Dynamics of exciton formation and relaxation in GaAs quantum wells

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We show that excitons form with a time constant $\tau \leq 20$ ps following the creation of electron-hole pairs by subpicosecond optical excitation. The excitons are initially formed in large-wave-vector states. At low temperatures, these *nonthermal* excitons relax in ≈ 400 ps to the $K \approx 0$ states, which couple directly to light by interaction with other excitons and acoustic phonons. This leads to a slow rise of exciton luminescence and an unusual dependence of this rise time on temperature, excitation density, and excitation energy.

The optical properties of excitons in quantum wells have been the subject of intense research in recent years for fundamental[1] and applied[2] reasons. Many fundamental properties of excitons have been investigated by using ultrafast laser spectroscopy. For example, the dynamics of exciton ionization[3] and the ac Stark effect of excitons induced by an intense optical field[4,5] have been investigated using excite-and-probe spectroscopy. The homogeneous linewidth of excitons, and the influence of temperature and various collisions on this linewidth, have been investigated by four-wave-mixing experiments.[6] The recombination dynamics of excitons has been investigated by time-resolved luminescence spectroscopy.[7]

In spite of this intense interest in excitons, one important aspect of excitons, the dynamics of formation of bound states of excitons following photoexcitation of electron-hole pairs, has remained essentially unexplored. The recent results of Kusano *et al.*[8] are largely dominated by *extrinsic* effects. The complex process of formation of intrinsic excitons has been identified as an important problem since the introduction of the concept of excitons in solids, but has not been addressed either experimentally or theoretically. Photoexcited electron and hole (either from a geminate or a nongeminate pair) can form an exciton by interaction with acoustic and optical phonons, and also by carrier-carrier interactions. The relaxation of photoexcited pairs within the bands proceeds simultaneously with the exciton formation process. Also, the excitons can be initially formed in the ground as well as excited states, and in the singlet as well as triplet states (corresponding to the orthohydrogen and parahydrogen states). Furthermore, the excitons are very likely created with a large total momentum wave vector K, corresponding to the center-of-mass motion of excitons in the quantum-well planes. The relaxation of these nonthermal excitons into the singlet $K=0$ state (the only state that can directly couple to the photons) must also be considered. It is clear that an understanding of these aspects of excitons is a fundamental importance in the physics of elementary excitons in solids.

We present in this article the first results on the dynamics of exciton formation and relaxation, which provide insight into many facets of exciton physics that have not been considered before. All results presented in this letter deal with *intrinsic* excitons. We probed exciton formation dynamics in GaAs quantum wells as a function of temperature, excitation density, and excitation photon energy, using luminescence spectroscopy with time resolution better than any previous study. We find that the formation time of $K=0$ singlet excitons, τ_f, defined as the time required for the exciton luminescence to reach a maximum, is surprisingly long (400 ps at low excitation densities), and decreases slowly above a certain excitation density. τ_f is nearly independent of the excitation photon energy in the range investigated (10–100 meV above the band gap); in particular, there are no resonances at the light-hole energy and for excess energy equal to the LO-phonon energy. Finally, τ_f shows a dramatic decrease from ≈ 400 to <20 ps as the sample temperature is increased from 5 to 60 K. Our time resolution allows us to show for the first time that excitons are created *rapidly* ($\tau \leq 20$ ps) in large K and higher excited states, and that the long τ_f results from a slow relaxation into the $K=0$ state. We further show that the distribution of excitons is *nonthermal*. We emphasize that these are *intrinsic* effects and the general results are relevant to all excitonic systems in semiconductors.

Two high-quality $GaAs/Al_{1-x}Ga_xAs$ multiple-quantum-well (MQW) samples were investigated; for sample A, the MQW was in the i region of a p-i-n structure and had 50 periods, a well thickness of 50 Å and Al concentration of 0.35 in the barriers. Sample B had 50 periods, a well width of 80 Å, and an Al concentration of 0.3 in the barriers. Both samples gave nearly identical results, except that the helium temperature decay time for excitons was 500 ps for sample B and 300 ps for sample A. All the data presented in this paper are for sample B unless indicated otherwise.

The inset in Fig. 1 shows the cw luminescence and photoluminescence excitation spectra of sample B at 10 K. The luminescence spectrum shows two narrow lines caused approximately by a one-monolayer (1-ML) fluctuation in the well thickness. The excitation spectrum shows split heavy- and light-hole excitons as well as the corresponding band-to-band features. The complete overlap between the luminescence and heavy-hole excitons (i.e., the absence of Stokes shift), the narrowness of

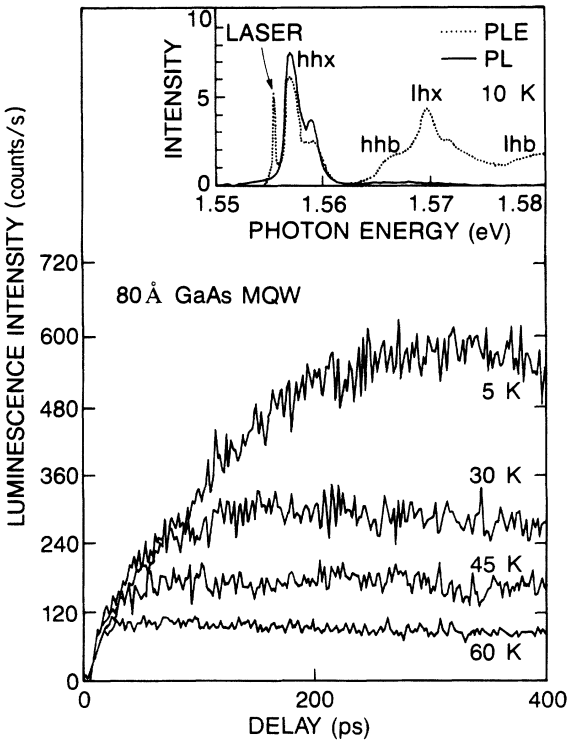

FIG. 1. Time evolution of exciton luminescence intensity at the spectral peak (1.557 eV) for various temperatures. The system time resolution is <1 ps. The inset shows the cw luminescence and luminescence excitation (PLE) spectra at 10 K. hhx and lhx are the heavy-hole and light-hole excitons and hhb and lhb are the corresponding band-to-band transitions.

the lines (0.65 meV at 2 K), the observation of several well-defined features in the spectra, and the absence of impurity-related luminescence even at very low excitation intensity attest to the extremely high quality of the sample. Sample A showed similar results. This inset demonstrates that all results reported here relate to the *intrinsic* properties of excitons. This should be contrasted with the results of Kusano *et al.*,[8] which are dominated by extrinsic effects such as localization kinetics.

Time-resolved measurements were performed using luminescence up-conversion technique[9] using an LD751 dye laser, synchronously pumped with the second harmonic of a compressed, mode-locked YAG laser (YAG denotes yttrium aluminum garnet). The laser was tunable between 720 and 800 nm and the pulsewidth was ≤ 0.7 ps. Luminescence time evolutions were obtained with a spectrometer centered at the exciton line; the spectrometer resolution of 2 meV encompassed both the sharp features observed in the cw luminescence (inset of Fig. 1). Time-resolved spectra showed no shift in the exciton peak position with time, once again demonstrating the intrinsic nature of the results presented here. Most of the data were obtained at an excitation density of 1×10^{10} cm^{-2} per well to avoid any complications arising from screening of excitons and band-gap renormalization effects.

Figure 1 shows the time evolution of exciton luminescence at various temperatures. τ_f, defined as the time required for the exciton luminescence to reach the maximum intensity, is nearly 300 ps at 10 K and decreases dramatically with increase in the lattice temperature. The initial increase in the exciton luminescence intensity is the same at all temperatures but the peak is reached much sooner and the maximum intensity is much smaller at higher temperatures. τ_f is ≤ 20 ps at 60 K.

Figure 2 shows the time evolution of exciton luminescence for three different excitation densities. The density range of 2×10^9 to 5×10^{10} cm^{-2} per well was investigated in this study. With increasing excitation density, τ_f increases and then saturates at ≈ 400 ps for excitation density $<5\times10^9$ cm^{-2} per well. We have investigated the dependence of τ_f on the excitation photon energy in the range 17–100 meV above the excitation energy and specifically investigated the excitation at the light-hole exciton energy and also at one LO phonon above the exciton energy. The data show that, within the experimental uncertainty, the time evolution of exciton luminescence is *independent* of the excitation energy in this range. Representative time evolution curves for sample A, with larger separation between the heavy- and the light-hole excitons, are shown in the inset of Fig. 2.

We begin the analysis of the data by recalling that only those excitons within the homogeneous linewidth (Δ) of $K=0$ can directly couple to radiation.[10] We visualize that the relaxation of photoexcited electron-hole pairs into $K=0$ excitons may be affected by three processes:

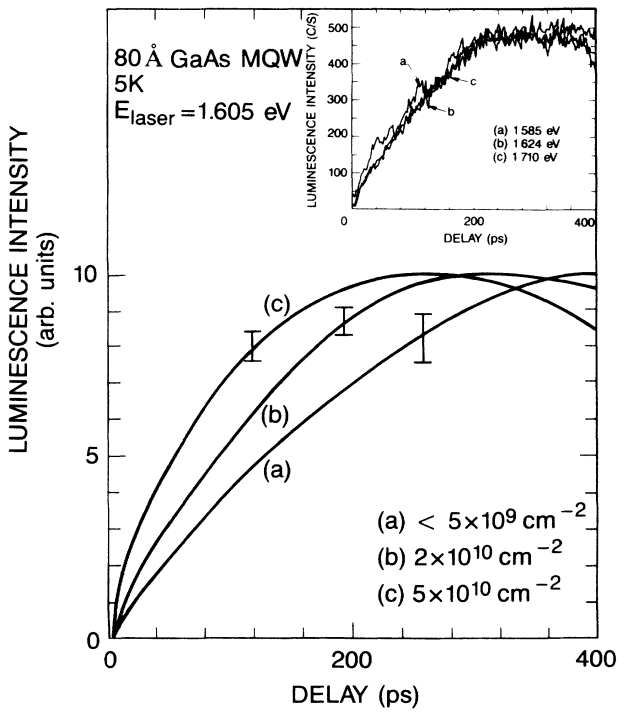

FIG. 2. Time evolution of exciton luminescence at the spectra peak (1.557 eV) for three different excitation densities. The inset shows time evolution of exciton luminescence at the spectral peak (1.568 eV) of sample A for three different excitation photon energies.

(1) initial thermalization and the subsequent cooling of the photoexcited pairs, (2) emission of acoustic or optical phonons by an electron-hole pair leading to the formation of excitons, preferentially at large L vectors, and (3) relaxation of the large K excitons into the $K=0$ excitons.[11,12]

To investigate which process dominates, we determine the relative density of electron-hole pairs and excitons as a function of time by analyzing the spectral shape of the luminescence, which is a superposition of the $K=0$ exciton luminescence and the electron-hole–pair luminescence. The emission from the excited states ($n>1$) of the exciton is negligible compared to that from the ground state because the oscillator strength decreases as $(n-\frac{1}{2})^{-3}$. In the spectra in Fig. 3(a), the spectral peak corresponds to the exciton luminescence while the high-energy tail corresponds to the band-to-band luminescence. We find that, even at the shortest time delays (≤ 1 ps), the excitonic luminescence dominates the free-carrier luminescence. However, this does not imply that the density of excitons is higher than the density of electron-hole pairs because the ratio of intensities depends not only on the densities and the relative oscillator strengths (or absorption coefficients), but also on the distribution functions of the electron-hole pairs and the excitons. Since the distribution functions are not known, the observed intensity ratios cannot be used to determine the ratio of densities accurately.

We monitor the electron-hole pair density by measuring the temporal evolution of the homogeneous linewidth of excitons, which is strongly influenced by the presence of electron-hole–pair density.[6,13] We consider that the exciton line shape at a given time [Fig. 3(a)] is a convolution of the Gaussian line shape observed at long times [full width at half maximum (FWHM) of 7 meV] with a Lorentzian whose width is adjusted to give a good fit to the low-energy side of the spectrum. This procedure allows us to determine the width of the Lorentzian within ± 0.5 meV. The electron-hole luminescence spectrum is then determined by subtracting this exciton line shape from the measured spectrum. This procedure is illustrated in Fig. 3(b) for the spectrum at 6.7 ps. The FWHM of the Lorentzian determined in this manner (inset, Fig. 3) shows a rapid initial reduction followed by a more gradual decrease. Since exciton-electron collisions[14] are about an order of magnitude more efficient in broadening excitons than exciton-exciton collisions,[6] the rapid initial reduction is attributed to the decay of electron-hole pairs into excitons and the more gradual decrease at later times to relaxation and decay of excitons. This analysis shows that the density of electron-hole pairs decreases with a time constant $\tau \leq 20$ ps, considerably shorter than the measured τ_f. This conclusion is also supported by the rapid decay of the integrated electron-hole–pair luminescence intensity and the cooling of the electron-hole temperature with time determined from the high-energy tail of electron-hole luminescence. We therefore conclude that the electron-hole pairs form excitons with a time constant *less* than 20 ps. Formation of excitons from electron-hole pairs occurs primarily by emission of acoustic phonons. Energy and momentum conservation require that excitons initially form in large K states (near 6 meV). This highly nonthermal initial exciton distribution does not couple to light in spite of the large FWHM of excitons at short times. The primary cause of the long rise time of exciton luminescence is the slow relaxation of large K excitons to $K=0$ excitons.

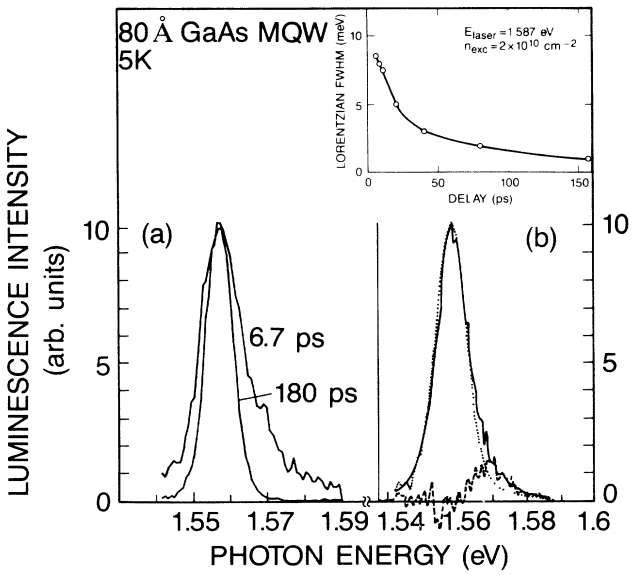

FIG. 3. (a) Time-resolved luminescence spectra at two different delays. (b) Line-shape analysis of the observed spectrum. The solid curve is experimental, the dotted curve is a Gaussian-Lorentzian fit, and the dashed curve is 2 times the difference between the two, representing the band-to-band recombination. The inset shows the time dependence of FWHM of the Lorentzian from such fits.

The data presented in Figs. 1 and 2 strongly support this conclusion. To understand the temperature dependence, we note that the measured intensity is proportional to R, the rate of radiative recombination of excitons where $R=n_{x0}/\tau_r$, n_{x0} is the density of excitons within Δ of $K=0$ and τ_r is the exciton radiative recombination lifetime, determined by the exciton oscillator strength. At low temperatures (10 K), the thermalized exciton distribution is sharply peaked near $K=0$, and it takes a long time for the initial distribution of large K excitons to relax towards the thermalized distribution. This explains the long rise for the exciton luminescence at 10 K. Since n_{x0} is large for a sharply peaked distribution near $K=0$, the maximum luminescence intensity is large. On the other hand, at higher temperatures (e.g., 60 K) the thermalized exciton distribution is spread out and the initial distribution of large K excitons approaches this distribution quite rapidly. At such temperatures, ionization of excitons by acoustic-phonon absorption also contributes to the dynamics. In this case the rise of luminescence is rapid and may in fact be limited by the capture of electron-hole pairs into excitons. Also, n_{x0} is relatively small because only a small fraction of all excitons are near $K=0$; therefore, the peak luminescence intensity is considerably smaller than for 10 K. The data at intermediate temperatures can be qualitatively explained by

similar arguments.

The relaxation of large K excitons to those that can radiate takes place via exciton-exciton collisions and exciton–acoustic-phonon collisions. The decrease of τ_f with increasing density (Fig. 2) for density greater than 4×10^9 cm^{-2} per well leads to the qualitative that exciton-exciton collisions are important above this density while exciton–acoustic-phonon collisions dominate below this density. Assuming collisions between hard disks, the exciton-exciton collision time is inversely proportional to the exciton density and velocity (and hence $\sqrt{T}$). At the above density and $T=10$ K, this time is estimated to be 30 ps. We conclude that the effective exciton–acoustic-phonon collision time for exciton relaxation is about 30 ps. While exciton–acoustic-phonon interactions relevant to exciton linewidth have been investigated,[15–17] relaxation of excitons within the exciton branch remains to be explored, and no comparison with calculations is possible at this time. It is also interesting to note that in the presence of exciton-exciton collisions, the exciton distribution remains *nonthermal* and continues to relax towards the lowest-energy exciton state until all excitons recombine. The observed density dependence also implies a nonthermal distribution of excitons.

We note that polariton effects are not expected for an isolated quantum well for light propagating perpendicular to the quantum-well plane. Furthermore, polariton effects in bulk GaAs are also weak because the splitting between longitudinal and transverse excitons is only 0.08 meV. Therefore the results reported here are not related to the polariton bottleneck effects observed in bulk II-VI semiconductors.

The observation (Fig. 2, inset) that the formation time is *independent* of the initial excess energy of the photoexcited electron-hole pairs strongly supports the earlier conclusion that the relaxation within the exciton branch is the primary cause of the slow rise of the exciton luminescence. It also supports the idea that the exciton distribution is nonthermal. Perhaps a more interesting aspect of the data is that no resonance is observed when the photon energy coincides with the light-hole exciton or when the photon energy is exactly one LO-phonon energy larger than the exciton. Since an electron-hole pair can emit a phonon in about 100 fs, why is the formation time not shortened? We believe that one possible answer is that since the homogeneous linewidth is considerably smaller than the inhomogeneous linewidth, only a small fraction of the absorbed photons can directly create $K=0$ excitons. This will considerably dilute the effect of the resonance. Our results are consistent with the recent report that LO-phonon resonance in the excitation spectra is observable only when tunneling of electrons out of the quantum well is extremely rapid.

In conclusion, we have presented the first investigation of the dynamics of the exciton formation and relaxation in a semiconductor. We have shown that excitons form rapidly ($\tau\leq20$ ps) in states with large K which do not couple to light directly, and that this formation time is independent of the excitation energy. We have demonstrated that the surprisingly long rise time for the exciton luminescence results from the slow relaxation of these nonthermal excitons within the exciton branch, mediated by exciton-exciton and exciton–acoustic-phonon interactions. These interaction times are determined from our studies. We also emphasize that our results provide new insights into $K\neq0$ excitons, for which there is no suitable theory. Finally, the results presented depend only on the intrinsic properties of excitons and have general validity.

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[10]The wave vector of the incident exciting photon is perpendicular and that of the emitted photon is nearly perpendicular to the quantum-well plane. Therefore, the electron-hole pairs are created with the total in-plane mometum $K=0$ and only $K=0$ excitons emit light.

[11]For a photon propagating normal to the quantum-well plane, the relative wave vector k of the photoexcited pair is the same as k_e and will have an uncertainty related to the spectral width of the excitation pulse. From the uncertainty principle, we estimate that the spatial extent of the electron-hole wave packet varies from about 200 to 600 Å for the excitation energies used in our experiment. If there are frequent long-range Coulomb collisions, then the excitons will be created from the geminate pair and there will be no triplet excitons. For less-frequent collisions, a rapidly moving electron will go away from its geminate hole, excitons can be formed from nongeminate pairs, and triplet states may play an important role.

[12]An electron-hole pair can form an exciton without losing any energy; however, such an exciton can autoionize just as easily. We therefore consider only those excitons whose kinetic energy is less than the exciton binding energy.

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