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Femtosecond study of exciton tunneling in (Zn,Cd)Se/ZnSe asymmetric double quantum wells

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We have studied, both experimentally and theoretically, exciton tunneling in a (Zn,Cd)Se/ZnSe asymmetric double quantum-well structure. The large exciton binding energy of these structures allows us to elucidate the role of the electron-hole interaction. Subsequent to resonant femtosecond pulse excitation, we observe fast (1 ps) exciton tunneling out of the narrow well, although LO-phonon scattering is forbidden for holes in a single-particle picture. Our theoretical analysis shows, however, that tunneling of the exciton as a whole entity with the emission of only one LO phonon is very slow. Instead, the exciton tunnels via an indirect state in a two-step process whose efficiency is dramatically enhanced by Coulomb effects. [S0163-1829(96)09219-3]

Carrier tunneling in semiconductor heterostructures is a topic of current research interest because of its fundamental and applied aspects.[1–4] Previous research concentrated mostly on (Ga,Al)As/GaAs and (Ga,In)As/(Al,In)As asymmetric double quantum wells (ADQW's), because these structures were available with the required quality. In a typical III-V ADQW, electrons tunnel rapidly via longitudinal optical (LO) phonon emission since the energy separation between the lowest electron subbands in the wide well (WW) and narrow well (NW) is larger than the LO-phonon energy.[5] Hole tunneling is normally slow[6] because the separation between the heavy-hole subbands is usually smaller than LO-phonon energy and the wave functions are more localized in the respective wells due to the larger hole mass. It has been pointed out[7] that Coulomb interaction does not play a significant role in the tunneling process. Thus, in III-V ADQW's electrons and holes tunnel independently rather than as excitons due to the relatively small exciton binding energy in these heterostructures.

Exciton binding energies of wide-gap II-VI semiconductors are almost an order of magnitude larger compared to those of typical III-V materials. Thus, they are ideal candidates to study the influence of excitonic effects on the tunneling process. In addition, II-VI compounds are more ionic so that the Fröhlich electron-phonon interaction is markedly enhanced. Previous studies[8–11] on carrier tunneling in II-VI ADQW's utilized CdTe-based structures and time-resolved photoluminescence (PL) with 10-ps time resolution. Here, we report an investigation of exciton tunneling in a (Zn,Cd)Se/ZnSe ADQW structure. The use of nonlinear absorption to monitor the tunneling transients enabled us to improve the time resolution up to the femtosecond time scale. ZnSe-based QW's exhibit exciton binding energies as large as 40 meV,[12] which is comparable with the LO-phonon energy ($\hbar\omega_{\mathrm{LO}}=31.7$ meV for ZnSe) and the electron and hole subband separations. We have designed and fabricated a structure anticipated to behave completely analogously to the above discussed III-V ADQW's: fast electron but slow acoustic-phonon-assisted hole tunneling. In contrast to this expectation, we observed that both particles escape from the NW with a time constant of 1 ps.

The (Zn,Cd)Se/ZnSe ADQW sample was grown by molecular-beam epitaxy on a (001) undoped GaAs substrate with a 1-μm ZnSe buffer layer. It comprises five periods of ADQW's separated by 850-Å ZnSe barriers wide enough to ensure that each ADQW structure is decoupled from the others. A single ADQW consists of $\mathrm{Zn}_{0.82}\mathrm{Cd}_{0.18}\mathrm{Se}$ narrow (13 Å) and wide (25 Å) wells separated by a 42-Å ZnSe barrier (see inset of Fig. 1). Phase-locked epitaxy was employed to achieve high interface quality and reproducibility of each period. For transmission experiments, the GaAs substrate and a part of the buffer layer were removed by chemical etching and the residual structure was mounted on a glass plate. Steady-state PL and PL excitation (PLE) measure-

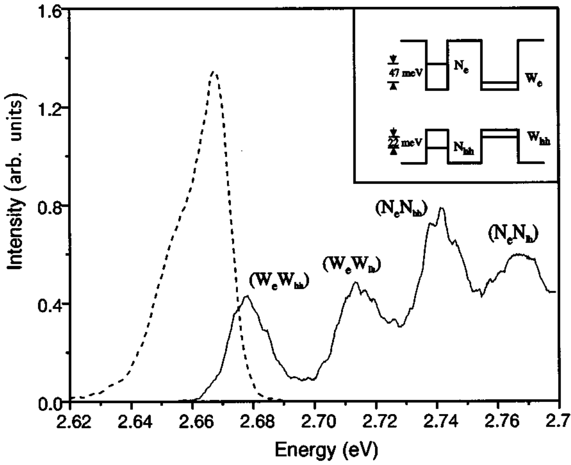

FIG. 1. Photoluminescence (dashed) and photoluminescence excitation (solid) spectra of the (Zn,Cd)Se/ZnSe ADQW. *W* and *N* refer to wide and narrow wells, respectively, and *e*, hh, and lh refer to electron, heavy hole, and light hole, respectively. The inset shows the sample design and energy levels of the uncorrelated particles.

TABLE I. Calculated energy levels of single carriers and excitons for the 13/42/25 (Zn,Cd)Ze/ZnSe ADQW.

Quantum state	Confinement energy (meV)	Binding energy (meV)	Exciton energy (eV)
W_e	85		
N_e	132		
W_{HH}	30		
N_{HH}	52		
(W_e, W_{HH})		29	2.673
(N_e, N_{HH})		27	2.744
(N_e, W_{HH})		11	2.738
(W_e, N_{HH})		11	2.713

ments were performed with a tunable dye laser. The time-resolved setup was based on a Kerr lens mode-locked Ti:sapphire laser which provided a 100-MHz train of 120-fs pulses tunable between 780 and 920 nm. Its output was divided into pump and probe beams which were frequency doubled in 2-mm $\mathrm{LiB_3O_5}$ crystals. The duration of the blue pulses increased to 300 fs because of group velocity mismatch in the nonlinear crystals. Pump and probe with spectral width of 2 nm were tuned to the NW heavy-hole exciton (455 nm at 77 K) and chopped at different frequencies. The transmitted probe was measured using lock-in detection at the sum frequency.

PL (dashed) and PLE (solid) spectra of the ADQW structure are shown in Fig. 1. The single PL band originates from the WW heavy-hole exciton recombination. The very small bound-exciton contribution indicated by a low-energy shoulder demonstrates the excellent sample quality. No PL was observed from the NW because, as will be shown by the pump-probe results, the tunneling-controlled lifetime of these excitons is very short. The PLE spectrum exhibits heavy- and light-hole (HH and LH) exciton features from both the NW and WW. These features also dominate in the linear absorption of the sample. The detection energy for PLE in Fig. 1 is slightly below the maximum of the WW PL band. Thus, the occurrence of the HH and LH absorption resonances of the NW in the PLE spectrum directly demonstrates that the excitons tunnel out of the NW and indeed appear in the WW where they eventually recombine. The PLE spectrum was recorded at 5 K to enable a direct extraction of the relevant energy separations, but apart from an overall energy shift no essential change is found up to 77 K. Table I summarizes calculated single-particle and exciton energies derived from a comparison of the PLE data and numerical calculations described in more detail below. Here, we merely note that our initial assumption about the different tunneling mechanisms for electrons and holes is quantitatively confirmed. The separation between the lowest single-electron levels in the NW and WW $[E(N_e)-E(W_e)=47$ meV$]$ is appreciably larger than the LO-phonon energy of $\hbar\omega_{\mathrm{LO}}=30.2$ meV for the present Cd fraction, whereas the opposite relation holds for the heavy hole $[E(N_h)-E(W_h)=22$ meV$]$ and hole tunneling is thus possible only via acoustic phonon emission. However, as we will demonstrate in the remainder of this paper, the true picture is entirely different as a result of the electron-hole Coulomb interaction.

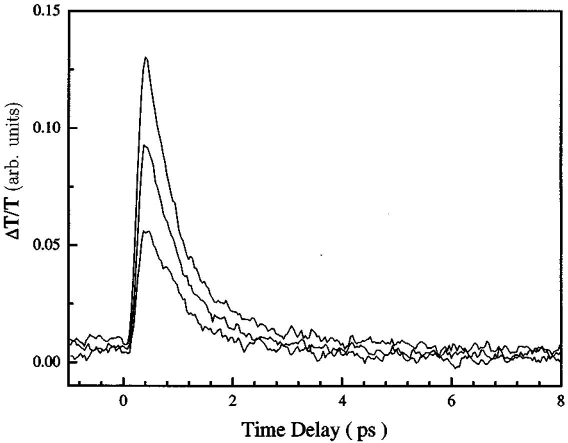

FIG. 2. Spectrally integraded, time-resolved differential transmission change of the NW heavy-hole exciton resonance at different carrier densities of, from bottom to top, 3×10^{10}, 6×10^{10}, and 9×10^{10} cm^{-2}.

Time-resolved pump-probe data at various excitation levels are displayed in Fig. 2. The rise of the probe transmission corresponds to the generation of excitons in the NW by the pump pulse. A striking feature in these data is the fast and complete recovery of the transmission change even at relatively high excitation densities. In time-resolved PL, the signal reflects the product of the electron and hole densities $n_e n_h$. Its decay is thus dominated by the shorter living electron. Conversely, time-resolved pump-probe measurements provide access to both carrier lifetimes since the absorption change is related to (n_e+n_h). Therefore, in conjunction with the PLE data (see Fig. 1), the complete absorption recovery proves unambiguously that both electrons and holes tunnel very rapidly from the NW to the WW. A fit of the absorption transients assuming a monoexponential decay yields a time constant of 1 ps with only a very slight change when the excitation level is increased. The exciton lifetime measured by time-resolved PL for a single QW with the same design as the NW is in the 100-ps range and thus has no influence on the tunneling dynamics.

The theory of phonon-assisted tunneling of individual electrons and holes in the absence of Coulomb interaction is well elaborated.[13,14] Based on formulas derived in Ref. 14, we estimate for the present ADQW a tunneling time of some 100 ps for the heavy holes via elastic scattering with longitudinal acoustic phonons. The contradiction with the experimental findings is evident. In what follows, we present a theoretical analysis of exciton tunneling in ADQW's. The Hamiltonian describing the coupling of excitons and phonons is a linear combination,[15,16]

$$H_{X\text{-ph}}=H_{e\text{-ph}}(r_e)-H_{e\text{-ph}}(r_h), \tag{1}$$

where $H_{e\text{-ph}}$ is the Fröhlich interaction potential. The exciton wave function is taken in the form

$$\begin{gathered}\Phi_X(\mathbf{r}_e,\mathbf{r}_h)=\exp(i\mathbf{K}\mathbf{R}_X)\Psi_X(\mathbf{r}_e\mathbf{r}_h),\\ \Psi_X(\mathbf{r}_e,\mathbf{r}_h)=\psi_e(z_e)\psi_h(z_h)\phi(z_e,z_h,\rho),\end{gathered} \tag{2}$$

where $\hbar\mathbf{K}$ is the exciton momentum, $\mathbf{R}_X$ and $\boldsymbol{\rho}=\boldsymbol{\rho}_e-\boldsymbol{\rho}_h$ are the in-plane center-of-mass and relative coordinate, respectively, and $z_{e,h}$ is the electron or hole coordinate in the

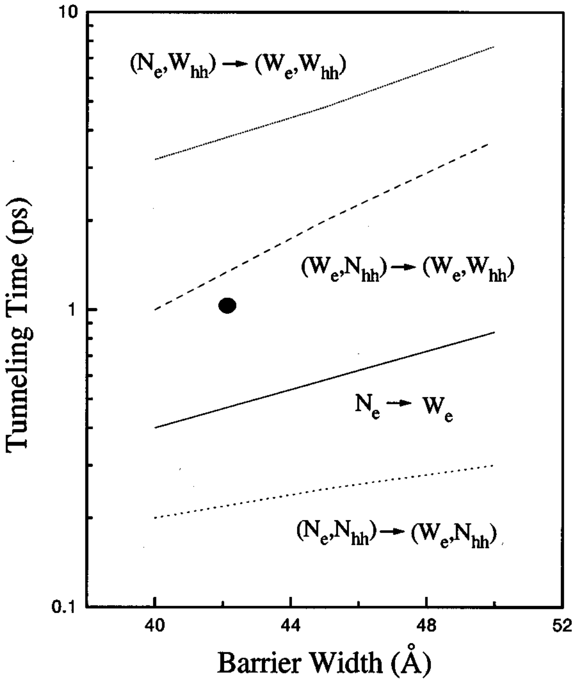

FIG. 3. Calculated LO-phonon-assisted tunneling times for electrons (solid) and excitons (dashed and dotted) versus barrier width for a 13-Å/L_b/25-Å ADQW structure. The dot marks the experimental value for the present ADQW.

growth direction. The wave functions $\psi_e(z)$ and $\psi_h(z)$ are the solutions of the single-particle Schrödinger equations for the ADQW potential without Coulomb interaction and were calculated by the transfer matrix method.[17] The electron-hole correlation is condensed in $\phi(z_e,z_h,\rho)$. After integration over the exciton final-state momentum, Fermi's golden rule yields for Fröhlich coupling the following expression for the tunneling rate:

$$\frac{1}{\tau}=\frac{Me^2\omega_{\mathrm{LO}}}{2\pi\hbar^2}\left(\frac{1}{\varepsilon_\infty}-\frac{1}{\varepsilon_0}\right)\int_0^{2\pi}d\theta\int_{-\infty}^{+\infty}dq\,\frac{|V(Q,q)|^2}{q^2+Q^2},\qquad(3)$$

with

$$V(Q,q)=\int d^2\boldsymbol{\rho}\int dz_e\int dz_h\Psi^*_{X,i}[\exp(i\alpha_h\mathbf{Q}\boldsymbol{\rho}+iqz_e)-\exp(-i\alpha_e\mathbf{Q}\boldsymbol{\rho}+iqz_h)]\Psi_{X,f}\qquad(4)$$

between the exciton states $\Psi_{X,i}$ and $\Psi_{X,f}$ of energy separation ΔE. Here, $\hbar\mathbf{Q}=\hbar(\mathbf{K}_i-\mathbf{K}_f)$ is the momentum change, e the electron charge, ε_0 (ε_∞) the static (dynamic) dielectric constant, $M=m_e+m_{hp}$ the exciton translational mass, $m_{hp}=m_0/(\gamma_1+\gamma_2)$ the heavy-hole in-plane mass, and $\alpha_{e,h}=m_{e,h}/M$. For optical excitation we may set $K_i=0$ and the energy conservation reads as $K_f^2=Q^2=2M(\Delta E-\hbar\omega_{\mathrm{LO}})/\hbar^2$.

It is straightforward to recover the LO-phonon-assisted tunneling rates for independent electrons and holes[13,14] from (3) and (4) using an uncorrelated plane wave ansatz for the in-plane function and single-particle energies. For completeness, we have also calculated the time constant for electron tunneling (with the hole staying in the NW) as a function of the barrier width L_b (solid line in Fig. 3). It is markedly shorter than the experimentally observed tunneling time.

Now we discuss the general structure of the exciton tunneling rate. In an ADQW, one has direct and indirect exciton states. For direct states, the electron and hole are located in the same QW [$\Psi_X\propto\psi_{Ae}(z_e)\psi_{Bh}(z_h)$, $A=B=N,W$]. The $\psi_{e,h}(z)$ are single particle eigenfunctions of the total ADQW structure so $\int dz\,\psi_{Ne,h}(z)\psi_{We,h}(z)=0$. Using this orthogonality relationship it is easy to see that the tunneling rate between direct excitons via LO-phonon emission is equal to zero when the Coulomb correlation along the growth direction is ignored, that is, when $\phi(z_e,z_h,\rho)=\phi(\rho)$. This frequently used ansatz covers the leading contribution from the Coulomb interaction as long as the excitons are truly quasi two dimensional. Therefore, tunneling between direct exciton states with the emission of only one LO phonon is normally not efficient. This is a consequence of charge neutrality of the exciton.

In contrast, tunneling between direct and indirect states (electron and hole in different wells, $A\neq B$) is very rapid. This process corresponds to separate electron or hole tunneling. However, the Coulomb interaction causes a profound renormalization of the energy spectrum so that transitions forbidden in the single-particle scheme become allowed. To demonstrate this quantitatively we have calculated exciton energies and tunneling rates using a variational procedure based on the ansatz[18,19]

$$\phi(z_e,z_h,\rho)=C(Z,R)\exp\left[-\frac{\sqrt{\rho^2+Z^2}}{R}\right],\qquad(5)$$

$$C(Z,R)=\frac{2}{R\sqrt{2\pi(1+2Z/R)}}\exp\left[\frac{Z}{R}\right]\qquad(6)$$

($Z=|z_e-z_h|$), with the single parameter R. By varying R, the binding energies of the two direct and two indirect relevant exciton states, further denoted by (A_e,B_{HH}), were calculated. The parameter set used (electron mass $m_e=0.16m_0$, Luttinger parameters $\gamma_1=4.3$, $\gamma_2=1.3$, conduction and valence band offsets $V_c=163$ meV and $V_v=70$ meV, respectively, $\varepsilon_0=9$, $\varepsilon_\infty=6.3$) is consistent with previously published data and yields reasonably good agreement between computed and experimental values of the total HH exciton energies for both the NW and WW. Table I shows that the following LO-phonon-assisted transitions are energetically allowed: (i) direct exciton tunneling $(N_e,N_{\mathrm{HH}})\rightarrow(W_e,W_{\mathrm{HH}})$, (ii) direct to indirect exciton tunneling $(N_e,N_{\mathrm{HH}})\rightarrow(W_e,N_{\mathrm{HH}})$, and (iii) indirect to direct exciton tunneling $(W_e,N_{\mathrm{HH}})\rightarrow(W_e,W_{\mathrm{HH}})$ or $(N_e,W_{\mathrm{HH}})\rightarrow(W_e,W_{\mathrm{HH}})$. In marked contrast to the single-particle scheme, LO-phonon-assisted tunneling is now allowed for heavy holes. The critical role of the Coulomb interaction is illustrated by the fact that heavy-hole tunneling occurs only when the electron is in the WW.

Using the wave function (5), and integrating over the in-plane variables, the matrix element $V(Q,q)$ takes the form,

$$\begin{aligned}V(Q,q)=\int dz_e\int dz_h\frac{2\pi}{R_{\mathrm{eff}}}C(R_i,Z)C(R_f,Z)\\ \times\psi^*_{e,i}(z_e)\psi^*_{h,i}(z_h)\psi_{e,f}(z_e)\psi_{h,f}(z_h)\\ \times[\exp(iqz_e-\zeta_hZ)\zeta_h^{-3}(1+\zeta_hZ)\\ -\exp(iqz_h-\zeta_eZ)\zeta_e^{-3}(1+\zeta_eZ)],\end{aligned}\qquad(7)$$

with $1/R_{\text{eff}}=1/R_i+1/R_f$ and $\zeta_{e,h}^2=(\alpha_{e,h}Q)^2+(1/R_{\text{eff}})^2$. When direct exciton states are considered for the initial ($i=N_e,N_{\text{HH}}$) and final ($f=W_e,W_{\text{HH}}$) states, it is simple to verify that $V=0$ for $R_i=R_f$. In the present ADQW, the R parameters of these excitons are almost the same (43 and 44 Å, respectively) so that the numerical calculation yields direct exciton tunneling times in the nanosecond range. We arrive, thus, at the conclusion that direct exciton tunneling is not significant.[20] On the contrary, tunneling processes where one of the involved states is a direct and the other is an indirect exciton are very efficient. Tunneling times for these transitions are also depicted as functions of L_b in Fig. 3. There are two transitions corresponding to electron tunneling, $(N_e,N_{\text{HH}})\rightarrow(W_e,N_{\text{HH}})$ and $(N_e,W_{\text{HH}})\rightarrow(W_e,W_{\text{HH}})$. The first process is very fast since the energy separation between initial and final states is almost equal to the LO-phonon energy and hence the momentum change is small. We find tunneling times (200–300 fs) even shorter than those computed for individual electrons without Coulomb interaction. Thus, the absorption recovery in the pump-probe measurements is controlled by the transition $(W_e,N_{\text{HH}})\rightarrow(W_e,W_{\text{HH}})$ corresponding to hole transfer from NW to WW. The calculated tunneling time for the present ADQW is 1.2 ps (see Fig. 3), in excellent agreement with the experimentally observed value.

The theoretical approach described above can be easily modified for other scattering mechanisms. For example, we estimated impurity-assisted exciton tunneling times to be in the nanosecond range for the impurity concentration of 10^{10} cm^{-2}.

In summary, we have studied free carrier versus exciton tunneling in a ZnSe/(Zn,Cd)Se ADQW structure. Unlike in III-V semiconductors, tunneling of electrons and holes as uncorrelated particles cannot explain the complete recovery of the NW absorption within 1 ps. We have derived a general expression for the rate of LO-phonon-assisted tunneling between exciton states and computed exciton wave functions, binding energies, and the time constants for various tunneling processes. Though our approach is based on a simple ansatz with only one variational parameter, and more elaborate treatments are desired, we believe that it provides the correct order of magnitude of the tunneling times. We found, in contrast to the common notion, that the exciton does not tunnel as a whole entity in a single event, though energetically allowed. Tunneling rather takes place in a two-step process. The strong Coulomb correlation in II-VI semiconductors renormalizes the energy spectrum so that transitions forbidden in a single-carrier scheme become very efficient. Tunneling of the hole can start from an indirect exciton state (electron in the WW) which is formed within 200 fs. In this way, the entire exciton is indeed transferred from the NW to the WW in 1 ps by the emission of two LO phonons. It will be interesting to study other designs of ZnSe-based ADQW's in this regard.

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[20] For the same reason, tunneling between the direct N_{HH} and W_{LH} exciton states only slightly energetically forbidden for the present ADQW is generally of low probability. It is also easy to see from (6) that a transition from the direct NW exciton to a direct but uncorrelated electron-hole pair from the WW exciton continuum may be disregarded, since R_f goes to infinity and V to zero in this case.