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Nonthermal occupation of Γ and X states in GaAs/AlAs superlattices

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We have studied the photoluminescence (PL) emission from a GaAs/AlAs asymmetric-double-well superlattice with indirect band gap as a function of temperature and applied electric field. The PL spectrum consists of two peaks, with a separation of only 21 meV, originating from the recombination of wide-well heavy holes with either X electrons of the barrier or Γ electrons of the wide well, respectively. The PL intensity ratio of the two peaks shows a strong nonthermal population between Γ and X states near flatband, because in this sample the transfer from Γ to X after photoexcitation can be induced only by absorption of phonons with a large momentum. The small Γ-X separation and the long recombination time of X electrons results in the filling of the X states that are at the same energy as the Γ minimum, blocking Γ-X transfer by phonon emission or interface (roughness) scattering.

Short-period GaAs/AlAs superlattices[1-4] are very interesting systems because they offer the possibility of exhibiting indirect band gaps, very long recombination lifetimes,[5-7] and nonlinear optical effects.[8,9] Unlike GaAs, bulk AlAs is an indirect-band-gap material with the conduction-band minimum at the X point of the Brillouin zone. Therefore, when quantum wells are thin enough so that the lowest electron level of the well (which is at the Γ point) is above the lowest electron level of the barrier (which is at the X point), the superlattices have an indirect gap in k space.[5,10,11] Moreover, the gap is also indirect in real space (type-II superlattices), because the associated transition involves a hole in the well and an electron in the barrier. Light absorption occurs mainly through direct transitions at the Γ point, which have a much larger oscillator strength. However, light emission takes place mainly through *thermalized* electrons and holes, i.e., recombination of the lowest X electron states with the Γ hole states. Therefore, the Γ-X transfer of electrons is very important in photoluminescence (PL) and has received considerable attention.[7,12,13] The transfer from Γ to X can be induced by three mechanisms,[7,13] phonon absorption (PA), phonon emission (PE), and interface (roughness) scattering (IS). Momentum conservation requires phonons near the zone edge.

Previous PL experiments in GaAs/AlAs indirect superlattices[14-16] have shown a thermal distribution of electrons between Γ and X levels. In both cases the Γ-to-X integrated PL intensity ratio increased with temperature, following an Arrhenius-type behavior, as the higher electron states at the Γ point become more populated. In these experiments[15,16] the splitting between the X and Γ minima was larger than 50 meV. In this paper we show that for a much smaller separation a nonthermal occupation of the conduction-band states (Γ and X) occurs. This nonthermal population is observed by performing PL experiments at various temperatures and electric fields.

The sample is a p-i-n diode grown by molecular beam epitaxy on a (100) n^+-type GaAs substrate. Apart from the substrate, the n side is formed by four layers doped with Si (donor concentration about 10^{18} cm^{-3}). The layers and their thicknesses are, following the growth direction, 1000 Å GaAs, 1700 Å $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$, 3000 Å $\mathrm{Al}_{0.5}\mathrm{Ga}_{0.5}\mathrm{As}$, and 700 Å $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$. x changes linearly between adjacent layers. Similarly, the p-side sequence is 700 Å $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$, 3000 Å $\mathrm{Al}_{0.5}\mathrm{Ga}_{0.5}\mathrm{As}$, and 85 Å GaAs, doped with C (acceptor concentration about 10^{19} cm^{-3}). The intrinsic region consists of a superlattice sandwiched between two 250 Å GaAs layers. The superlattice contains 60 periods of 14 Å AlAs, 17 Å GaAs, 14 Å AlAs, and 28 Å GaAs, plus another 14 Å AlAs barrier at the superlattice end. The unit cell represents an asymmetric double-quantum-well structure (see Fig. 1).

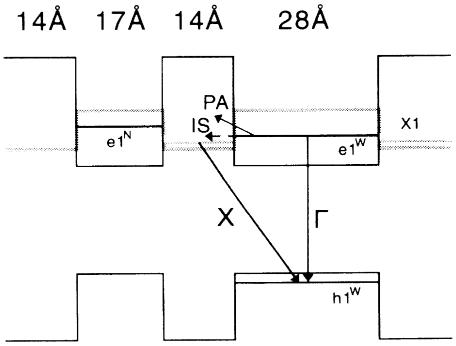

FIG. 1. Schematic potential profile for one period of the GaAs/AlAs double-well superlattice at flat band. Black and gray lines stand for the Γ and X band edges, respectively. Energies are not drawn to scale.

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In this superlattice the Γ states of two consecutive wide wells are decoupled, because they are separated by two barriers and a narrow well. At the same time the barriers are narrow enough to have the quantum-well level of the barrier at the X point slightly below the Γ level of the wide well. We prepared devices by evaporating AuGe/Ni/Au and Cr/Au contacts on the n^+ and p^+ regions, respectively, and by etching 120-μm-diameter mesa structures down to the substrate. When the diode is reverse biased with a voltage V, the electric field in the superlattice is homogeneously distributed and given by $\mathcal{E} = (V_{\text{BI}} - V)/W$, where $V_{\text{BI}} \approx 1.5$ V is the built-in voltage (determined as the voltage for which the photocurrent crosses the zero value) and $W = 4894$ Å is the intrinsic-region width. PL was excited with the 6471 Å (1.916 eV) or the 4762 Å (2.604 eV) line of a Kr$^+$ laser. The laser power was reduced to keep the photocurrent at -5 V smaller than 20 μA.

The PL spectra exhibit two peaks at 1.821 and 1.842 meV (see Fig. 2). The high-energy peak (Γ) corresponds to the transition between the first electron state of the wide well ($e1^W$), which is at the Γ point, and the first heavy-hole state in the wide well ($h1^W$). This is a direct transition in k space (arrow labeled Γ in Fig. 1). The low-energy peak (X) corresponds to the transition between the first electron state in the barrier ($X1$), which is at the X point, and the first heavy-hole state in the wide well, which is an indirect transition in real and in k space (arrow labeled X in Fig. 1). The lattice constant of AlAs is slightly smaller than the lattice constant of the GaAs substrate. Therefore, the AlAs layers are under uniaxial stress and the X edge of the barriers splits[10,11,18] into X_z and X_{xy} edges with crystal momentum k parallel and perpendicular, respectively, to the growth direction z. For AlAs barriers thinner than 60 Å the lowest edge[11] is X_z. Furthermore, the recombination of X_{xy} electrons is characterized by strong phonon replicas,[7] which are absent in our PL spectra. Therefore, the low-energy PL peak is ascribed to recombination of electrons in an X_z state. To check the assignments we have calculated the position of electronic levels with a generalized Kronig-Penney model in the envelope-function approximation.[19] The best fit for the Γ transition energy as measured by photocurrent spectroscopy is obtained for a wide-well width of 26 Å. Scaling all the widths in accordance, the calculated confinement energies are listed in Table I. The corresponding calculated transition energies are 1.817 eV for the $X1$-$h1^W$ transition and 1.846 eV for the $e1^W$-$h1^W$ transition, in good agreement with the observed peak energies. The calculated separation between the two PL peaks is 29 meV, which is similar to the observed one. The Stokes shift between the Γ peaks in PL emission and photocurrent is 11 meV, which is a typical value.[4]

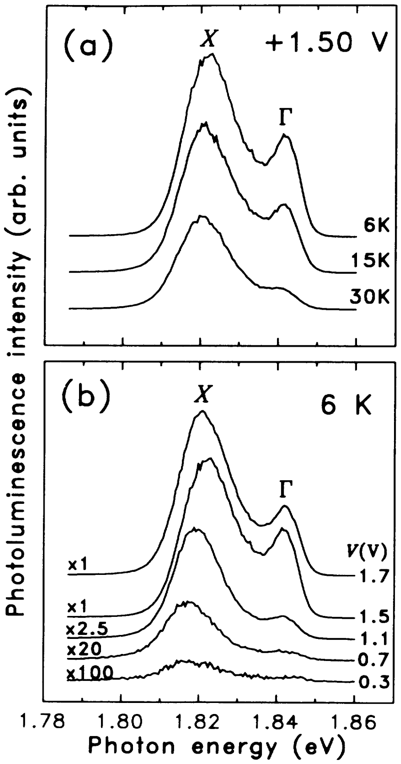

FIG. 2. Photoluminescence (PL) spectra measured (a) at zero electric field (applied voltage of 1.5 V) for different sample temperatures and (b) at 6 K for selected values of the applied voltage. The excitation energy was 1.916 eV. Spectra have been offset vertically for clarity.

We measured the PL spectra for a series of applied voltages at 6, 15, and 30 K. At zero electric field (applied voltage of 1.5 V) the evolution with temperature [Fig. 2(a)] shows that the intensity of both peaks decreases when the temperature increases, but the reduction of the Γ peak intensity is larger than that for the X peak. Furthermore, the Γ peak disappears above 30 K. In Fig. 2(b) the field dependence of the PL is shown at the lowest temperature. The Γ peak intensity is more strongly reduced than the X peak intensity when the applied electric field is increased (between an applied voltage of 1.7 and 0.3 V). The PL intensity of both lines decreases with increasing electric field due to the field-induced separation of electrons and holes. A closer look at the spectra shows that the X peak shifts to lower energies with increasing electric field, while the Γ peak does not. This observation is additional evidence for the assignment of the low-energy peak as the indirect transition between the $X1$ state and the $h1^W$ state.

In the following we will focus on the relative intensities of these two transitions. Since the two peaks partially

TABLE I. Calculated confinement energies of the electron ground state at the X minimum of the barrier ($X1$) and at the Γ minimum of the wide well ($e1^W$) and the narrow well ($e1^N$) with respect to the conduction-band edge of bulk GaAs; and calculated confinement energies of the heavy-hole ground state of the wide well ($h1^W$) and the narrow well ($h1^N$) with respect to the valence-band edge of bulk GaAs.

$X1$	214 meV
$e1^W$	243 meV
$e1^N$	425 meV
$h1^W$	84 meV
$h1^N$	164 meV

overlap we have fitted the spectra with two Gaussians. The ratio of integrated intensities for the two Gaussians as a function of temperature is represented in Fig. 3(a). Intensities of the Γ and X PL peaks are proportional to the electron populations in the $e1^W$ and $X1$ states, respectively, because the matrix elements between the $h1^W$ and $X1$ or $e1^W$ states are temperature independent.[7] Previous investigations on short-period GaAs/AlAs superlattices have shown[14,15] that at zero electric field (no field dependence was studied) the population of both states was thermal. The higher the temperature, the larger was the population of $e1^W$, which is at higher energy. Furthermore, the Γ-X PL intensity ratio followed an Arrhenius behavior.[14,15] In our experiments (Fig. 3), for large electric fields the Γ-X ratio also increases with temperature, although it does not follow a perfect Arrhenius behavior. However, near flatband the ratio clearly decreases with temperature, evidencing a nonthermal distribution of electrons between the two levels.

Our explanation is based on the small energy separation between the Γ and X levels, which rules out two of the three possible mechanisms for Γ-X transfer near flatband. Absorbed photons excite electrons mostly at the Γ states of the quantum wells because type-II indirect transitions to the X states have much smaller oscillator strengths. Photogenerated electrons relax very quickly to the $e1^W$ state of the wide well. Once at the bottom of the Γ state they can be transferred into the $X1$ state via PA, PE, or IS. Except for nonradiative processes, recombination of $h1^W$ holes with electrons in the $e1^W$ and $X1$ state produces the Γ and X PL peaks, respectively. The relative electron populations will depend on the Γ-X transfer. When the transfer can occur by PA, PE, and IS, there is a very good thermalization between the Γ and X states, because the latter two mechanisms allow for a good transfer at any temperature. However, in our case two of these mechanisms are not possible near flatband. PE and IS are probably blocked by charge buildup in the $X1$ band.[13] There are two reasons for the buildup: First, the rather long recombination times of the $X1$ state, and second, the larger density of states for the X valley, which makes Γ-X transfer an order of magnitude larger than X-Γ transfer. The charge buildup leads to recombination of $X1$ electrons at higher energies, which produces the slowly decaying tail on the high-energy side of the X PL peak (Fig. 2).

Then the only remaining mechanism for Γ-X transfer is PA, which is strongly temperature dependent. Its probability is proportional to the phonon density,[7] i.e., to the Bose-Einstein occupation number $n(T) = [\exp(E_{\text{ph}}/k_BT) - 1]^{-1}$, where E_{ph} is the phonon energy, which can vary between 10 and 31 meV for GaAs zone-edge phonons,[17] and k_B is the Boltzmann constant. At 6 K there are almost no phonon states populated and the Γ-X transfer is small, but at 30 K the number of occupied phonon states becomes appreciable and more electrons are transferred to the $X1$ state. Therefore, the larger the temperature, the smaller the relative population of the higher state ($e1^W$) with respect to the lower state ($X1$). In other words, there is a nonthermal occupation of the conduction-band levels near flatband.

For finite electric fields, the Γ-X PL intensity ratio increases with temperature [shadowed area of Fig. 3(a)], although it does not follow a straight line in an Arrhenius plot. This means that PA is no longer the only mechanism for Γ-X transfer; either PE or IS is coming into play. Considering that intrawell Stark shifts are negligible,[20] the electric field increases the separation between the $e1^W$ and one of the neighbor $X1$ levels by $\Delta E(\text{meV}) = e\mathcal{E}d$, e and d being the electron charge and the distance between the barrier and the wide-well centers ($d = 21$ Å). The larger separation lowers the filled X states with respect to the Γ minimum and can trigger Γ-X transfer by IS or PE processes. This implies that at low temperatures the Γ-X PL intensity ratio should decrease with the electric field. This is in fact observed [cf. Fig. 2(b)]. Figure 3(b) shows the Γ-X PL intensity ratio as a function of electric field for 6, 15, and 30 K. For the two lowest temperatures the ratio decreases when the electric field increases. The decay saturates within the experimental error at around 10 kV/cm. At 30 K the intensity ratio increases smoothly with the field. The reason for this behavior is not clear yet.

In summary, we have studied the photoluminescence emission from a GaAs/AlAs asymmetric-double-well superlattice with indirect band gap and a small Γ-X splitting. In contrast to previous experiments with a larger Γ-X separation, we have found that near flatband the Γ-X transfer can occur in our sample only via phonon absorption, which increases sharply with temperature and results in a nonthermal occupation of the Γ and X conduction-band levels.

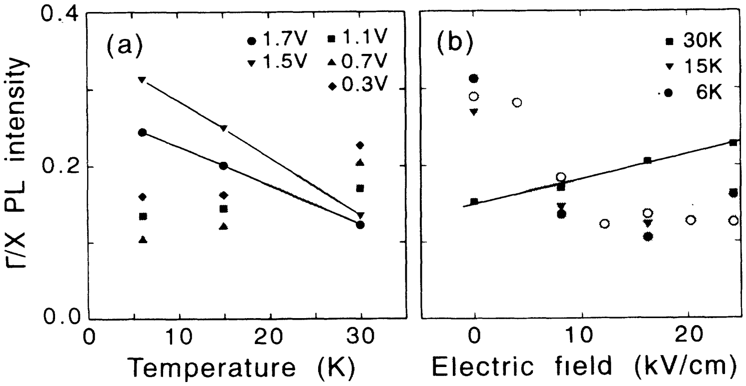

FIG. 3. Γ-to-X integrated PL intensity ratio vs temperature for different applied voltages (a) and vs electric field at 6, 15, and 30 K (b). The excitation energy was 1.916 eV for the full symbols and 2.604 eV for the empty symbols. Lines and shadowed areas are only a guide to the eye.

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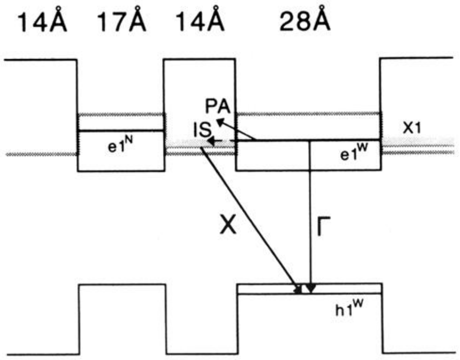

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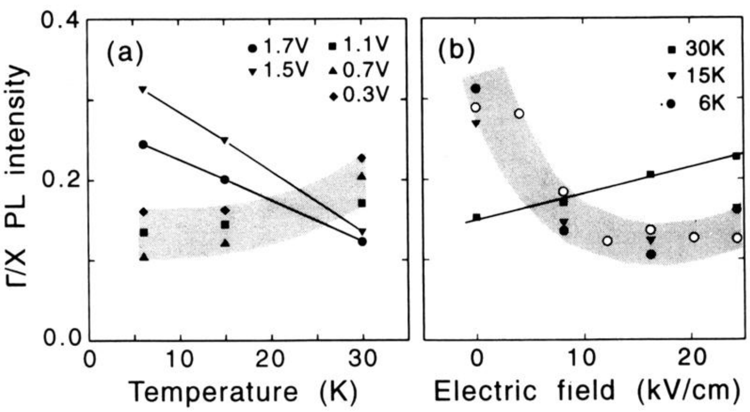

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