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Hole delocalization in $CdTe/Cd_{1-x}Zn_xTe$ quantum wells

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We report on femtosecond pump-probe absorption measurements in $CdTe/Cd_{1-x}Zn_xTe$ quantum wells with an unusual distribution of band offset: almost all the band-gap difference between the two constituent materials is found as a conduction-band offset. We have observed a blueshift of the exciton energy due to hard-core repulsion between excitons and an intriguing redshift in the presence of free electron-hole pairs. We evaluate the redshift due to different mechanisms and conclude that the redshift observed is due to hole delocalization throughout the structure resulting from the very shallow valence-band potential wells.

Heterostructures made with II-VI materials are receiving increasing attention due to their large range of band gaps leading to applications, such as blue-green lasers.[1] On the other hand, they have also been the object of many fundamental studies because of their differences from the more common III-V heterostructures, such as larger exciton binding energies and unusual distribution of the band-gap difference between the conduction and valence band. The strained-layer $CdTe/Cd_{1-x}Zn_xTe$ system, in particular, is characterized by a very small valence-band offset in the absence of strain. The potential wells formed in the valence band are thus mainly due to the strain and, for small Zn concentrations, are shallow.[2] Therefore, this system exemplifies a remarkable configuration where electrons are well localized, while holes are only weakly localized and can be easily delocalized in the whole structure.

In this work, we investigate the effects of excitons and electron-hole pairs on the exciton energy in $CdTe/Cd_{1-x}Zn_xTe$ multiple quantum wells (MQW's) using femtosecond pump-probe absorption. The observed blueshifts of the exciton absorption line are attributed to short-range hard-core repulsion between excitons, while the more unusual redshifts observed are explained in terms of hole delocalization.

Several $CdTe/Cd_{1-x}Zn_xTe$ MQW's with similar parameters were used in this study. They were grown by molecular-beam epitaxy lattice-matched on (100) $Cd_{1-x}Zn_xTe$ substrates with Zn concentration about half that of the barrier.[3] Thus the CdTe and $Cd_{1-x}Zn_xTe$ layers experience strain of opposite sign. This gives rise to potential profiles localizing heavy holes (hh) in the CdTe layers (to be called wells) and light holes (lh) in the $Cd_{1-x}Zn_xTe$ layers (to be called barriers). Thus hh excitons are direct in real space while lh excitons are indirect.[2] A schematic band diagram of the sample 1 on which we will concentrate is shown in the inset of Fig. 1.[4] This sample consists of 20 periods of 170-Å CdTe wells and 254-Å $Cd_{1-x}Zn_xTe$ ($x=10.8\%$) barriers grown on a substrate with $x=5.8\%$. An interesting detail is that the confined hh and lh levels are at about the same energy within a few meV. Due to the larger exciton binding energy of the direct hh excitons, however, the structure is clearly type I (that is, the energetically lowest exciton transition is spatially direct) with the exciton energy (1.604 eV at 1.8 K) being 12 meV below that of lh excitons. Note that while the electron

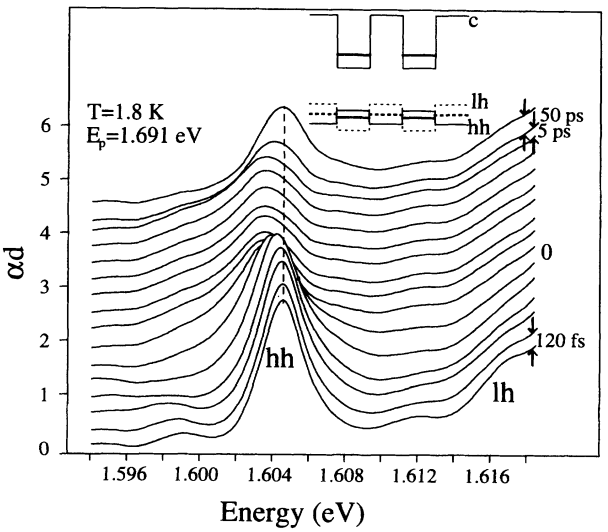

FIG. 1. Absorption spectra αd for nonresonant excitation $E_p=1.691$ eV and for several pump-probe delays. The zero of delay corresponds to pump-probe coincidence within approximately 300 fs. The temporal step is 120 fs except for the last two curves where it is 5 and 50 ps, respectively. The spectra have been displaced for clarity. The dashed vertical line shows the exciton peak position at negative delay times. The corresponding exciton peak shift is shown in curve (e) of Fig. 2. The inset shows a schematic band diagram of the sample.

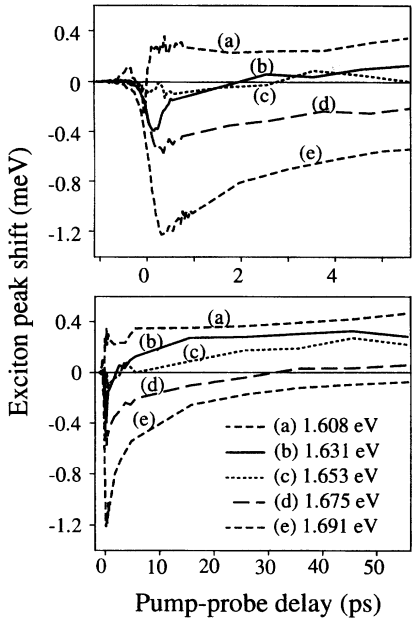

FIG. 2. The exciton peak shift as a function of pump-probe delay for several excitation energies. The upper part shows an enlargement of the lower part for small delay times. Positive (negative) values of the exciton shift correspond to a blueshift (redshift).

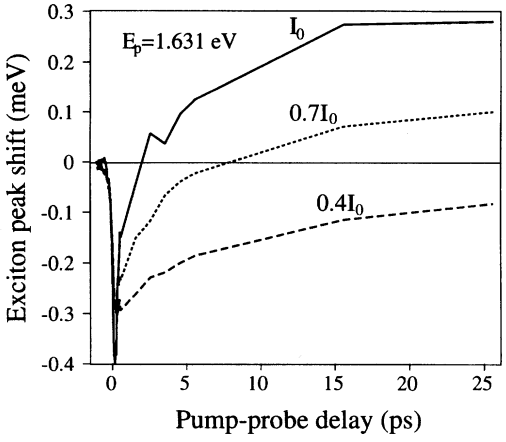

FIG. 3. The exciton peak shift as a function of pump-probe delay for three different excitation intensities at $E_p = 1.631$ eV. The curve for I_0 is the same as curve (b) in Fig. 2 and corresponds to an electron-hole pair density of approximately 4×10^{11} cm^{-2}.

level is situated 42 meV below the barrier, the hh levels lies only 11 meV below.

The pump-probe absorption setup is based on a colliding pulse mode-locked laser amplified at 6.5 kHz with the green line of a copper vapor laser.[5] Focusing of the amplified pulses on an ethylene glycol jet leads to the formation of a spectral continuum with a duration of about 100 fs, a portion of which is used as the probe pulse. The pump pulse is obtained after amplification of part of the continuum selected with an interference filter and has a bandwidth of about 17 meV and a duration of approximately 200 fs. Pump pulses with energy on the order of 0.1 nJ were focused down to 60 μm onto the sample from the quantum-well side to create carrier densities of 10^{11}–10^{12} cm^{-2}. The samples were placed in a liquid-He cryostat. We verified that the modifications of the pump spectrum due to self-phase modulation in the liquid He were negligible.

The absorption spectra for different pump-probe delays and for a pump energy of $E_p = 1.691$ eV are shown in Fig. 1. The absorption background at high energies is due to the substrate absorption. The hh and lh exciton lines are observed while the structure between the two is attributed to an excited state of center-of-mass confinement.[6] In the following we will concentrate on the influence of the pump on the hh exciton. The behavior of the lh exciton would also give valuable information but, unfortunately, it is almost completely screened at very early times (due to its small binding energy) and the evaluation of changes in energy is not possible. At positive delay times we observe a redshift of the hh exciton as well as a bleaching and broadening due to the presence of carriers created by the pump. The redshift reaches a maximum and then decreases with time while at much longer delay times (comparable to the exciton recombination time) the exciton starts recovering its initial oscillator strength and linewidth. The oscillations appearing on the low-energy side of the hh exciton for negative delay times (the probe arriving on the sample before the pump) are due to coherence effects,[7] namely, to the perturbation by the pump pulse of the polarization induced by the probe pulse.

The pump-probe experiments were performed for several pump excitation energies: (a) $E_p = 1.608$ eV, in resonance with the hh exciton, (b) $E_p = 1.631$ eV, 27 meV above the hh exciton energy, (c) $E_p = 1.653$ eV, close to the hh and lh barrier exciton transitions at 1.658 and 1.645 eV, respectively, (d) $E_p = 1.675$ eV, and (e) $E_p = 1.691$ eV, above the barrier exciton. The results for the various excitation energies are summarized in Fig. 2, where we show the exciton peak shift, obtained by a polynomial fit of the exciton absorption peak around the absorption maximum, as a function of delay. The exciton bleaching at long times was similar for cases (a)–(e) (the oscillator strength was about half the initial one) indicating comparable carrier densities.

Let us first concentrate on curves (a) and (b). For resonant excitation (a) a blueshift appears simultaneously with the pump pulse. Blueshifts of the exciton energy have been observed in GaAs/$Ga_{1-x}Al_xAs$ quantum wells[8] and attributed to a renormalization of the exciton self-energy due to the exciton-exciton repulsion inside a dense exciton gas.[9] The net shift is blue because the blueshift due to the Pauli exclusion principle is only partially compensated by the redshift due to screening. We believe that the blueshift we observe is of the same origin. The fact that it appears simultaneously when excitons are resonantly created [curve (a)] while it shows up at later times when electron-hole pairs are injected [curve (b)] is consistent with this assumption. Furthermore, the magnitude of the blueshift increases with pump intensity (see Fig. 3) in agreement with the theoretical predictions.[9]

For excitation 27 meV above the exciton energy [curve (b)] a redshift sets in initially and then turns into a blueshift. Given an exciton binding energy of about 11 meV,[10] free electron-hole pairs are created with a 16-meV kinetic energy. Assuming a fast redistribution of kinetic energy between

electrons and holes and due to the presence of lh levels in the barrier, the holes can rapidly become transiently delocalized in both the CdTe and $Cd_{1-x}Zn_xTe$ layers. We therefore attribute the observed redshift to the delocalization of the holes.[11] Before speculating on the exact mechanism through which hole delocalization causes a redshift, we present some further evidence supporting this claim. We have performed nonresonant excitation experiments under similar conditions in a 50-Å GaAs/50-Å $Ga_{0.7}Al_{0.3}As$ superlattice as well as in a 47-Å CdTe/950-Å $Cd_{0.83}Mn_{0.17}Te$ MQW structure. In both of these structures, the valence-band offset being about 40% of the gap difference, both electrons and holes are well localized in deep potential wells (100–130 meV for the holes). Only blueshifts of the exciton line were observed, reaching their maximum value with a time constant of about 3 ps.

Let us now consider through which mechanisms hole delocalization can lead to a lowering of the exciton energy. First of all, the spatial separation of electrons and holes results in the violation of charge neutrality within each well or barrier layer and in the appearance of a local electric field that causes band bending. A redshift observed in photoluminescence spectra of type-II long-period $Ga_{0.66}Al_{0.34}As/AlAs$ MQW's was attributed to band bending induced by real-space charge transfer.[12] In a crude model, neglecting many-body effects, we assumed a hole charge uniformly distributed throughout both CdTe and $Cd_{1-x}Zn_xTe$ layers and an electron charge uniformly distributed throughout the CdTe layers, and added the resulting potential to the square-well potential of the structure. We obtained a redshift of 0.8 meV for an electron-hole pair density of 4×10^{11} cm^{-2} by numerically solving Schrödinger's equation for the lowest energy level for electrons and holes. Obviously, the redshift calculated is overestimated mainly due to the assumption of complete hole delocalization and of uniform charge distributions but is of the same order of magnitude as the one observed experimentally in curve (b) of Fig. 2 (0.4 meV for approximately 4×10^{11} cm^{-2} electron-hole pairs). The band bending will also decrease the exciton binding energy leading to a blueshift whose magnitude, however, is only a small fraction of the redshift calculated.[13]

The redshift due to band bending should saturate at large densities due to carrier screening of the electric field which is indeed what is observed in Fig. 3, where the exciton peak shift as a function of delay is shown for three different excitation intensities. While the intensity is increased by a factor of 2.5, the maximum redshift increases only from 0.3 to 0.4 meV. As the excitation energy is increased (Fig. 2), the redshift should also increase reaching a maximum for above-barrier excitation [curve (d)] for which complete hole delocalization is achieved. This reasoning, however, does not explain why the observed redshift continues to grow when the excitation energy is further increased [curve (e)].

The reason for this increase may be the following additional electric-field effect: owing to the large absorption coefficient α of our structure, there is a longitudinal concentration gradient throughout the 20 periods of the structure. While the electrons remain confined in the wells, this concentration gradient will cause the delocalized holes to diffuse towards the substrate. It should be noted that, for above-barrier excitation, both electrons and holes are initially delocalized but we expect electrons to be captured much faster in their deeper potential wells. Throughout the whole structure the positive charges will be displaced with respect to the negative charges thus giving rise to a longitudinal macroscopic electric field E. The hole current $J=qp\mu E-qD\ dp/dz$, where q is the hole charge, p the hole density, D the diffusion coefficient $D=\mu kT_p/q$ (kT_p corresponds to the excess kinetic energy of the particle), and μ the hole mobility, becomes zero when the electric field due to the displacement compensates the driving force of the concentration gradient. This "equilibrium" macroscopic electric field $E=\alpha kT_p/q$ depends only on the absorption coefficient of the structure at the given excitation energy and on the excess kinetic energy and induces an exciton Stark redshift.[14] It is interesting to point out that, due to the exponential absorption law, this macroscopic electric field is constant throughout the structure. Since the macroscopic electric field is proportional to the hole kinetic energy, this Stark redshift effect becomes important only for large excitation energies: for excitation at 1.691 eV [curve (e) of Fig. 2], with $\alpha=4\times10^4$ cm^{-1} (see Ref. 15 for the absorption in ZnTe which has material parameters very similar to those of CdTe) and $kT_p=38$ meV (we assume that holes rapidly possess half the kinetic energy available) we obtain an electric field of 1.5 kV/cm. Using the finite-quantum-well, weak-field expression of Ref. 14 we find a redshift of 0.1 meV while an electric field of 3.5 kV/cm is necessary to explain the 0.6-meV increase of the redshift maximum from curve (d) to curve (e) (the Stark-shift dependence on electric field is quadratic for weak fields). The difference may be due to the oversimplified model we use to estimate the electric field which neglects the role of the potential wells in the diffusion and assumes a diffusion coefficient valid for a nondegenerate particle gas.

Curve (c) surprisingly shows a smaller redshift than that of curve (b). We have no definitive explanation for this behavior but it is possibly related to the fact that electrons are excited in a delocalized manner with only a small excess energy with respect to the barrier transition energy. Under these conditions, the electron capture time may be comparable to that of the holes in which case no charge separation and band bending appear.

A third mechanism that may be of some relevance should be mentioned: recently, the observation of two electrons bound to one hole (X^-) was reported in $CdTe/Cd_{0.86}Zn_{0.14}Te$ quantum wells with an excess of electrons in the wells created either optically[16] or by modulation doping.[16,17] These negatively charged excitons appear as an absorption line about 3 meV below the free exciton line and are attributed to a $e+h\nu\rightarrow X^-$ process. In some absorption spectra of our samples we have observed a shoulder on the low-energy side of the exciton which we believe is of the same origin. The shoulder appears only after excitation with the pump and during several ps after it which is consistent with our interpretation of hole delocalization leading to a transient presence of excess electrons in the wells. Part of the redshift observed may be due to an unresolved contribution of the X^- line but in both cases the physical cause is hole delocalization. The observation of X^- in undoped samples under above-barrier excitation was attributed to capturing of holes at acceptor sites in the barrier.[16] This process is negligible in our case since the acceptor density in the barrier (estimated to be less than 10^{16} cm^{-3}, that is 2.5×10^{10}

cm^{-2} for our barrier width) is low compared to our carrier densities and since the time constants involved in this case are much longer, of the order of a μs.[18]

Finally, the possible role of many-body effects (other than space-charge effects) in the appearance of the redshift should be considered. It is well known that the band-gap renormalization is partially compensated by a reduction of the exciton binding energy yielding a bound state of slightly blueshifted energy.[19] To our knowledge, there are no theoretical predictions of *exciton* redshifts due to many-body effects even in cases of charge separation.[20] The small redshift of the 1*s* magnetoexciton under excitation at the 2*s* resonance observed in Ref. 21 is due to the magnetic-field-induced reduction of the exciton-exciton interaction.

The evolution of the redshift as a function of pump-probe delay time should give information on the decay of the electric field and the delocalization of the holes. However, it is difficult to draw clearcut conclusions since it proceeds at the same time as the establishment of the blueshift due to exciton formation. Nevertheless, there is a clear tendency of slower recovery for higher excitation energies (see Fig. 2) which may be due to capturing of holes in wells adjacent to those in which they were created and a slower tunneling-related return to the initial wells.

In conclusion, we have observed a redshift of the exciton energy that we attribute to transient hole delocalization related to the unusual band structure of $CdTe/Cd_{1-x}Zn_xTe$ quantum wells. While band bending due to carrier separation seems to be responsible for the redshift, a Stark shift related to the concentration gradient in the sample starts contributing for large excess energies. Femtosecond pump-probe experiments give us access to a configuration intermediate between type I and type II that occurs in a transient manner with electrons localized in the wells and holes delocalized in both wells and barriers.

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