Exciton formation rates in GaAs/$Al_xGa_{1-x}As$ quantum wells

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A theoretical investigation of the exciton formation process from free carriers in a single GaAs/$Al_{1-x}Ga_xAs$ quantum well is presented. The mechanism for the formation processes is provided by the interaction of the electrons and holes with phonons. The contributions from both the acoustic and optical phonons are considered. The relative importance of exciton creation from a thermalized electron-hole gas (bimolecular formation) versus a direct creation of excitons from the crystal ground state through the electromagnetic field (geminate formation) is discussed. The formation process is analyzed for different densities and temperature of the free carriers, and for different intensities of the exciting optical pump. The results compare reasonably well with recent experiments. [S0163-1829(97)03303-1]

In a nonresonant photoluminescence (PL) experiment, the optical pump excites free-carrier pairs, which eventually relax to form excitons. The investigation of exciton formation is therefore relevant for the understanding of some features of PL in the bulk as well as quantum wells (QW's). During the last few years, several experiments have been carried out in order to clarify the exciton formation process both in bulk and QW semiconductor systems. Most experiments are based on time-resolved techniques, which include time-resolved PL,[1,2] time resolved Raman spectroscopy,[3] and nonlinear cross-correlated PL.[4,5] Zhu *et al.*[6] have also considered the continuous-wave PL in QW's in the presence of a magnetic field. However, the results of time-resolved experiments do not allow a clear identification of the exciton formation rate, because in the dynamics it is difficult to distinguish between this and other relaxation processes. In this report we propose a theoretical approach to the problem of exciton formation in PL. To the authors' knowledge, only a partial theoretical investigation of these rates including only acoustic phonons is available.[7] Recently, a Monte Carlo approach to the problem of relaxation of coupled free carriers and exciton in bulk systems has been proposed.[8]

Here we provide an exhaustive discussion of all the possible contributions to the rate of exciton formation, and calculate the different characteristic rates of this process. These results should help to better understand the role of the exciton formation rate in the dynamics of time-resolved PL experiments. When a photon from the pump pulse is absorbed by the sample, an electron hole pair is created. The electron and the hole in this pair are strongly correlated because they have opposite momentum, but this correlation is rapidly lost through scattering with the other carriers and with phonons. These scattering mechanisms provide also a fast thermalization within the free carriers, and are responsible for the transitions from the free carriers to excitons. Consequently we distinguish between two different cases: direct formation of the exciton from the initially created electron hole pair before correlation is lost (geminate formation) and indirect formation from thermalized electron-hole pairs (bimolecular formation). The rate of geminate formation is proportional to the created pairs density, and is therefore linear in the pulse intensity. The bimolecular formation rate is proportional to the probability that the thermalized electrons and holes interact, and is therefore proportional to the product of electron and hole densities. This is valid for a nondegenerate Fermi gas, as is the case in most experiments. The geminate and bimolecular exciton formation rates in a single GaAs/$Al_{1-x}Ga_xAs$ QW with $x=0.4$ are presented here in a detailed calculation. We considered all the possible relaxation mechanisms in the system, and found that in the range of carrier densities of 10^8-10^{11} cm^{-2}, the carrier-phonon interaction dominates in the exciton formation process. We include in the calculation the contribution from the acoustic phonons due to the deformation potential interaction, and the contribution from the optical phonons through the Fröhlich interaction.

The dynamics of the exciton formation is considered in the framework of the Boltzmann equation for a system containing free electrons, free holes, and excitons. The residual Coulomb interaction between the free carriers is neglected, which is justified in the range of temperatures and densities considered. In this paper we focus on the exciton formation mechanism and do not discuss the relaxation of the three species within their respective bands, the electron-hole scattering, and radiative recombination. We denote the occupation numbers for electrons, holes, and excitons by $f_e(\mathbf{k}_e), f_h(\mathbf{k}_h)$, and $f_{\mathrm{ex}}(\mathbf{k}_{\mathrm{ex}})$, respectively, where $\mathbf{k}_e$, $\mathbf{k}_h$, and $\mathbf{k}_{\mathrm{ex}}$ are the in-plane wave vector for electrons, holes, and excitons. For the bimolecular formation, the scattering terms in the Boltzmann equation process read

$$\left(\frac{df_e(\mathbf{k}_e)}{dt}\right)_{\mathrm{form}} = -\sum_{\mathbf{k}_{\mathrm{ex}},\mathbf{k}_h} F_{\mathbf{k}_e,\mathbf{k}_h\to\mathbf{k}_{\mathrm{ex}}} f_h(\mathbf{k}_h) f_e(\mathbf{k}_e), \quad (1)$$

where the $F_{\mathbf{k}_e,\mathbf{k}_h\to\mathbf{k}_{\mathrm{ex}}}$ represents the the probability per unit time for a free electron with wave vector $\mathbf{k}_e$ to bind to a free hole with wave vector $\mathbf{k}_h$ giving rise to an exciton with a wave vector $\mathbf{k}_{\mathrm{ex}}=\mathbf{k}_e+\mathbf{k}_h$. An equation analogous to Eq. (1)

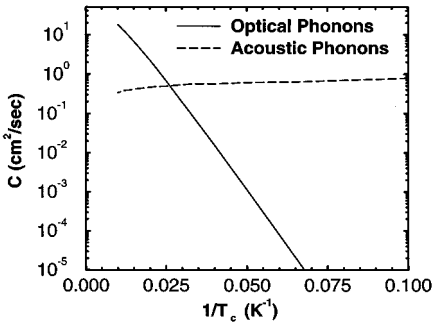

FIG. 1. The exciton formation coefficient C as a function of the carrier temperature T_c, at a fixed lattice temperature $T_l=10$ K. Other parameters are given in the text.

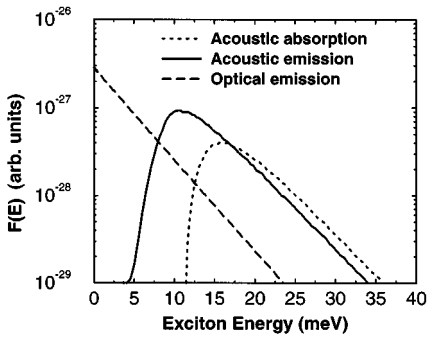

FIG. 2. The formed exciton distribution $F(E)$, as a function of the exciton energy E, for optical and acoustic phonon processes. The free carrier temperature is 50 K.

holds also for the hole and exciton distribution functions. The formation rate F is evaluated using the Fermi golden rule. For the exciton we used a two-dimensional hydrogenic-like wave function and plane waves for the free carriers. For the parameters of the exciton wave function and the deformation potentials we refer to Ref. 10. During the evolution of the system, the free electrons and holes are thermalized at the same temperature T_c. This thermalization is produced by fast carrier-carrier scattering. Typical thermalization times in GaAs QW are found to be of the order $\sim$ 100 fs for carrier density above 10^{10} cm^{-2},[11] which are faster than all the other scattering times, in particular when compared to the exciton formation time. In the scattering term of Eq. (1), we use for $f_e(\mathbf{k}_e)$, and $f_h(\mathbf{k}_h)$ equilibrium Boltzmann distribution function at T_c. Consequently, by summing Eq. (1) over $\mathbf{k}_e$, we obtain an adiabatic equation for the evolution of the electronic density $n_e=[\Sigma_{\mathbf{k}_e} f_e(\mathbf{k}_e)]/S$:

$$\frac{dn_e}{dt}=-\sum_{\mathbf{k}_{\rm ex}} F(\mathbf{k}_{\rm ex})n_e n_h \equiv C n_e n_h . \tag{2}$$

The coefficient C is the bimolecular formation coefficient, which depends on both T_c and the lattice temperature T_l through the interaction with the phonons, and $F(\mathbf{k}_{\rm ex})$ is defined as

$$F(\mathbf{k}_{\rm ex})=\left(\frac{2\pi\hbar^2}{k_B T_c}\right)^2 \frac{1}{m_e m_h S} \times \sum_{\mathbf{k}_e,\mathbf{k}_h} F_{\mathbf{k}_e,\mathbf{k}_h\to\mathbf{k}_{\rm ex}} e^{-[E_e(\mathbf{k}_e)+E_h(\mathbf{k}_h)/k_B T_c]}.$$

The carrier temperature T_c immediatly after the pump pulse depends on the excess energy $\Delta E=E_{\rm pump}-E_{\rm gap}$, and is defined by $k_B T_c=\Delta E/2$. However, in the dynamics, T_c approaches the lattice temperature T_l through emission of phonons showing two characteristic times: a short one associated to the emission of optical phonons and a longer one associated to acoustic phonons. The optical phonon dominates for T_c above 50 K. We do not consider the evolution of the temperature T_c, which may be experimentally measured,[9] and we evaluate the formation coefficient C as a function of T_c and T_l. In Fig. 1 we report C as a function of $1/T_c$ for a fixed lattice temperature $T_l=10$ K, for a GaAs QW of 50 Å. The two contributions from the acoustic and optical phonons are shown separately, the optical phonon dominates for temperatures larger than 40 K. The Arrhenius plot in Fig. 1 shows an activation energy of 25 meV for the optical phonon process. This energy corresponds to the difference between the optical phonon energy ($\hbar\omega_{\rm LO}=$ 36 meV) and the exciton binding energy ($E_b=$ 10 meV). We conclude that the formation process is therefore mainly governed by optical phonon emissions. For the acoustic phonon process, we do not find any activation energy. In fact, both the emission and absorption of acoustic phonons contribute to exciton formation. The difference between the two processes appears clearly in their dependence on the lattice temperature T_l. The optical phonon contribution does not depend on T_l, whereas the acoustic phonon one increases linearly with T_l. The qualitative difference between exciton formation by the optical and acoustic phonons is also clearly shown in Fig. 2, where $F(E)=F(k_{\rm ex}=\sqrt{2ME/\hbar^2})$ is plotted as a function of the energy E of the created exciton. The thermalized carrier distribution relaxes to form excitons through emission of optical phonons. Since optical phonons are dispersionless, this transition is vertical in energy and produces excitons at the free-carrier temperature T_c. The energies exchanged by acoustic phonon emission and absorption are of the order of 1 meV, and the excitons are created through quasielastic transitions. Therefore, excitons from this process are formed close to the bandedge, at an energy E close to E_b.

Comparison of these results with experiments is not straightforward. Strobel *et al.*[4] find $C=6\pm 2$ cm^2/s in an experiment where $\Delta E=112$ meV and $T_l=8$ K. Since ΔE is much larger than the optical phonon emission threshold, we expect that T_c will rapidly decrease in a few ps as assessed by experiment.[2,9] The measure of C is performed on a time scale of $\sim$10 ps, which is of the same order of the time variation of T_c. Therefore from the experiment one obtains a time-averaged value for C. We find the same formation rate C at $T_c=$ 60 K, which can be considered as the average temperature during the formation process. However, in order to perform a closer comparison, the carrier temperature evolution also has to be measured. Robart *et al.*[2] find C larger than 14 cm^2/s, using $\Delta E=$ 25 meV, and $T_l=$ 1.7 K. In this last experiment, the carrier temperature has been measured, and has been found to decrease from 60 K after 10 ps from the excitation, to 10 K after 100 ps. The dynamics at short times is therefore also needed in order to make a quantitative

comparison with the present calculations. Recent confirmation of the order of magnitude of C has been also established by Colocci and Emiliani.[12]

The geminate formation process can be described as follows: excitation of an electron hole pair by a photon, propagation of the created pair through the crystal with total momentum close to zero, and finally conversion of the correlated pair into the exciton via interaction with phonons. The rate of creation is therefore proportional to the density of pump photons. We stress the fact that the electron-hole pair has total zero momentum, whereas in the bimolecular case the total momentum of the electron and hole is not constrained. In fact we notice from Eq. (1) that a given electron interacts with all the populated hole states to form the exciton. In the geminate process, two interactions coexist: the carrier-phonon interaction V_p and the carrier-photon interaction V_γ. The formation rate of an exciton with a given center-of-mass wave vector $\mathbf{q}$, produced by a photon with energy $\hbar\omega$, is calculated by second-order perturbation theory. The emission of optical phonons gives the dominant contribution to this formation rate, and has a threshold at $\hbar\omega = E_{\rm gap} - \hbar\omega_{\rm LO} - E_b$. The contribution from the acoustic phonons in the geminate formation is four orders of magnitude smaller, according to our evaluation. The formation rate for optical phonons reads

$$R(\hbar\omega \rightarrow \mathbf{q}) = \frac{2\pi}{\hbar}\sum_{q_z}\left|\sum_{\mathbf{k}_r}\frac{\langle 0|V_\gamma|\mathbf{k}_r\rangle\sqrt{(n_p+1)}\langle \mathbf{k}_r|V_p|\mathbf{q}\rangle}{\hbar\omega - E_{\rm gap} - \hbar^2|\mathbf{k}_r|^2/2\mu + i\Gamma}\right|^2 \times \delta\left(\hbar\omega - \hbar\omega_{\rm LO} - E_{\rm gap} + E_{\rm bin} - \frac{\hbar^2|\mathbf{q}|^2}{2M_{\rm exc}}\right). \tag{3}$$

Here $|0\rangle$ is ground state, $|\mathbf{k}_r\rangle$ represents an electron-hole state with relative momentum $\mathbf{k}_r$, and $|\mathbf{q}\rangle$ is the exciton state. All the intermediate states have zero center-of-mass momentum and we sum only on the relative momentum $\mathbf{k}_r$ of the electron-hole pair. Furthermore, the in-plane wave-vector conservation implies that the created exciton and the emitted optical phonon have opposite momentum. The factor n_p is the Bose occupation number for optical phonons, which is negligible in the range of lattice temperature T_L considered. The sum over q_z of the final phonon is due to the breaking of the translational symmetry in the growth direction. The energy Γ gives the broadening of the intermediate states, and is assumed to be energy independent. The broadening is produced by the same process that thermalizes the carriers, as explained above. We have investigated the effect of this broadening on the total rate of the process. We have found that for Γ larger than $\simeq$ 10 meV, the geminate rate decreases rapidly. This is related to the loss of correlation in the intermediate pair for Γ larger than the exciton binding energy E_b. In the following, we assume Γ to be smaller than 10 meV. The total rate of formation is then obtained from Eq. 3 by summing over all the final exciton states, and can be written as a function of the pump power P and the pump frequency ω as

$$\left(\frac{dn_{\rm ex}}{dt}\right)_{\rm gem} = \alpha_{\rm gem}(\hbar\omega)P(\hbar\omega). \tag{4}$$

We obtain for a QW of 50 Å a coefficient $\alpha = 1.4\times 10^{15}(\mathrm{W\,s})^{-1}$, for an excitation energy of 40 meV above the band edge. We have found that $(dn_{\rm ex}/dt)$ is slowly dependent on the excitation energy above the energy threshold. For a 1-ps pump pulse and 1-KW/cm^2 power, about 10^6 cm^{-2} excitons are formed by the geminate process. In order to quantify the importance of the geminate formation process, we compare it with the total formation rate of free carriers for the same excitation conditions, and obtain

$$\frac{(dn_{\rm ex}/dt)_{\rm gem}}{(dn_e/dt)_{\rm carr}} = \frac{\alpha_{\rm gem}(\hbar\omega)P(\hbar\omega)}{\alpha_{\rm carr}(\hbar\omega)P(\hbar\omega)} \simeq 0.05. \tag{5}$$

Here the total free-carrier rate $\alpha_{\rm carr}(\hbar\omega)P$ is related to the free-carrier absorption, and is energy independent for excitation above the band edge.

The characteristics of the two processes are different. The geminate formation exists only during the pump pulse, whereas the bimolecular formation takes place also at later times, and depletes the carrier population during the exciton formation. Due to the quadratic dependence of the rate on the density of free carriers, the temporal evolution of n_e is not given by a simple exponential. However, a characteristic formation time for $n_e = n_h$ may be defined as $(Cn_e)^{-1}$. Typical values for this time are in the range of 1–20 ps for n_c of 10^{10} cm^{-2}. For later times, the dynamics becomes more complex because of exciton and carrier temperature relaxation processes, and of the dissociation of the excitons. In order to compare the geminate and bimolecular exciton formation rates, a given experimental condition of pump power P, pump duration Δt, carrier temperature T_c, and lattice temperature T_l has to be considered. As discussed above, the carrier temperature T_c is not simply related to the excess excitation energy ΔE. Here, the excess energy is always above the geminate generation threshold. Therefore, we consider a typical range of possible carrier temperatures T_c from 50 to 100 K, which may result after the excitation.[9,2] The geminate formation rate is written in terms of the carrier density n_e created by the pulse by approximating $(dn_e/dt) \sim n_e/\Delta t$ and using Eq. (5) to obtain

$$\left(\frac{dn_{\rm ex}}{dt}\right)_{\rm gem} \simeq \frac{\alpha_{\rm gem}}{\alpha_{\rm carr}}\frac{n_c}{\Delta t F_S}, \tag{6}$$

where F_S is a form factor due to the shape of the laser pulse. We consider a Gaussian pulse of full width at half maximum equal to Δt, and we average the geminate rate over the temporal width of the pulse. The correspondig F_S is 1.426. In Fig. 3 we report both the geminate and bimolecular formation rates at short times as a function of n_e, for $\Delta t = 1$ ps and $T_c =$ 50 and 100 K, and $T_l = 10$ K. Clearly, at large carrier density, the bimolecular formation rate dominates over the geminate rate. The crossing of the two rates depends on both Δt and the carrier temperature T_c. For the chosen parameters, the crossover corresponds to $n_c = 10^9$ cm^{-2}. The crossover density decreases with increasing Δt as shown in Eq. (6). Measurements by Amand *et al.*[13] on the relative weight of the two processes confirm that for carrier density n_e above 10^9 cm^{-2}, the geminate process is negligible.

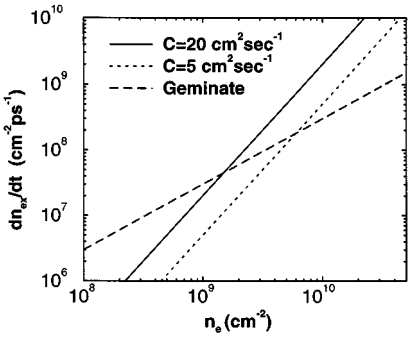

FIG. 3. Geminate and bimolecular exciton formation rates as functions of the carrier density n_e. Other parameters are given in the text.

Other formation processes assisted by carrier-carrier scattering (Auger processes) and scattering by disorder and impurities take place in any available sample. The first process has a cubic dependence on n_e, and should have a small influence for densities lower than 10^{11} cm^{-2}, as shown experimentally.[4] Both a direct contribution and a correction to the calculated phonon-assisted rates exist due to the interface disorder and impurities. Clearly, correction to the optical phonon-assisted rates is negligible, due to the large energy exchanged in the process compared to the typical disorder broadenings. Acoustic phonon-assisted processes may be slightly modified by the presence of disorder, especially when the broadenings are larger than the typical exchanged energies of 1 meV. For these large inhomogeneous broadenings, we expect also that the disorder-assisted formation process becomes relevant, and comparable to the acoustic phonon-assisted process.

In conclusion, we have calculated the phonon-assisted exciton formation rate for both the bimolecular and geminate case. We have considered both the optical and acoustic phonons. In the bimolecular formation, we have found a substantial difference between the two contributions. This difference is related to the large energy exchanged in optical phonon scattering (36 meV), compared to the energy exchanged in acoustic phonon scattering (of the order of ~ 1 meV). Therefore, the distribution of excitons reflects the thermalized free-carrier distribution in the first case, while excitons close to the band edge are created in the second one. We have also found that for carrier temperature T_c larger than 40 K the optical phonon contribution to the bimolecular formation dominates over the acoustic phonon one. In the geminate formation, the direct creation from the correlated electron-hole pairs has been calculated. The process is linear in the pump intensity. It follows that for low pump intensities, the geminate formation dominates over the bimolecular formation for short times. The role of carrier-carrier scattering, interface roughness, and impurities in the formation process has also been discussed.

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