes more relevant when a third charge is added. For hydrogen ions, the binding energy of H_2^+ is 2.8 eV, whereas for H^- it is 0.75 eV. Hence, the electronic affinity is significantly larger for the heavier charge than for the lighter one.[1]

In a semiconductor, the electronic affinity of the third carrier involved in the formation of charged excitons (so-called trions) is expected to show a similar behavior.[2,3] Positively charged ($X^+ = 2$ holes + 1 electron) and negatively charged trions ($X^- = 2$ electrons + 1 hole) form when excitons are present in an environment with excess holes or electrons, respectively. They were initially investigated theoretically[1–3] and later observed in semiconductor quantum well (QW) structures.[4–6] The binding energy of the second electron, $E_{b,e}$, or second hole, $E_{b,h}$, is a few meV, and increases with the quantum confinement.[7] However, theory and experiments have provided conflicting evidence about the relative magnitudes of $E_{b,e}$ and $E_{b,h}$ in QW's.[8–11] The measured binding energies for X^+ and X^- are rather similar.[10] In some cases, $E_{b,h}$ is about 10% larger than $E_{b,e}$,[9] in other cases smaller.[11] This disagrees with theoretical predictions[3] that suggest that $E_{b,h}$ should be about 30% larger than $E_{b,e}$ in GaAs QWs due to the heavier hole effective mass.

Recent theoretical work[12,13] has considered other possible mechanisms involved in the binding energy of the third carrier. They suggest that the disorder due to well-width fluctuations may lead to a significant increase of the trion binding energy in narrow QW's where interface defects become relevant. The different electron and hole localization at the defect site is responsible for the distinct increase of the X^- and X^+ binding energies, which is larger in the case of X^- than of X^+. In narrow QW's, this effect could therefore perturb the expected value of $E_{b,h}$ and $E_{b,e}$ when the degree of quantum confinement is increased.[7] In self-assembled quantum dots, which can be regarded as an extreme limit of interface roughness, the difference between the X^+ and X^- binding energies is of particular significance and interest.[14]

This paper examines the formation and binding energies of charged excitons in a narrow GaAs QW structure in which the relative concentrations of electrons and holes can be adjusted in a controlled way. This is achieved by using a double-barrier resonant tunneling diode (RTD) in which the GaAs QW is embedded between thin AlAs barriers. Under an applied bias, electrons can tunnel into the QW from *n*-doped GaAs layers placed on either side of the barriers. By illuminating the device with above-band-gap light under bias, the photogenerated holes can also tunnel into the well (see Fig. 1, inset). By varying the bias, *V*, and the intensity of illumination, we can control the number of electrons and holes tunneling through the barriers. Thus, we can precisely tune the charge state of the QW from hole-rich through charge-neutral to electron-rich conditions. This allows us to

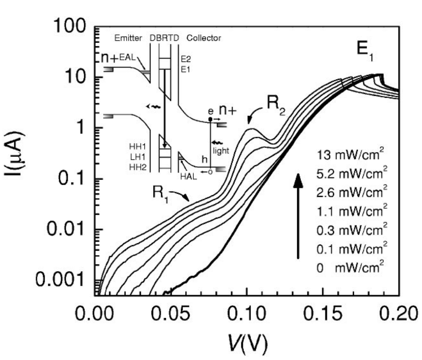

FIG. 1. $I(V)$ characteristics at 4.2 K in forward bias under illumination by a 760-nm laser line for different powers between 0 (bottom) and 13 mW/cm^2 (top). Inset: The schematic band diagram showing how the photocreated electron-hole pairs drift in opposite directions under an applied electric field.

create, in the same QW, different environments that favor the formation of positive, neutral, and negatively charged excitons, respectively. In this way, we can compare the values of $E_{b,e}$ and $E_{b,h}$ in the *same* structure without resorting to making difficult comparisons between spectra of different modulation-doped samples, in which there can be unintended small differences in the well width.

We investigate the current-voltage characteristics, $I(V)$, and the photoluminescence (PL) of a *n-i-n* GaAs/AlAs resonant tunneling diode under laser illumination over a wide range of bias. The device was grown by molecular beam epitaxy at 550 °C on a semi-insulating (100) GaAs substrate. It has a symmetric layer sequence, incorporating two 6-nm AlAs barriers and a 9-nm GaAs QW in the undoped intrinsic region. Undoped GaAs spacer layers of 20 nm separate the barriers from *n*-type doped contact layers with Si doping graded from 2×10^{16} (51 nm thick) through 2×10^{17} (80 nm) to 2×10^{18} cm^{-3} (100 nm). Optical lithography and wet etching were used to process circular mesas of diameter 100, 200, and 400 μm with a metal-free window at the top to provide optical access for PL measurements.

Under bias, a two-dimensional electron accumulation layer (EAL) forms in the GaAs spacer layer on the negatively biased (electron emitter) side of the device (see inset of Fig. 1). At low temperatures, the electron gas in the EAL is degenerate, as confirmed by the Shubnikov–de Haas-like oscillations observed in the tunnel current when a magnetic field is applied perpendicular to the electron sheet.[15] Figure 1 shows typical $I(V)$ curves at $T=4.2$ K for a 400-μm-diam device under different levels of laser light illumination (760-nm line). In dark conditions, the device shows a peak in $I(V)$ at $V\approx+0.185$ V, corresponding to resonant tunneling of conduction electrons from the EAL into the lowest energy subband E_1 of the QW. At the onset of the E_1 resonance ($V\approx+0.070$ V), the electron charge buildup of the QW increases and is a maximum at the resonant peak position. The $I(V)$ curves are symmetric in forward and reverse bias. Under illumination, two new resonances,[16] R_1 and R_2, appear in $I(V)$ at bias voltages $V_{R1}\approx+0.065$ V and $V_{R2}\approx+0.100$ V, significantly below the peak of the E_1 resonance. They appear only for photon energies larger than the GaAs band gap and their amplitudes depend strongly on the illumination intensity, as shown in Fig. 1.

To understand the effect of illumination we refer to the band profiles of the device shown in inset of Fig. 1. In forward bias, corresponding to the top n^+ GaAs layer biased positive, photocreated electrons in the GaAs depletion region beyond the right-hand barrier are swept into the doped collector region, but photocreated holes drift towards the collector barrier where they form a hole accumulation layer (HAL). This process has been discussed previously in the context of PL of RTD's.[17] The space charge of the HAL modifies the electrostatic profile in the device and accounts for the observed shift to lower bias of the threshold and peak of the E_1 resonance. The line shapes of R_1 and R_2 are similar in both bias directions but their amplitudes are smaller in reverse bias because of optical absorption effects. We ascribe the R_1 and R_2 resonances to hole tunneling through the heavy hole and light hole state QW subbands (HH_1 and LH_1) respectively, in analogy to the assignment of hole resonances below E_1 observed in *p-i-n* tunneling diodes.[18] Assuming a similar escape rate for electrons and holes from the QW, the ratio of electron/hole charge is approximately given by $Q_e/Q_h=I_e/I_h$. Therefore, comparing the $I(V)$ curves in dark conditions and under illumination, we estimate that the hole density into the QW is an order of magnitude larger than the electron density at bias V_{R2} for the highest illumination conditions.

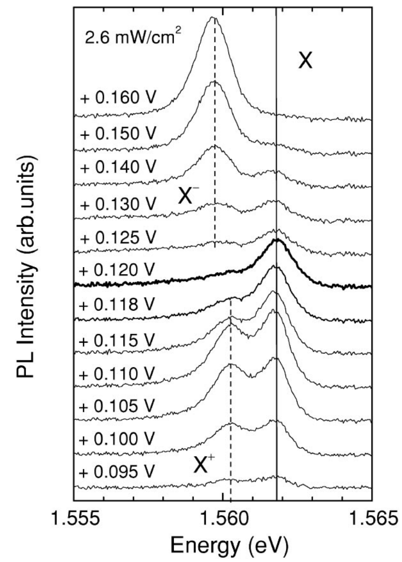

FIG. 2. PL spectra at 4.2 K at different forward biases under illumination by a 760-nm laser line with power=2.6 mW/cm^2. Spectra are displaced vertically for clarity.

With increasing bias beyond the threshold of the E_1 resonance, electron tunneling is more efficient and electrons progressively become the majority carriers in the QW. In this way, hole-rich and electron-rich conditions occur on the R_2 and E_1 resonances, respectively. When electrons and photocreated holes injected from EAL and HAL enter the QW, they recombine leading to PL emission. The bias-dependent tunability of the QW charging allows us to control the relative populations of the neutral and charged excitons as is clearly revealed in the optical response of the QW.

For a given illumination power (e.g., 2.6 mW/cm^2), the PL spectra are very sensitive to the carrier charge buildup of the QW, which can be tuned with the applied bias. No PL signal from the QW was detected at zero or low applied bias. As shown in Fig. 2, the threshold for detecting PL emission from the QW is at $V\sim+0.090$ V, corresponding to the low bias edge of the resonance R_2. On this resonance, the photocreated holes are efficiently injected into the QW and thermalize into HH_1 where they can recombine with the small number of electrons that start to tunnel into the QW in this bias range. This recombination in the QW has an excitonic nature as revealed by the diamagnetic shift of the PL spectra under the magnetic field.[19] The number of emission lines and their relative intensities are sensitive to the charge state of the QW. Thus, between $V=+0.090$ V and +0.120 V, in the vicinity of V_{R2} where holes are majority carriers in the QW, we can resolve two PL peaks at 1.5603 and 1.5618 eV. We

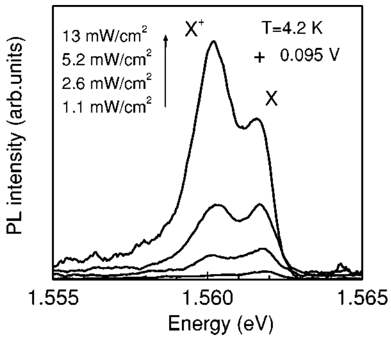

FIG. 3. Illumination power dependence of the PL spectra under illumination by a 760-nm laser line for $V=+0.095$ V at 4.2 K.

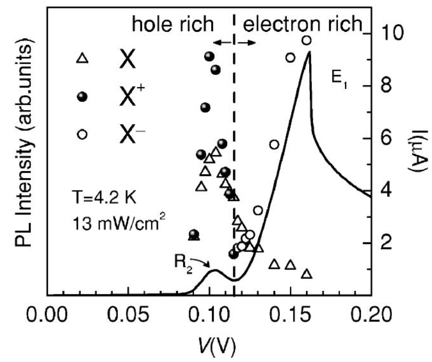

FIG. 4. Bias dependence of PL intensities of lines X (1.5618 meV), X^+ (1.5603 meV), and X^- (1.5597 meV) under illumination by a 760-nm laser line for a fixed illumination power of 13 mW/cm^2 at 4.2 K. The PL intensity dependence is compared with the forward bias $I(V)$.

identify them as X^+ and X, respectively. Within this bias range, any increase of hole density would favor X^+ formation. Figure 3 shows the PL spectra for different illumination powers for a bias $V=+0.095$ V. It is clear that the X^+ formation is favored when the hole density in the QW is enhanced at high illumination powers. Despite their relative intensity changes in the PL spectrum over this bias range, the energy positions of the X^+ and X PL lines do not change. When the bias is increased to $V=+0.120$ V, which corresponds to the minimum in current between R_2 and E_1, only the neutral exciton peak remains. A further small increase of bias towards the peak of E_1 gives rise to another well-resolved emission line at lower energy (1.5597 eV). With a further increase in bias, the electron density in the QW increases and the new emission line becomes dominant for bias $V>+0.130$ V, whereas the neutral exciton PL quenches at the approach of the peak of the E_1 resonance. The fact that the new line is favored by electron charging of the QW identifies it as arising from X^- recombination.

Still higher bias leads to changes in the relative intensity, but the energy position of the PL lines remains identical. Note that for the whole range of bias up to the peak of the E_1 resonance, the energy position of the X PL line remains constant, i.e., the quantum confined Stark effect is negligible, as expected in a 9-nm-thick QW at these modest applied electric fields.[20]

The evolution with bias of the PL spectrum from X^+ through X to X^- emission is a clear signature of the electrical charging state into the QW. The resulting PL can therefore be used to monitor the tunneling of electrons and holes into the QW as a function of bias. In Fig. 4, we compare the tunnel current flowing through the device with the PL intensities of neutral exciton and trions as a function of bias for fixed illumination power (13 mW/cm^2). The evolution of these PL lines is clearly correlated to the hole and electron tunneling. The X^+ PL intensity increases from a threshold at $V=+0.090$ V to a maximum at +0.100 V and then decreases, disappearing at $V=+0.120$ V. Note that the peak of the X^+ PL intensity coincides with that of R_2. Thus, we conclude that R_2 in $I(V)$ is associated with resonant tunneling of photogenerated holes into the QW. The X^- line appears at $V>+0.120$ V, and its PL intensity increases, to reach a maximum at $V=+0.160$ V, which coincides with the main peak in $I(V)$ due to electron tunneling into the E_1 subband.

The maximum intensity of the X PL line also coincides with the current peak of the R_2 resonance at $V=+0.100$ V and falls off gradually with increasing bias, disappearing close to the threshold of the main resonant peak E_1 due to the increasing amount of electronic charge in the QW. The bias dependences of the X^+ and X^- PL peaks provide a clear signature of the changing carrier environment in the QW and is consistent with a model of trion formation involving a dynamical equilibrium between trions, neutral excitons, and free carriers, and the respective recombination times.[21] Interestingly, at $V=+0.120$ V and for the laser excitation condition shown in Fig. 2, the PL spectrum is dominated by the X PL line, indicating that neutral-charge conditions prevail in the QW. This condition can be shifted slightly to lower bias by increasing the laser intensity. Since the holes entering the QW from the HAL arise mainly from photogeneration in the GaAs collector layer, by varying the illumination power we can enhance the formation of X^+ as is confirmed by the PL spectra shown in Fig. 3.

The PL spectra in Fig. 2 provide us with values of the the binding energies of X^+ and X^- in the *same* QW: $E_{b,h}=1.5$ meV and $E_{b,e}=2.1$ meV. It is of particular interest that $E_{b,e}$ is $\sim$40% larger than $E_{b,h}$, especially as a similar result has also been reported for trions in quantum wires.[22] A larger value of $E_{b,h}$ than $E_{b,e}$ is expected[2,3] in analogy with the relative binding energies of H_2^+ and H^-. On the other hand, a previous experimental study comparing trion binding energies in a wider 20-nm GaAs QW[10] gave $E_{b,h}=E_{b,e}=1.10$ meV. These values are significantly smaller than those we have obtained in a 9-nm QW. In the case of X^+, the observed increase of 35% of $E_{b,h}$ for our narrow QW can, in principle, be explained by the reduction of the quantum well width.[7] However, an increase of 90% for $E_{b,e}$ is difficult to explain by considering confinement effects only.

Our results suggest that other mechanisms may cause the large increase of $E_{b,e}$ for a narrow QW, and compared with the $E_{b,h}$ value. Recent calculations suggest that fluctuations in the well width produce disorder, which tends to increase the binding energy of the third carrier.[12,13] They predict a larger increase of the trion binding energy compared to calculations, which neglect disorder effects.[7] Thus, when the effect of disorder is included the expected value of $E_{b,e}$ in narrow GaAs QW's is a factor of 2 larger than for the case when confinement effects only are considered.[7,13] In addition, the influence of disorder is expected to be different for X^+ and X^- as is observed in quantum dots.[14] Due to its smaller effective mass, the spatial extent of the electron wave function in the interface defect is larger than that of the hole.[7,13] This leads to a larger $E_{b,e}$ than $E_{b,h}$. Since interface roughness is particularly important in narrow QWs, disorder effects may become more significant than the quantum confinement effect as the QW width is decreased. This could explain our observation of a significantly larger value of $E_{b,e}$ than $E_{b,h}$ in a narrow GaAs QW.

In conclusion, we find strong evidence for a larger binding energy for X^- than for X^+ in narrow QWs. Our experiments indicate that interface defects may enhance the binding energy of the third carrier in trions, as recently predicted.[12,13] We demonstrate that a RTD is a useful system for studying trion formation, since it is possible to precisely tune the electron and hole densities in the QW by a combination of voltage-controlled injection and optical excitation. We also identify the origin of a photoinduced resonant peak in $I(V)$. Finally, we suggest that further insights into the effect of disorder on the positive and negative trion binding energy could be gained by studying similar RTDs but with controlled amounts of interface disorder, e.g., by introducing a small concentration of Al near the QW-barrier interfaces.

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