Optical- and acoustical-phonon-assisted hopping of localized excitons in CdTe/ZnTe quantum wells

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Interaction with both acoustical as well as optical phonons contributes to the relaxation of excitons in tail states of coherently strained CdTe/ZnTe quantum wells. The contribution of acoustical phonons is most important in the thinnest well of 1.8 monolayers. Hopping down, which involves the emission of acoustic phonons, leads to a redshift of the luminescence band of about 10 meV within the first 200 ps after excitation. A comparison of the experimental data with results of a quantitative theory allows us to evaluate the concentration of localized states involved in the relaxation process.

I. INTRODUCTION

The relaxation of localized carriers or excitons within disorder-induced electronic tail states in materials like semiconductor alloys, amorphous or heavily-doped semiconductors, or quantum-well structures typically involves the interaction with acoustical phonons.[1-7] The involvement of optical phonons in the relaxation of localized excitons is, however, quite unusual owing to the large phonon energy with respect to the localization depth and the weak coupling in nonpolar materials. Recently, optical phonons were found to contribute efficiently to the initial relaxation of free excitons into localized states[8] and, in the case of thin wells, to the migration of excitons between localized sites[9] in II-VI quantum wells.

Both acoustical as well as optical phonons contribute to the relaxation of excitons localized at interface fluctuations in coherently strained CdTe/ZnTe single quantum wells. In this paper we want to discuss the relative contributions of both types of phonons to this relaxation and to identify the corresponding migration mechanisms. We find an efficient hopping relaxation of the excitons involving the emission of acoustic phonons in the thinnest well of 1.8-monolayer thickness, the temporal development of which can be modeled by a quantitative theory. The most efficient relaxation mechanism in all coherently strained wells is the hopping via the emission of optical phonons. A thermalization of the exciton distribution cannot be achieved by the latter process but requires the thermal population of acoustical-phonon modes.

II. EXPERIMENT

The samples are thin single quantum wells of CdTe between thick (600 Å) ZnTe barriers. The average thicknesses of the wells under investigation are 1.8, 2.5,

and 4.3 monolayers, which is below the critical thickness for the onset of strain relaxation by misfit dislocations in this high-lattice-mismatch system.[10] The CdTe wells are thus coherently strained and strain fluctuations in the well resulting from thickness variations can be neglected. A localization of optically generated excitons will thus solely be a result of the interface roughness. The samples are mounted to a cold finger in a He-flow cryostat where any lattice temperature between 5 and 300 K can be achieved.

The quantum wells are optically excited by pulses from a synchronously pumped dye laser [5 ps full width at half maximum (FWHM)]. The luminescence is analyzed by a combination of a synchroscan streak camera connected to the exit of a 0.32-m spectrometer. The two-dimensional readout of the streak tube simultaneously provides a spectrally and temporally resolved luminescence signal with resolutions of 1.1 meV and 12 ps, respectively.

III. RESULTS AND DISCUSSION

A. Hopping assisted by acoustical phonons

The role of acoustical phonons in comparison to optical phonons is most important in the thinnest well of 1.8 monolayers (ML). This finding is evident from contrasting the luminescence dynamics in different wells. The temporal developments of the luminescence signals in the 1.8- and 4.3-ML wells are displayed in Figs. 1 and 2, respectively. The excitation energy in each case is closely below the so-called mobility edge (ME), which separates excitons with extended wave functions from ones with spatially restricted wave functions.[1,11] The energy of the mobility edge can be determined from the decay of luminescence resonant to the laser energy. Details of these measurements are given elsewhere.[9,12] Three luminescence bands are observed for the 1.8-ML quan-
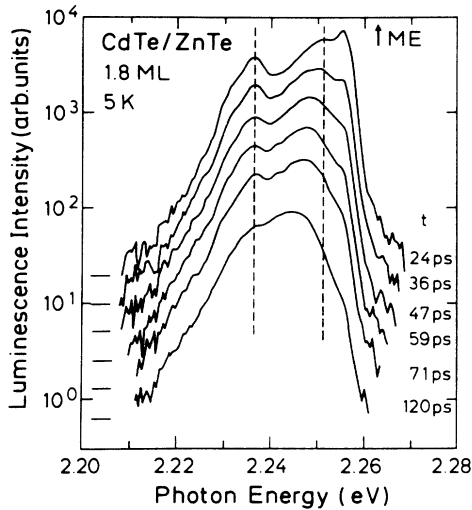
FIG. 1. Temporal evolution of the luminescence in a 1.8-ML CdTe/ZnTe quantum well. The spectra are not normalized but shifted with respect to each other for clarity.

tum well (see Fig. 1): (1) a narrow luminescence band resonant to the laser energy at $\hbar\omega_L = 2.255$ eV, (2) a redshifting band, which actually emerges from the signal at $\hbar\omega_L$, and (3) a phonon sideband to the energy of the laser (around 2.237 eV) shifted by energies in the range of the optical phonons in the CdTe/ZnTe system. In contrast, the redshifting band (2) is missing in the thicker quantum wells (see Fig. 2) while features (1) and (3) are still present.

Several replicas of the laser energy are observed in the thicker wells as a result of the increase of spectral extent of the range of localized states with well thickness.[12] In all three quantum wells under investigation we find a substructure in the replicas at 19 and 24 meV below the laser energy, which can be assigned to an interface mode and a LO mode in strained CdTe (see also Fig. 5).[13] The dynamics of the replica in the 4.3- and 2.5-ML wells reflect an efficient migration of the excitons between localized
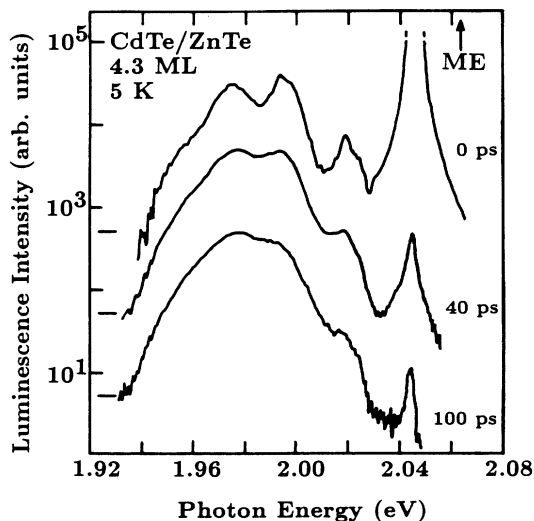
sites assisted by optical phonons,[9] in contrast to the strong localization found in freestanding CdTe/ZnTe superlattices.[14] Only one replica is found in the 1.8-ML well. Its temporal evolution shows an onset which is the integral over the temporal shape of the laser pulse. The initial relaxation into the localized states via emission of optical phonons is thus much faster than our time resolution, even when several phonons have to be emitted and when the excitation is far above the mobility edge. These findings are similar to what has been reported for the case of $Cd_xZn_{1-x}Te/ZnTe$ quantum wells.[8]

The presence of the redshifting luminescence band (see Fig. 1) in the 1.8-ML well indicates a relaxation mechanism which is unimportant in the thicker wells. This band emerges as a shoulder from the signal due to scattered light from the laser (not shown). A significant redshift of about 10 meV occurs within the first 200 ps. The luminescence band finally merges into the optical-phonon replica to form at long delay time a featureless luminescence line with 15 meV FWHM and a line shape similar to the emission observed under cw excitation. No further redshift occurs for the optical-phonon replica, i.e., excitons deep in the tail states (see Fig. 1). This mechanism is also not found in the thicker quantum wells (see Fig. 2), where most of the excitons relax deep into the tail states on a 10-ps time scale.

In Fig. 3, we plot the shift $\Delta E = E_{ME} - E_{max}$ of the maximum of the redshifting luminescence in the 1.8-ML well with respect to the mobility edge at 2.263 eV as a function of time t. It is reasonable to expect that at low temperatures the redshift of the whole carrier distribution is caused by the hopping relaxation of excitons through localized states, which arise here from the roughnesses of the quantum-well interfaces.[15] Moreover, at such low temperatures only hops down in energy should be considered. Indeed, a change of the lattice temperature from 5 to 20 K does not change the dependence $\Delta E(t)$ significantly, which means that the temperature does not influence the relaxation process.

An analogous theory for the hopping relaxation of

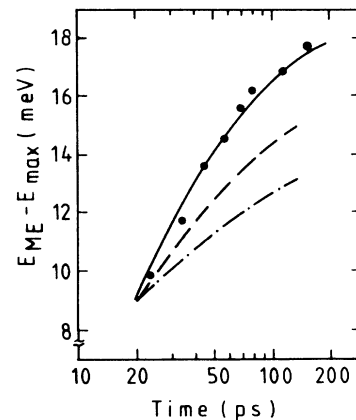FIG. 2. Temporal evolution of the luminescence in a 4.3-ML CdTe/ZnTe quantum well.

FIG. 3. Temporal shift of the maximum intensity of the redshifting luminescence with respect to the mobility edge. Dots: experimental points; solid line: fit using the DOS in Fig. 4 with $N_0\alpha^2 \simeq 1.6$, $\nu_0 \simeq 0.2$ ps^{-1}; dashed line: $N_0\alpha^2 \simeq 0.6$, $\nu_0 \simeq 0.47$ ps^{-1}; dashed-dotted line: $N_0\alpha^2 \simeq 0.2$, $\nu_0 \simeq 2.5$ ps^{-1}.

electrons through localized states has been developed for some particular shapes $g(\varepsilon)$, e.g., purely exponential[3] or Gaussian,[16] of the density of states (DOS) as a function of the quasiparticle energy with respect to the mobility edge. For our CdTe/ZnTe quantum wells, however, some specific form has been deduced (see Fig. 4). The DOS for localized excitons in the 1.8-ML well has a maximum at about 8 meV below the mobility edge. A nearly exponential tail follows starting at about 20 meV below ME. This shape of the DOS can be demonstrated from a deconvolution of the time-integrated luminescence at a lattice temperature of 100 K. At this temperature conditions close to thermalization are reached which is proven by comparison to spectra at higher lattice temperatures (e.g., 150 K). The luminescence line shape is then given by the DOS times the Boltzmann factor. The thermal gap variation between 5 and 100 K was taken into account by a shift of the whole DOS by 14 meV. The shape of the DOS is also reflected in the luminescence signal as a function of laser photon energy (Fig. 5), as will be discussed below. We develop here a quantitative theory of the hopping relaxation of excitons in this particular DOS.

Excitons lose their energy by hopping to lower states. The time of the hop $\tau(r)$ depends exponentially on the distance r between the involved localized states,

$$\tau(r) = v_0^{-1} \exp(2r/\alpha) , \qquad (1)$$

where v_0 is the attempt-to-escape frequency, typically of the order of 1 ps^{-1}, and α is the localization radius of excitons.

In order to develop a quantitative theory of hopping relaxation, it is not sufficient to know the normalized DOS $g(\varepsilon)$. Also, the total interface concentration N_0 of the localized states involved in the relaxation process is needed, as well as the values of the length α and the frequency v_0. We consider these quantities as free parameters and will find them from a comparison with the experimental data.

At a current observation time t, the excitons have relaxed within the tail states via a certain number of hops. The average hop time τ of each of these hops is consider-
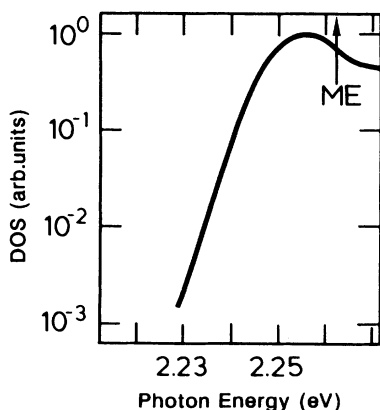
ably shorter than t. At time t, the excitons form a distribution around an average energy ΔE below the mobility edge corresponding to the spectral maximum of the luminescence. At this time, the hop time for the next hops starting from this particular energy position within the tail states will be much larger than t. The energy ΔE of the packet is thus related to the time t by the equality

$$\tau(r(\Delta E)) \approx t , \qquad (2)$$

where

$$[r(\Delta E)]^{-1} = \sqrt{\pi N(\Delta E)} \qquad (3)$$

is the average distance between localized states with energies deeper than ΔE and having an interface concentration

$$N(\Delta E) = N_0 \int_{\Delta E}^{\infty} g(\varepsilon) d\varepsilon \qquad (4)$$

with $g(\varepsilon)$ being normalized such that

$$\int_0^{\infty} g(\varepsilon) d\varepsilon = 1 . \qquad (5)$$

Using Eqs. (1)–(4) we obtain a relation between the redshift ΔE and the corresponding time t,

$$\int_{\Delta E}^{\infty} g(\varepsilon) d\varepsilon = \frac{4/\pi}{(N_0 \alpha^2) \ln^2(v_0 t)} . \qquad (6)$$

This equation is solved numerically for various values of the parameters $N_0 \alpha^2$ and v_0, and a set of dependencies ΔE vs $\ln(t)$ is obtained. The best fit to the experimental results at 5 K is given by the values $N_0 \alpha^2 \simeq 1.6$, $v_0 \simeq 0.2$ ps^{-1}. It appears that a relatively small change of the parameters $N_0 \alpha^2$ and v_0 modifies the dependence $\Delta E(t)$ considerably (see Fig. 3) so that the parameters $N_0 \alpha^2$ and v_0 can be found accurately from a comparison of the theoretical curves with the experimental data if the shape $g(\varepsilon)$ is known.

In order to demonstrate the sensitivity of the theoretical results to the particular shape of the DOS, we have carried out this calculation also with the DOS

FIG. 4. The density of states (DOS) in the localized regime of the 1.8-ML well as extracted from time-integrated luminescence.
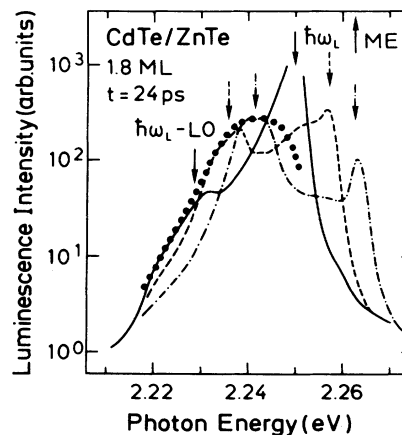
FIG. 5. Luminescence spectra at a delay time of 24 ps for three different excitation energies $\hbar\omega_L$ as indicated by the arrows. The phonon replicas are marked correspondingly. The dots represent the low-energy part of a luminescence spectrum taken at long delay time (400 ps).

$$g(\varepsilon) = [c(\beta)/\varepsilon_0]\exp[-(\varepsilon/\varepsilon_0)^\beta] \qquad (7)$$

with various β and ε_0 and the normalization factor of $c(\beta)$ to satisfy Eq. (5). Among the dependencies $\Delta E(t)$ we obtained, the best fit to the experimental data is given by the values $\beta = 1$, $\varepsilon_0 \simeq 6.2$ meV, $N_0\alpha^2 = 1.8$, and $v_0 \simeq 0.3$ ps^{-1}. We note that the values of the parameters $N_0\alpha^2$ and v_0 are not too far from those found for the DOS of Fig. 4. This allows us to conclude that the experimental dependence $\Delta E(t)$ in fact determines the found values of the parameters v_0 and $N_0\alpha^2$.

The extracted parameter $N_0\alpha^2$ reflects a rather large density of localized states, where an exciton at the energy of the mobility edge finds at $t = 0$ an average number of $\pi N_0\alpha^2 \approx 4.5$ localized states within a disk of radius α. This is consistent with the conclusions drawn from the excitonic luminescence linewidth, namely, that the interface fluctuations occur on a length scale smaller than the spatial extent of the exciton.[9] The extremely large modulation of the free-exciton energy on the order of 100 meV for a 1-ML thickness change results in a localization radius α probably much smaller than the excitonic Bohr radius. The interface roughness has, then, a length scale of few atoms in this narrow well.

At this point a comment on the interpretation of picosecond temporal shifts of luminescence bands is necessary. Besides the rather strong relaxation as described above, a minor redshift of 2 meV is found for replicas and the resonant luminescence in the 4.3-ML quantum well. The temporal evolution of this small shift is found to follow a logarithmic law in time.[9] On first sight, the latter behavior might suggest a multiple-trapping relaxation of the excitons, for which such a temporal shift of the exciton distribution is predicted.[7] Multiple trapping, however, requires an activation of the excitons across the mobility edge by absorption of acoustic phonons. Such an activation can be excluded at low lattice temperature especially for excitons deep in the tail states. The observed small temporal shift can be attributed to relaxation into local energy minima via hopping down involving the emission of acoustic phonons. Close inspection of the data and theory in Fig. 3 for excitons in the vicinity of ME actually demonstrates that the hopping mechanism leads to a nearly single-logarithmic behavior for the first 100 ps. We want to point out here, that a classification into hopping and multiple trapping according to single- or double-logarithmic temporal shifts of the exciton distribution, respectively, as proposed by theory,[3,7] only applies for certain conditions. The hopping theory, for one, is only valid for strictly exponential shapes of the density of localized states [as in Eq. (7) with $\beta = 1$]. Such a DOS is definitely not found for the excitons in the vicinity of the mobility edge and is only approximately given for the excitons deep in the tail states of our quantum wells. But more importantly, single- and double-logarithmic temporal shifts are not easily distinguishable on a time scale of 100 ps. The identification of the relaxation mechanism has to be based on a full numerical analysis as demonstrated above. The same arguments hold for the picosecond relaxation of carriers in amorphous semiconductors.[17,18]

B. Optical- versus acoustical-phonon-assisted relaxation

Emission of both optical and acoustic phonons contributes to the relaxation of the localized excitons in the thinnest quantum well. The relative strength of these processes is strongly dependent on the energy of the excitation laser. This is reflected in the spectra of Fig. 5 which were recorded shortly after the laser pulse under exactly identical conditions except for $\hbar\omega_L$. Excitation at $\hbar\omega_L = 2.25$ eV (solid arrow) leads to a rather weak replica but an extremely strong resonant luminescence (truncated line), the broad low-energy tail of which originates from excitons relaxing via the emission of acoustic phonons. Increasing of $\hbar\omega_L$ (dashed and dash-dotted arrows) results in a strong increase of the replicas while the resonant luminescence as well as the redshifting band weaken significantly. This reflects directly the increasing density of final states for the optical-phonon assisted process. Consistently, the line shape of the luminescence at very long delay times, i.e., close to thermalized conditions as described above (see dots in Fig. 5), forms an envelope over the low-energy tails of the replica luminescence.

The relative intensity of the two luminescence bands demonstrates that the relaxation via the emission of optical phonons is much more important than the acoustical phonon-assisted hopping mechanism. The intensity of the replica is about equal to or even larger than the intensity of the redshifting band, although the density of states is significantly smaller for the former in comparison to the latter (see Fig. 4). We already noted that the hopping of excitons in the vicinity of ME is not found in the thicker wells. Here, the density of localized states has a much larger extension to lower energies.[12] As a result the relaxation to deep states via optical-phonon emission is so efficient that almost no excitons close to the mobility edge are left after the excitation pulse (see Fig 2). We have not yet included a comparison of the hopping via both types of phonons into the theory, but the relative weakness of the exciton-acoustic-phonon interaction in states deep in the tail at low temperature is directly evident from the temporal development of the luminescence signal in all three quantum wells. Sharp replica structures persist in the thicker quantum wells for several hundred picoseconds, and no significant broadening of the resonant luminescence line is found within its lifetimes.[9] Further, the line shape of the low-energy tail of the luminescence is continuously changing within the observation time. These findings demonstrate that the thermalization of the excitons during their lifetime is impossible at low temperature when the dominant relaxation process is associated with the emission of optical phonons. This is a direct consequence of the fact that dispersion curves of optical phonons are very flat so that almost the same energy is always emitted or absorbed.

This situation, however, change completely when the lattice temperature is elevated. Even deep states become increasingly affected by inelastic processes involving the rising number of acoustic phonons. This tendency is demonstrated in Fig. 6. Here, we show spectra taken at fixed delay time and fixed excess energy of the laser with respect to the maximum of the luminescence at long de-
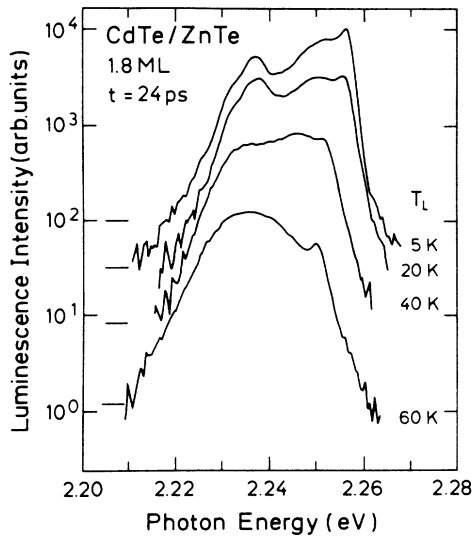
FIG. 6. Luminescence spectra at fixed delay for various lattice temperatures T. The spectra are normalized and shifted for clarity.

lay, i.e., the temperature-dependent shift of the band gap is compensated for. The pronounced structures related to the different relaxation processes get increasingly washed out even at very short delay times. Due to the increasing population of acoustic-phonon modes, the thermalization process speeds up such that the excitons have relaxed to deep tail states right after the picosecond excitation and no redshifting band is observed for temperatures higher than 60 K. A comparison of spectra at short and long delay and also with cw spectra[10] shows

that a thermalized distribution of the excitons is not completely reached until a lattice temperature of at least 100 K.

IV. CONCLUSIONS

In conclusion, interaction with both optical and acoustical phonons contributes to the relaxation of excitons localized at interface fluctuations in coherently strained CdTe/ZnTe quantum wells. Hopping down involving the emission of optical phonons dominates the relaxation process. A significant contribution of interaction with acoustical phonons to the relaxation process is found in the thinnest well. This contribution is well described by a quantitative theory of hopping relaxation through localized tail states. The relative efficiency of relaxation via optical or acoustic phonons is shown to depend strongly on the density of final states for the relaxation. The temporal development of the luminescence spectra shows that the optical phonons are inadequate for thermalization of the exciton distribution owing to their large energy. Thermalization via acoustic phonons is extremely inefficient at low-temperatures and is only achieved within the exciton lifetime at temperatures of 100 K or higher.

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