Exciton dynamics in disordered quantum wells: Localized and delocalized regimes

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The electronic states in a disordered solid may be localized or delocalized, depending on their energy and the disorder potential. By examining exciton dynamics with transient four-wave mixing experiments we show that low-energy excitons in CdTe/(Cd,Mg)Te quantum wells are localized, while higher-energy excitons are not. In the delocalized regime the excitonic dephasing rate decreases with increasing energy, a theoretically predicted, but experimentally unreported result.

Semiconductor mixed crystals and semiconductor nanostructures very often exhibit disorder, which results in a modification of their electrical and optical properties in comparison to an ideally ordered system. One manifestation of disorder is the localization of carriers, which may arise due to either, classically, confinement in a potential minimum or, quantum mechanically, due to a destructive interference between forward and backward imperfection scattered components of the wave function (Anderson localization). The later was first described by Anderson[1] to explain the disappearance of the conductivity at zero temperature in a disordered system, despite there being no energy gap between the occupied and unoccupied states, i.e., the Fermi level lies in a band. Banyai[2] suggested that in either case the localized and delocalized states are separated by a mobility edge at an energy E_m, a concept that was later extended by Mott.[3,4] These approaches consider the ratio between the width of the energetic distribution of localized states and the strength of the intersite coupling. E_m is the energy above which the coupling between sites becomes sufficiently strong such that the particle wave functions become extended.

Studying the effects of disorder on excitons in semiconductors is particularly interesting because excitons are neutral particles and, therefore, overcome the difficulties in the interpretation of transport data using charged particles, which are typically obscured by the presence of interaction induced localization mediated by the interparticle Coulomb forces.[5] Furthermore, the strong optical activity of excitons in direct gap semiconductors makes them accessible to optical spectroscopy. In a quantum well (QW) heterostructure the confinement increases the exciton binding energy and oscillator strength. In an ideal QW the excitons would be localized in the growth direction and extended in the plane of the well. In a real quantum well, however, nonideal growth conditions result in well width fluctuations. As a consequence of this disorder the local exciton energy varies, leading to exciton localization in the plane of the well and inhomogeneous broadening of the absorption line.[6] Experimental studies suggest that in GaAs/(Al,Ga)As QW's the transition energy between localized and delocalized excitonic states is near the absorption line center.[7]

We present here optical studies of low-temperature exciton dynamics in semiconductor QW's using transient four-wave mixing (TFWM). TFWM allows a direct determination of exciton dephasing times (i.e., inverse homogeneous linewidth) even in the presence of inhomogeneous broadening.[8] An incident laser pulse excites a macroscopic polarization in the sample, which decays with time as the phases of the individual microscopic oscillators (excitons) get out of step with each other. Dephasing is this loss of the initial macroscopic polarization. Of course, inhomogeneous broadening causes a decay of the macroscopic polarization, but this merely reflects the distribution of excitons energies and is not of interest here. The decay of the polarization at a given energy, which TFWM is sensitive to, is of interest as it reflects the stochastic interaction of the excitons with their environment. Because localization of the exciton wave function influences its interaction with the environment by modifying its spatial extent and mobility, the dephasing time is very sensitive to exciton localization. The particular microscopic interactions between the exciton and its environment that result in dephasing include scattering with phonons and other carriers and disorder. For reviews of the use of TFWM to study disorder induced dynamics in quantum wells see Ref. 9. Previous TFWM studies observed that localized excitons dephase more slowly than delocalized ones[10] and that in the localized regime the excitonic dephasing rate increases with increasing energy,[7] in agreement with theoretical predictions.[11]

The energetic region above E_m has not, to our knowledge, previously been experimentally investigated. Although the theoretical predictions indicate that the excitonic dephasing rate in the presence of disorder due to width fluctuations should *decrease* with increasing energy in this region, experimental difficulties have hindered confirmation. In particular, it is necessary to avoid excitation of energetically higher-lying exciton and continuum states, and hence a material with a large exciton binding energy is advantageous, such as wide gap II-VI materials.[12] In II-VI CdTe/(Cd,Mg)Te structures we are

able to measure the energy dependence of the dephasing both above and below E_m and observe that the dephasing rate increases with increasing energy below E_m and decreases with increasing energy above it. The presence of a mobility edge is verified by the observation of the characteristic temperature dependence of the dephasing rates below E_m for the localized excitons and that for delocalized excitons above E_m.

We investigated $CdTe/Cd_{0.56}Mg_{0.44}Te$ multiple-quantum-well structures (75 periods) with nominally 75 Å thick well and barrier layers. The structures were grown by molecular-beam epitaxy on (100)-oriented CdTe;[13] transmission electron microscopy and x-ray diffraction show them to have high structural quality[14] (for growth details see Ref. 15). Figure 1(a) shows the photoluminescence excitation (PLE) spectrum, measured at 6 K. At about 1.656 eV and 1.6595 eV the split resonance of the $n = 1$ heavy-hole exciton (hh) is observed. The splitting arises from large-scale interface islands[16] and the 3.5 meV energy spacing between the peaks is consistent with one monolayer well width fluctuations. The samples are not homogeneous across the entire structure.[14,16] Thus, by moving the laser spot over the sample, the exciton energy and the shape of the hh-exciton resonance changes, showing either a double or a single peak.[16,17] In Fig. 1(a), we show a PLE spectrum with a split hh exciton resonance, which is also observed in the spectral dependence of the TFWM signal. The peak at 1.679 eV is the light-hole exciton. The relative efficiency of the TFWM is indicated by solid circles in Fig. 1(a). The TFWM signal has its maximum within the high-energy peak of the PLE spectrum. We focus on the spectral dependence of the TFWM within this high-energy peak, corresponding to a certain average well width. Within the low-energy peak the TFWM shows qualitatively similar results, however, the signal strength is low and the specific features are less distinct.

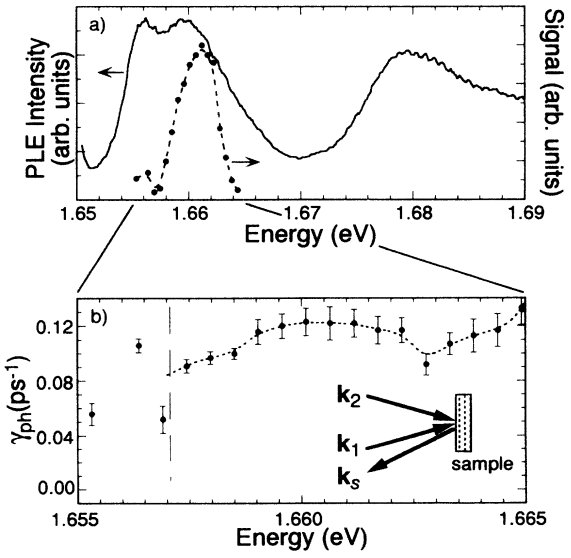

FIG. 1. (a) Low-temperature PLE spectrum of the 75 Å thick $CdTe/Cd_{0.56}Mg_{0.44}Te$ MQW. The filled circles are the relative efficiency of the TFWM signal. The dashed line is a guide to the eye. (b) Dephasing rate (dots) as a function of photon energy (the short dashed line is a guide to the eye). Note the different energy scales in (a) and (b). Inset in (b) is the experimental configuration. We focus on the energies above 1.659 eV, shown by the vertical dashed line.

The excitonic dephasing times T_2 were obtained by TFWM experiments in the two-pulse configuration in a reflected geometry.[18] In this configuration [see inset Fig. 1(b)] two succesive laser pulses with wave vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ and parallel polarization excite the sample at times $t = 0$ and $t = \tau$, respectively. The interaction of these two laser pulses creates a nonlinear third-order polarization that gives rise to coherent radiation, emitted in the direction $2\mathbf{k}_2 - \mathbf{k}_1$. In the reflected geometry, the reflection of this signal about the plane of the sample is observed. The exponential decay of this nonlinear signal as a function of the delay time τ is directly due to the decay of the initially created coherent, macroscopic polarization and hence yields the dephasing time T_2, i.e., the exciton scattering time.[8,19] Additionally, three-pulse experiments were used to measure the spectral relaxation time and to determine the nature of the broadening of the optical transition. In this second configuration three pulses, time delayed with respect to each other, excite the sample. We refer to the time delay between pulses 1 and 2 as τ_{21} while pulses 2 and 3 are seperated by τ_{23}. The three-pulse nonlinear signal is detected in the reflection of the direction $\mathbf{k}_3 + \mathbf{k}_2 - \mathbf{k}_1$.

The TFWM measurements were performed using two different laser systems, a synchronously pumped mode-locked dye laser with a saturable absorber, generating 1.5–2 ps pulses and a self-mode-locked Ti:sapphire laser producing 110-fs pulses. The dye-laser system exhibits a relatively narrow pulse spectrum and, therefore, allows experiments with high spectral resolution. The Ti:sapphire laser was used for the dephasing measurements at temperatures above 35 K, where the dephasing times become too short to be resolved by the dye-laser system. If not stated, the results were obtained with the dye-laser system. The measurements were performed in a temperature variable helium flow cryostat.

We employed a three-pulse experiment to determine the nature of the broadening of the optical transition. In the case of inhomogeneous broadening the three-pulse TFWM signal for finite τ_{23} as a function of τ_{21} is asymmetric (independent of the third pulse), while for homogeneous broadening it is symmetric.[20] In the structures studied here, the three-pulse TFWM signal is asymmetric as a function of τ_{21} and hence the hh resonance is inhomogeneously broadened.

Figure 1(b) shows the dephasing rates, $\gamma_{ph} = 1/T_2$, as a function of the exciting photon energy at 9 K and constant excitation intensity. In the following we focus on energies above 1.657 eV [vertical dashed line in Fig. 1(b)]. Between this energy and the PLE line center (~1.660 eV) γ_{ph} increases with increasing energy. Above 1.660 eV γ_{ph} decreases, reaches its minimum 2.8 meV above the line center and increases again at higher energies.[21]

The nonmonotonic spectral dependence of γ_{ph} can be understood on the basis of theoretical work by Takagahara[11] where the dephasing of localized and de-

localized excitons in quantum well structures was considered. Takagahara predicts that localized excitons dephase by phonon-assisted migration between localized sites (often designated phonon-assisted tunneling), or by thermal activation from localized to extended states. In the delocalized regime, the excitons dephase due to acoustic-phonon-mediated intraband scattering or by elastic scattering at the rough interface. The calculations based on these mechanisms showed that in the localized regime the dephasing rate increases with increasing exciton energy, whereas in the delocalized regime γ_{ph} decreases with the exciton energy, corresponding to our observation for energies between $\sim$ 1.660 and 1.663 eV.

The theoretical analysis that provides these predictions for the energetic dependence of the excitonic dephasing rate also predicts the temperature dependence. Consequently, by examining the temperature dependence, we are able to verify that an analysis based on a division into localized and delocalized regimes is plausible. In Fig. 2 we plot γ_{ph} as a function of temperature for these regimes. In both cases γ_{ph} increases with increasing temperature. However, it increases more rapidly for the delocalized as compared to the localized excitons. Below 50 K, a linear temperature dependence is expected for extended excitons with wave vectors $K \simeq 0$,[18]

$$\gamma_{ph} = \gamma_{ph}^{0} + (\gamma_{LA}/2\hbar)T, \tag{1}$$

where γ_{LA} is the coupling constant for exciton-acoustic phonon scattering, and γ_{ph}^{0} accounts for the interaction of the excitons with crystal imperfections and other excitons. This formula is for acoustic-phonon absorption, i.e., anti-Stokes scattering. Hence, it depends on the number of phonons (given by the Bose-Einstein statistics), which at low temperatures and for a given wave vector increases linearly with temperature. From a linear fit to the experimental data measured at 1.662 eV we obtain a γ_{LA} of 5 μeV/K.

For localized excitons a non-linear temperature dependence is expected, however at low temperatures the nonlinearity is very weak and difficult to distinguish from a linear temperature dependence. Consequently, it is necessary to employ a much larger temperature variation in the localized regime, in turn necessitating the use of the short pulses generated by the Ti:sapphire laser, due to the large dephasing rates at high temperatures. The results are shown in the inset of Fig. 2. The laser was tuned below the hh-exciton resonance in order to emphasize the localized excitons.[22] In the localized regime thermal activation and phonon-assisted tunneling contribute to the dephasing. Additionally, at temperatures above $\sim$ 50 K scattering with longitudinal optical phonons contributes. The solid line in the inset of Fig. 2 is a fit to

$$\gamma_{ph} = \gamma_0 + A\exp(-E_{act}/k_BT) + \gamma_{LO}[\exp(\hbar\omega_{LO}/k_BT) - 1]^{-1} \tag{2}$$

where γ_0 is the zero-temperature dephasing rate. The second term accounts for the activated behavior, E_{act} is the activation energy and A gives a measure of the strength for this process. The third term accounts for the scattering by longitudinal-optical phonons, γ_{LO} is the coupling strength for the exciton-LO phonon interaction and $\hbar\omega_{LO}$ is the energy of the LO-phonon in CdTe. The fit to our experimental results yields an activation energy of 4.6 meV.[23] This corresponds well to the energy difference between the peak energy of the exciting laser pulse used in the experiment and the center of the PLE line, confirming the interpretation in terms of a mobility edge. In this formula there is no contribution due to phonon-assisted tunneling, which has a temperature dependence $\exp(BT^{\alpha})$.[11] For theoretically expected values of B the temperature dependence of this term is quite weak and, consequently, it is difficult to clearly isolate a contribution due to phonon-assisted tunneling in the presence of the relatively strong thermal activation contribution. Phonon–assisted tunneling does still contribute at zero temperature and hence may be one of the processes we have lumped into γ_0.

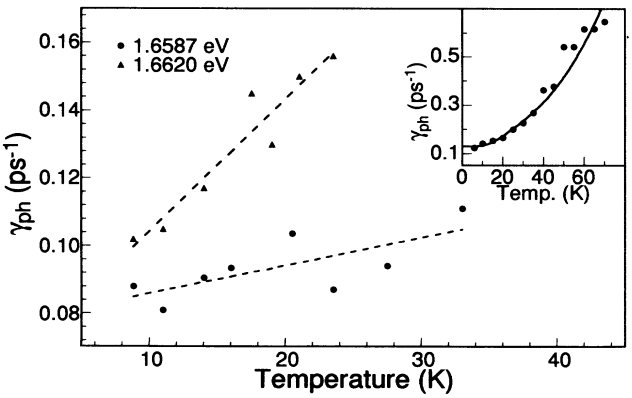

FIG. 2. Temperature dependence of the dephasing rate γ_{ph} for the localized (1.659 eV) and delocalized (1.662) excitons. The dashed lines are linear fits to the experimental data. The inset shows the temperature dependence for the localized excitons as measured with the 110-fs Ti-sapphire laser up to 70 K. The solid line is a fit to Eq. (2).

On the basis of these results we infer that, near the PLE line center, there clearly is a transition between localized and delocalized regimes. An abrubt mobility edge, however, is only expected at $T = 0$; at finite temperatures there is a continuous transition between the regimes. The increase of γ_{ph} with increasing energy in the localized regime is attributed to the increasing number of phonons with sufficient energy to activate the excitons above the mobility edge. The decrease of γ_{ph} in the delocalized regime is due to decreasing population of participating phonons with increasing energy. A decrease of the deformation potential and piezoelectric coupling, which determine the exciton-phonon interaction, is also predicted,[11] however, these effects depend on the particular material constants. Additionally, the elastic scattering of free excitons at the rough interface exhibits a K^{-2} dependence for the in-plane center of mass wave vector K of the free exciton, also resulting in a decrease of γ_{ph} with increasing energy. The observed increase of the dephasing rate with a further increase in the energy is due to multiphonon processes and intersubband scattering becoming important.

The theoretical treatment in Ref. 11 makes the simplifying assumption that above the transition region the exciton states can be classified by the in-plane center of mass wave vector K. Although this is not strictly correct,

because disorder will lead to a mixing of the excitonic eigenstates, a better treatment is currently not available. Actually, this mixing of eigenstates is a prerequisite for our optical experiments, since it also mixes the oscillator strength of the excitonic states, ensuring that exciton states away from $K \simeq 0$ are optically accessible.

One process that is not included in the theoretical analysis is the localization of initially delocalized excitons (trapping). Because this would represent an additional population relaxation channel for the delocalized exciton population, we measured the population relaxation time, T_1, in a three-pulse TFWM experiment, with ($t_{21} = 0$) and the diffracted signal is detected as a function of t_{23}. In this context, T_1 accounts for energy relaxation, recombination and spatial diffusion of the excitons. In our structures T_1 is on the order of 55 ps with no spectral dependence. Thus, the dephasing times given above are not related to relaxation of excitons from the delocalized to localized states.

In conclusion, we have performed transient four-wave-mixing experiments on $CdTe/Cd_{1-x}Mg_xTe$ multiple quantum wells. We observe a distinct spectral and temperature dependences of the dephasing rate in accordance with theoretical predictions for a disordered system with a transition from localized to delocalized states. We, therefore, conclude that a localized-delocalized transition takes place near the absorption line center. A complete theoretical description of excitonic dephasing above the mobility edge, including disorder has not been developed so far. We hope that our results will stimulate further theoretical effort in this direction.

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[22]The decay of the nonlinear signal in these experiments is multiexponential, since the broad spectrum of the Ti:sapphire laser (22 meV) excites the entire absorption line, and T_2 varies across the line, as shown in Fig. 1. However, the slowest component in the decay of the transients measured with the Ti:sapphire corresponds to the decay measured with the ps-dye laser system.

[23]For the fit, $\hbar\omega_{LO} = 21$ meV and $\gamma_{LO} = 13.4$ ps^{-1} were used. E_{act}, $\gamma_0 (= 0.132$ ps$^{-1})$, and $A (= 0.568$ ps$^{-1})$ were the fit parameters. γ_{LO} was obtained by measuring the FWHM of the PLE spectra between 1.6 and 270 K at a sample position where the resonance is not split (not shown here). At high temperatures homogeneous broadening due to LO-phonon scattering overcomes the inhomogeneous broadening, which dominates the linear spectrum at low temperatures. Hence a determination of γ_{LO} as a homogeneous broadening mechanism is possible; see, e.g., D. Lee, A.M. Johnson, J.E. Zucker, R.D. Feldman, and R.F. Austin, J. Appl. Phys. **69**, 6722 (1991).