Selective Exciton Formation in Thin GaAs/$Al_xGa_{1-x}As$ Quantum Wells

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We demonstrate experimentally that the exciton luminescence rise times in GaAs/$Al_xGa_{1-x}As$ quantum wells oscillate as a function of laser excess energy. We interpret these results as the occurrence of a selective optical-phonon assisted exciton formation. Experiments on doped quantum wells confirm our exciton formation model.

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Exciton spectra of the photoluminescence and photoconductivity of various semiconductors are well known to exhibit oscillatory behavior [1–9]. Since optical excitation gives rise to the direct generation of excitons or to free electrons and holes, the origin of these oscillations arises from the relaxation of either hot carriers [2,5,8] or hot excitons [1,3,4,6,7]. The oscillation directly reveals whether the relaxation of photogenerated carriers is dominated by hot excitons ($\hbar\omega_{LO}$) or hot carriers [$\hbar\omega_{LO}(1+m_e^*/m_h^*)$]. The creation of hot excitons with high momenta is an indirect process in which the large exciton wave vector is compensated for by the wave vector of a simultaneously created phonon. In II-VI semiconductors this indirect exciton formation process is dominant due to the large electron phonon coupling [1,3,4,6]. In III-V semiconductors no hot exciton effects have been reported and the observed oscillations were attributed to the relaxation of hot electrons [8,10] or resonant capture of hot electrons [11]. In this situation the dynamical properties of the excitons are governed by subsequent carrier cooling, exciton formation, and exciton relaxation.

The larger exciton binding energy in quantum wells with regard to bulk reduces the redissociation probability of the hot excitons and thus enhances the hot exciton relaxation effects. In II-VI quantum wells the creation of hot excitons at high momentum and their subsequent relaxation by LO-phonon emission has been demonstrated using picosecond time-resolved luminescence spectroscopy [12,13]. In III-V quantum wells no hot exciton effects have been observed [14] in spite of the larger exciton binding energy. Only in a coupled GaAs-(Al,Ga)As quantum-well system, where the relaxation rates could be modified by the tunneling through the barrier between the wells, hot exciton effects have been observed [15]. However, the question whether the exciton dynamics in III-V quantum wells are dominated by the direct formation and relaxation of hot excitons or by the relaxation of hot carriers with subsequent exciton formation and relaxation has not been clarified.

The dependence of the exciton luminescence on the energy and momentum of the participating electron and hole provides information about the dominant mechanism. For excitation energies below the band edge the reported dependence of the luminescence rise time on the photon energy was attributed to exciton relaxation effects [16–19]. From the fast initial rise of the photoluminescence for small excess energies exciton formation times of < 20 ps were deduced [16,18] and a time-resolved study on an asymmetric double quantum well [20] provided an exciton formation time of 14.4 ps. For photon energies exceeding the electron–heavy-hole band edge no dependence of the luminescence rise times on laser energy has been observed [16–18]. From the absence of an enhancement of the excitation formation for a laser energy of one LO-phonon energy larger than the exciton state, it was assumed that the formation of excitons was dominated by the emission of acoustic phonons [16]. However, no theoretical or experimental study is available which disentangles the various mechanisms of exciton formation.

A possible dependence of the exciton formation process on the laser energy is difficult to observe, since variations in the exciton formation time of < 20 ps are very small in comparison with the reported luminescence rise times of 400 ps [16–19] for wide quantum wells. These long rise times were attributed to the migration of excitons towards the lower energy positions in an inhomogeneous quantum well by emission of acoustic phonons [17], the intrinsic relaxation of excitons [16], and a drift-diffusion model driven by potential fluctuations in the quantum well plane [21]. By narrowing the quantum wells the slow exciton relaxation process can be enhanced substantially due to a decrease of the acoustic phonon scattering time, which varies linearly with the well width [22]. Furthermore, with increasing excitation density the rise times are reduced as a result of electron-exciton and exciton-scattering [16,18,19]. By calculating the broadening of the electron and hole distributions during the initial LO-phonon cascade, we obtained that an excitation density of 5×10^{10} cm^{-2} still gives rise to a spectral distribution of a few meV for the electrons.

In the present study we have investigated the luminescence rise times of thin (26 Å) GaAs/AlGaAs quantum well structures as a function of laser energy. The aluminum fraction in the AlGaAs layers is 0.3 (sample A) and 0.4 (sample B). For both aluminum fractions the quantum wells contain one electron bound state, one light-hole bound state, and two heavy-hole bound states. The exciton formation process has been studied by subpicosecond time-resolved luminescence experiments using an up-

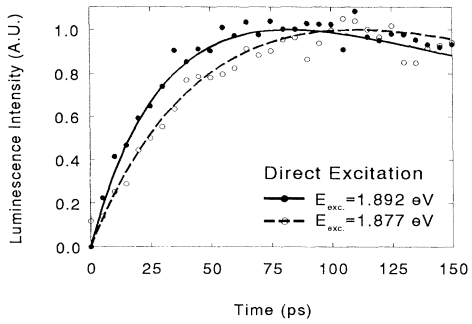

FIG. 1. Time evolution of the exciton luminescence of sample A at the spectral peak (1.705 eV) for two different excitation photon energies. The experiments were carried out at $T=8$ K with an excitation density of 5×10^{10} cm^{-2} in the quantum wells. The fitted curves, which are plotted as a solid and a dashed line, provide luminescence rise times of 27 and 32 ps for the laser energies of 1.892 and 1.877 eV, respectively.

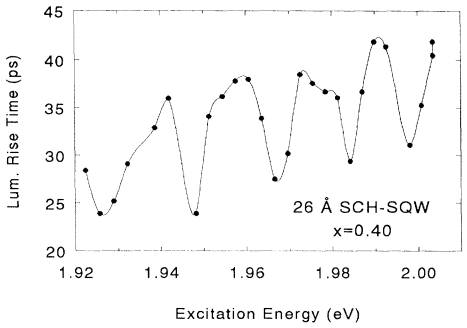

FIG. 2. Exciton luminescence rise times (●) at $T=8$ K as a function of excitation energy of sample B ($x=0.4$). The excitation density amounts to 5×10^{10} cm^{-2}. Oscillations between 25 and 40 ps in the exciton luminescence rise times are observed with a periodicity of about 20 meV. The solid line is a guide to the eye.

conversion light gate. In this up-conversion technique the luminescence excited by a short laser pulse (0.6 ps) is mixed with the laser itself in a nonlinear crystal to generate the sum or difference frequency radiation, providing time resolution comparable to the laser pulse. The time-resolved experiments have been carried out at $T=8$ K at an excitation density of 5×10^{10} cm^{-2} with laser energies lower than the barrier band gap. Our spectral window is determined by the phase-matching conditions in the nonlinear crystal and is limited to 2 meV. As a result we can only monitor the time-resolved behavior of the central part of the exciton luminescence peak.

In Fig. 1 the time evolution of the exciton luminescence of sample A after excitation with a subpicosecond laser pulse is shown for laser energies of 1.892 and 1.877 eV, which are both beneath the barrier band gap of sample A. For the different laser energies rise times of 27 and 32 ± 1 ps have been obtained, respectively. It should be noted that in the literature the rise time is often defined as the time for the luminescence to reach its maximum value [16,18], while we obtain our rise times from an exponential fit. In order to compare our rise times with reported values, they should be multiplied by a factor 3. For a quantum well width of 26 Å and an excitation density of 5×10^{10} cm^{-2} the exciton luminescence reaches its maximum value around 100 ps, in agreement with the results of Eccleston *et al.* [18], and becomes sensitive to the exciton formation time. This enables us to investigate the dependence of the exciton formation process on laser energy. Figure 2 shows the dependence of the exciton luminescence rise times on laser energy in the interval 1.92–2.00 eV for sample B. We observe an oscillating rise time of the exciton luminescence with a period of nearly 20 meV and a difference in amplitude of about 12 ps. Such an oscillating rise time has also been observed in sample A with the same periodicity.

Oscillations as a result of hot exciton relaxation would appear with a constant oscillation period of 36.8 meV. The decreasing period of the observed oscillations in Fig. 2 with increasing laser energy definitely indicates that hot exciton relaxation can be excluded as an explanation for the observed resonances. Furthermore, the resonances cannot be attributed only to hot electron effects [8] which should give rise to a constant oscillation period of 42 meV. The observed oscillating behavior strongly suggests that the exciton formation process of free electrons and holes is sensitive to the positions in momentum space of the electrons and holes after the initial LO-phonon cascade.

In order to find out whether such a concept of "sensitive spots" is realistic in our experimental conditions we have performed a series of Monte Carlo simulations [23]. The comparison between the calculated and observed structure in the luminescence rise time directly reveals information about the dominant exciton formation mechanism, the relevant conditions for energy and momentum (i.e., energy and momentum conservation and relative velocity of the participating electron and holes), and the role of carrier-carrier scattering during the LO-phonon cascade. In order to obtain the positions of the electrons and holes in their subbands after photoexcitation and during exciton formation we have used the dispersion relations of the various subbands in momentum space as calculated by means of an empirical pseudopotential method by Cuypers and van Haeringen [24]. After excitation both the electrons and holes will relax by means of a LO-phonon cascade until they are within one LO-phonon energy from their subband minima. The light holes will subsequently scatter to the heavy-hole subband, which process is still being fast due to the large density of states connected with the heavy-hole effective mass.

In Fig. 3 we compare the position of the photoexcited electrons from the light- (e_{lh}) and heavy-hole band (e_{hh}) after their LO-phonon cascade [Fig. 3(a)] with the observed and calculated rise times [Fig. 3(b)] as a function of laser energy. Our Monte Carlo study has revealed that

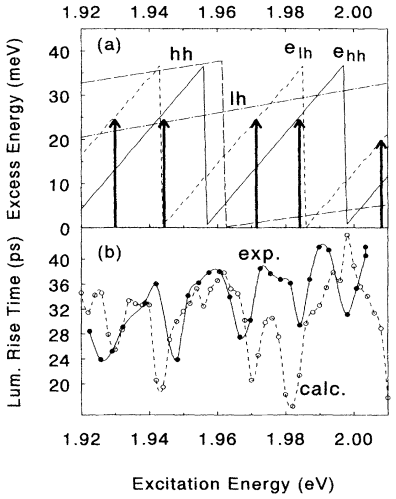

FIG. 3. Comparison between electron (e_{hh} and e_{lh}) and hole (hh and lh) excess energies (a) after the phonon cascade and exciton luminescence rise times (b) as a function of excitation energy. The electron excess energies continuously vary between 0 and 36.8 meV with a period of 42 meV. The excess energy of the light holes gradually increases from 20 to 33 meV as the excitation energy increases from 1.92 to 2.01 eV. A minimum in the exciton rise times is observed whenever free electrons and holes are able to form excitons by LO-phonon emission. The minima correspond to electron excess energies of about 25 meV, since holes are available at the subband maximum for all laser energies.

a structure which closely resembles the experimental data [23] is obtained by LO-phonon-assisted exciton formation whenever (i) the sum of electron and heavy-hole energy is equal to the LO-phonon energy minus the exciton binding energy and (ii) one of the participating particles has energy and momentum close to zero. As an example at a laser energy of 1.985 eV the excess energy of the electrons excited from the heavy-hole subband (e_{hh}) amounts to 25 meV with regard to the subband minimum, whereas the excess energy of the heavy hole is about 2 meV. By emitting a LO phonon of 36.8 meV, the electron-hole pair lowers its total energy by 10 meV, which is nearly equal to the exciton binding energy for our thin quantum well. With decreasing laser energy the next minimum occurs at 1.970 eV where the excess energy of the electrons excited from the light-hole subband amounts to 25 meV after the phonon cascade. From the amplitude of the oscillations we obtain a difference between LO-phonon-assisted exciton formation (1 ps) and acoustic-phonon-assisted exciton formation of 12 ps. The observed exciton formation time of 12 ps due to acoustic-phonon emission is in agreement with earlier reported exciton formation times [16,18,20].

Another important feature is that for laser energies smaller than 1.960 eV the excess energy of the heavy holes is close to the LO-phonon threshold. By means of carrier-carrier scattering, which is a fast process for the heavy holes as a result of their large effective mass, a part of the heavy holes exceeds the LO-phonon threshold and is immediately transferred to the subband minimum by LO-phonon emission. Above 1.96 eV the heavy holes end around $k=0$ after the LO-phonon cascade. So in the whole energy range we have heavy holes around $k=0$. The energy positions of the LO-phonon-assisted exciton formation, which are indicated by the arrows in Fig. 3(a), correspond within a few meV to the observed minima of the exciton luminescence rise times. Only the experimental minimum at 2.00 eV deviates from the calculated minima at 2.01 eV with 10 meV. However, it should be noted that the calculated positions strongly depend on the precise knowledge of the band structure, which is hard to obtain, especially for the various hole bands.

During and after the LO-phonon cascade the carriers spread out in momentum and energy space due to carrier-carrier scattering. As a result of the larger effective mass the carrier-carrier scattering and thus the diffusion in momentum space of the heavy holes are almost 1 order of magnitude larger than the scattering rate and diffusion of electrons. Because of this large hole scattering rate the condition that one of the participating particles (electron or heavy hole) has a small momentum is fulfilled in our experiments.

According to our model, we should also expect a minimum at a laser energy of 1.957 eV, where the excess energy of the holes originating from the light-hole subband amounts to 25 meV. However, since the holes are already spread out in energy before the electrons have completed their LO-phonon cascade, no minimum is observed at this laser energy. In a sample with n-doped quantum wells, however, this minimum should appear, since already electrons at the subband minima are available at the moment that the holes have completed their cascade and start to diffuse in momentum space. The experimental exciton rise times for an n-doped (1×10^{11} cm^{-2}) GaAs/AlGaAs multiple quantum well with a well width of 26 Å and an aluminum fraction of 0.4 is plotted in Fig. 4 as a function of laser energy. The exciton peak of the n-doped sample was shifted (9 meV) to a higher energy in comparison with the undoped sample, due to a somewhat smaller well width. Furthermore, the experiments on the doped sample were carried out at a lower excitation density (2×10^{10} cm^{-2}) with regard to the undoped sample (5×10^{10} cm^{-2}) resulting in a lower rise time. Therefore, in order to compare the rise times of both samples the laser energies of the n-doped sample are shifted 9 meV to lower energy. The excitonic behavior, which disappears at very high doping densities [25], is still present at our doping density. We observe that for the n-doped sample the maximum in the luminescence rise time at 1.957 eV of the undoped sample has disappeared, which strongly supports our model.

The diffusion of the carriers by means of carrier-carrier scattering in energy and momentum can also be enhanced by increasing the excitation density. We have found that with increasing excitation density from 5×10^{10} cm^{-2} to 5×10^{11} cm^{-2} (i) the oscillations of the rise times are re-

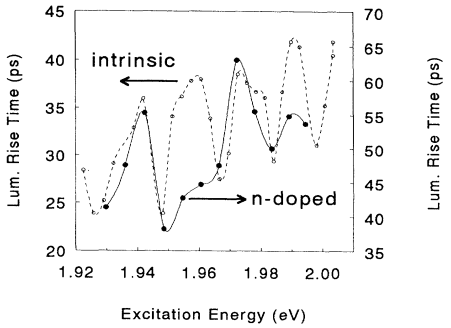

FIG. 4. Exciton luminescence rise times (●) as a function of excitation energy for a sample with *n*-doped quantum wells. The layer structure of the sample is identical to sample B and the dopant density is 1×10^{11} cm^{-2}. With regard to the intrinsic sample B (dashed line) no maximum is observed at laser energies of 1.96 and 1.99 eV, due to the LO-phonon emission induced exciton formation of holes (lh) with an excess energy of 25 meV and electrons at their subband minimum.

duced within our experimental error of ± 1 ps and (ii) the rise times decreased with a factor of 2 due to an increased electron-exciton and exciton-exciton scattering rate. As expected, we find that the amplitude of the oscillations decreases since at high carrier densities the carrier distribution is already smeared out due to carrier-carrier scattering before the phonon cascade is completed.

For wider quantum wells with more than one bound state we observed an expected [20] increase of the luminescence rise times from 30 ps (26 Å) to 80 ps (90 Å), but hardly any dependence of the exciton luminescence rise time on laser energy. For these wide wells the number of energy positions where carriers are created increases, which smears out the resonances. Furthermore, the carriers created in the highest subbands smear out in energy and momentum during the relaxation due to the intersubband scattering, which is about 1 order of magnitude slower than intraband scattering [26].

In conclusion we have observed oscillations in the exciton luminescence rise times as a function of laser energy. The origin of these oscillations is attributed to the LO-phonon-assisted exciton formation, a process which is dominant whenever the sum of the excess energies of the electrons and holes amounts to 25 meV with one of the participating particles at $k=0$. Furthermore, we have demonstrated that our model is consistent with experiments on *n*-doped samples, which show an additional minimum in the rise time. Finally the amplitude of the oscillations decreases with increasing excitation density as a result of the enhanced carrier-carrier scattering.

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