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Tunneling and energy transfer in ZnSe-based semimagnetic double quantum wells

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An asymmetric double-quantum-well structure has been fabricated by molecular-beam epitaxy, consisting of a semimagnetic (Zn,Cd,Mn)Se and a nonmagnetic (Zn,Cd)Se well, weakly coupled via a ZnSe barrier. Level crossing of the quantum well excitons is accomplished through an external magnetic field. The crossing is accompanied by reverse of the tunneling direction. The tunneling process is of *excitonic* nature. Besides the very efficient 2-LO-phonon scattering mechanism, indications for a radiationless resonance energy-transfer have been found. [S0163-1829(98)03823-5]

Tunneling of carriers in semiconductor heterostructures is of fundamental quantum-mechanical and practical interest. Measurements have been carried out on asymmetric double-quantum-well (ADQW) structures as well as on resonant tunneling diodes. Especially, for wide band-gap semiconductors, the role of excitons (including direct and spatially indirect excitons) and the underlying tunneling mechanism are under debate.[1–5] Semimagnetic II-VI heterostructures are ideal candidates for studying these questions, since the ‘‘giant’’ Zeeman effect associated with the s,p-d exchange interaction, between the extended band states and the localized moments of the magnetic ions, allows the continuous tuning of band-gap and exciton energies by an external magnetic field. Previous work has been mostly concentrated on CdTe/(Cd,Mn)Te (Refs. 1 and 2) and ZnSe/(Zn,Mn)Se,[6] where a nonmagnetic well (NMW) is embedded between semimagnetic barriers. In particular, tunneling of excitons and carriers has been investigated using ADQW structures based on CdTe/(Cd,Mn)Te.[1,2] However, problems arise in the interpretation of the data from those structures, as the field dependence of the inner barrier is a factor of considerable uncertainty. The paramagnetic behavior of this typically very thin layer, hardly accessible by optical measurements, is strongly influenced by interface effects.[7,8] The magnetically induced change of the barrier is only indirectly seen by the variation of the QW energy levels, leaving thus the actual tunneling conditions open. In this paper we report on a magneto-optical study on an ADQW structure formed by (Zn,Cd,Mn)Se/ZnSe (Zn,Cd)Se. Here, a nonmagnetic barrier separates a NMW from a semimagnetic well (SMW), with only the latter being affected by the external field. In addition, ZnSe-based structures offer larger exciton binding energies and allow us thus to pronounce Coulomb effects in the tunneling process.

The zinc-blende structures were grown by molecular-beam epitaxy on (001) GaAs in a phase-locked modus to improve interface quality.[9] A 1-μm-thick ZnSe buffer layer was deposited first before the growth of the ADQW started. The (Zn,Cd)Se NMW is followed by a nonmagnetic ZnSe barrier and a SMW, formed by the quaternary (Zn, Cd, Mn)Se, all of which have a thickness of 6 nm. The structure is completed by a 20-nm ZnSe cap layer. The ZnSe band gap is increased by the incorporation of Mn, while Cd provides the opposite trend. Therefore, using the same Cd concentration (x_{Cd}) for the NMW and SMW and adjusting properly the Mn concentration (y_{Mn}), the band gaps can be aligned so that $E_G[\mathrm{ZnSe}] > E_G[(\mathrm{Zn,Cd,Mn})\mathrm{Se}] > E_G[(\mathrm{Zn,Cd})\mathrm{Se}]$ holds (see also Fig. 4). For the present study, two compositions were selected: (a) $x_{\mathrm{Cd}}=0.18$ and $y_{\mathrm{Mn}}=0.15$ and (b) $x_{\mathrm{Cd}}=0.15$ and $y_{\mathrm{Mn}}=0.09$. We have performed photoluminescence (PL) and PL excitation (PLE) measurements using a tunable cw dye laser pumped by the UV line of an Ar$^+$ laser at $T=1.8$ K. A magneto-optical cryostat provided external fields up to 7.5 T, applied in Faraday geometry (field and light propagation along the ADQW axis).

In Fig. 1, PL spectra of sample (b) at various magnetic-field strengths are shown for excitation above the ZnSe barriers. The PL of the NMW consists of a dominant bound exciton line (D^0X) at about 2.622 eV and a high-energy shoulder due to the free heavy-hole ground-state exciton (hh1). These lines undergo virtually no shift up to 7.5 T. A third feature located at low fields on the high-energy side is due to the hh1 resonance of the SMW. This line is of less intensity, but exhibits a strong shift to lower energies with increasing magnetic field. Eventually, a crossing occurs between the NMW and SMW hh1 exciton levels. The ‘‘giant’’ Zeeman effect, responsible for the shift of the SMW exciton, is given in very good approximation by the field-induced shifts of the conduction and valence-band edges:[10]

$$\Delta E_c = a^{\mathrm{eff}} y_{\mathrm{Mn}} N_0 \alpha S B_S(\zeta) m_j , \tag{1}$$

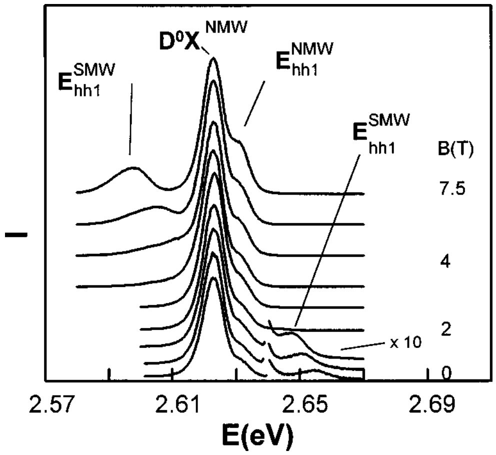

FIG. 1. PL spectra of an ADQW structure ($\mathrm{Zn_{0.85}Cd_{0.15}Se/ZnSe/Zn_{0.76}Cd_{0.15}Mn_{0.09}Se}$) with well and barrier widths of 6 nm at various magnetic-field strengths ($T=1.8$ K).

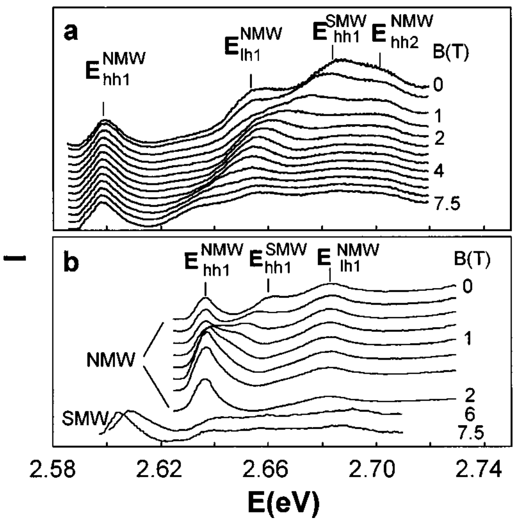

FIG. 2. PLE spectra of sample (a) ($Zn_{0.82}Cd_{0.18}Se/ZnSe/Zn_{0.67}Cd_{0.18}Mn_{0.15}Se$) and sample (b) (see Fig. 1) at various magnetic fields ($T=1.8$ K). The marks represent the results of energy calculations described in the text.

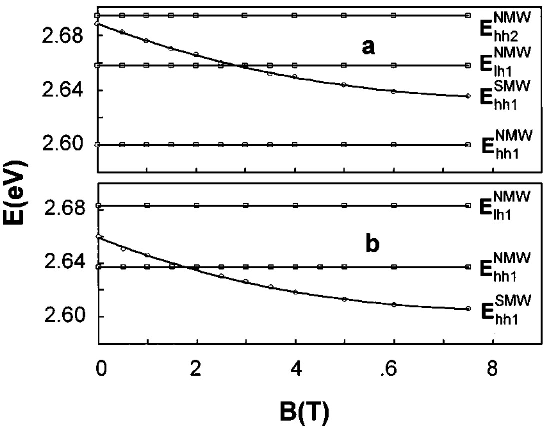

FIG. 3. Energetic positions of the exciton lines of the SMW (○) and NMW (□) of samples (a) and (b) vs magnetic-field strength. Curves are calculated. See text for details.

$$\Delta E_\nu = \tfrac{1}{3} a^{\text{eff}} y_{\text{Mn}} N_0 \beta S B_S(\zeta) m_j , \qquad (2)$$

where $N_0\alpha$ and $N_0\beta$ are the respective exchange integrals, $S=\frac{5}{2}$, $m_j=\pm\frac{1}{2}$, $\pm\frac{3}{2}$, and $B_S(\zeta)$ is the modified Brillouin function with $\zeta = Sg\mu_B B/k(T+\Theta)$. Θ and a^{eff} are phenomenological parameters, taking into account the formation of spin-correlated clusters.

Figure 2 summarizes PLE spectra of both samples at various magnetic fields in σ^+ polarization. The detection was on the D^0X line, except for sample (b) beyond the crossing field, where the low-energy tail of the SMW hh1 line is detected. For sample (a), no crossing is accomplished as a result of the increased zero-field separation between the NMW and SMW ground-state exciton, caused by the larger values of x_{Cd} and y_{Mn}. The PLE spectra uncover excited exciton states, associated with the light-hole band (lh1) or the second electron and heavy-hole subbands (hh2). The assignments given in Fig. 2 are based on ADQW energy calculations applying the transfer matrix formalism for the single-particle states and using for the exciton binding energy the formula derived in Ref. 11. The band gap of zinc blende (Zn,Cd)Se was taken from Ref. 12 and distributed by 70:30 between conduction and valence band.[13,14] As data for the ternary and quaternary layers are not available, we have used the deformation potentials[15] $a=5.4$ eV and $b=-1.2$ eV, the elastic compliance coefficients[16] $S_{11}=2.26\times10^{11}$ m^2/N and $S_{12}=-0.85\times10^{11}$ m^2/N, as well as the Luttinger parameters $\gamma_1=3.77$ and $\gamma_2=1.24$ of ZnSe, too. X-ray diffraction measurements have yielded that the lattice-misfit-induced strain is practically entirely adopted by the wells, defining the main origin of the hh-lh splitting of 60 meV (a) and 50 meV (b). The band-gap energies have been determined on thick (Zn,Mn,Cd)Se epilayers grown as reference. Nothing is actually known about the conduction-band–valence-band offset ratio at the (Zn,Cd,Mn)Se/ZnSe heterointerfaces. Using a ratio of 70:30 [the same as for (Zn, Cd)Se/ZnSe] enabled a very good fit of the experimental energy positions (see Fig. 2). In the context of tunneling, the PLE data clearly demonstrate that excitons excited in the SMW appear in the NMW and, beyond the crossing field, also a transfer in the opposite direction for sample (b). Though the NMW resonances appear less pronounced in the latter case due to an increased broadening, the absence of any fieldshift for the PLE bands represents direct evidence for this.

The energy positions of the various exciton states are plotted versus magnetic field in Fig. 3. The experimental points were extracted from the PLE spectra using a deconvolution procedure with Gaussian bands. It is again clearly seen that the features from the NMW maintain their position (within the present spectral resolution), whereas the exciton states of the SMW's exhibit a huge low-energy shift. This shift is also very well reproduced by the above described calculations, carried out now with the field-dependent band edges defined by Eqs. (1) and (2). Taking for the exchange integrals literature data of (Zn,Mn)Se ($N_0\beta=-1.31$ eV, $N_0\alpha=0.26$ eV),[17] we find an effective Mn concentration and a Curie-Weiss parameter of $a^{\text{eff}}=0.22$ and $\Theta=3.15$ K for sample (a) and $a^{\text{eff}}=0.33$ and $\Theta=2.58$ K for sample (b), respectively. The smaller a^{eff} and higher Θ of sample (a) are consistent with its larger nominal y_{Mn}, giving rise to an increased spin-glass transition temperature. The crossing field strength of sample (b) in PLE is $B_{\text{xc}}=1.8$ T

Figure 4 depicts schematically the band alignment across the ADQW structures, extracted from the fit of the experimental data. At zero field [Fig. 4(a)], both the electron and heavy-hole ground state of the SMW are higher in energy than the respective states of the NMW. The exchange integral of the valence band is about five times larger than that of

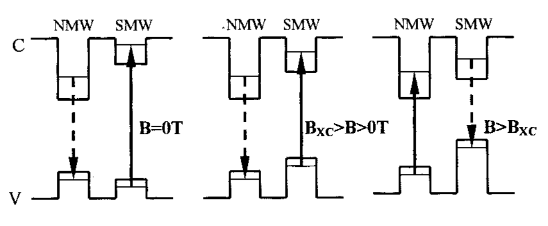

FIG. 4. Schematics of the conduction-band (C) and valence-band (V) alignments in σ^+ polarization. The full arrows mark excitation, the dashed luminescence.

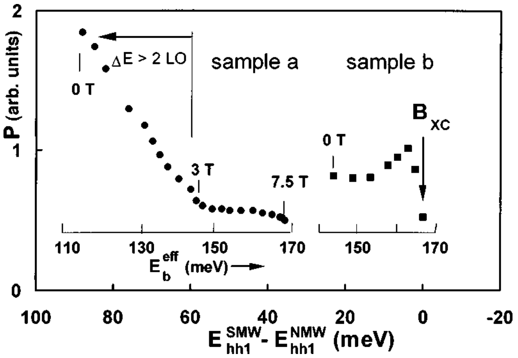

FIG. 5. Tunneling probability P (SMW→NMW) vs the energy separation of the hh1 states of both wells. The corresponding effective barrier heights and magnetic-field strengths are given, too.

the conduction band. Therefore, the hole levels of the NMW and SMW reverse their sequence first [Fig. 4(b)]. Regardless of the uncertainty in the valence-band offsets, this occurs definitely for both samples, though a reversing of the exciton levels is only observed on sample (b). In a single-particle picture, one would thus expect that hole tunneling from the SMW to NMW is increasingly inhibited above a certain field $B<B_{\mathrm{xc}}$, since the final state is now higher in energy. This is, however, in contrast with the experimental findings, signifying clearly a transfer of the exciton as a whole entity, for sample (b) as long as B is below B_{xc}. In the opposite case ($B>B_{\mathrm{xc}}$), the same discussion can be made for electron tunneling [Fig. 4(c)]. These results ultimately show that the tunneling process is solely controlled by the energy positions of the exciton states.

From the deconvoluted PLE spectra, the (relative) tunneling efficiency P between the exciton ground states of the SMW and NMW can be deduced. In Fig. 5, we have plotted this efficiency vs the energy separation of these excitons as well as vs the effective barrier height $E_b^{\mathrm{eff}}(B)=E_g^{\mathrm{ZnSe}}-E_{\mathrm{hh1}}^{\mathrm{SMW}}(B)$, both directly defined by the experiment. Note, these quantities are tuned into opposite directions by the external field. Sample (a) exhibits a roughly linear decrease of P with a marked change of the slope below the 2-LO-phonon threshold, indicating a change of the underlying tunneling mechanism. The decrease of the tunneling efficiency when the 2-LO-phonon threshold is approached from above signifies that the increasing barrier height overcompensates a possible rise of P caused by a closer separation of the tunneling levels. Sample (b) allows us to study the tunneling efficiency for a separation of these levels even distinctly less than one LO-phonon energy. Though the barrier becomes higher, an increase of P occurs first, reaching a maximum at a magnetic field, where the SMW-PL crosses the NMW absorption, followed by a sharp drop towards B_{xc}, defined by the crossing in absorption. The fact that the maximum is not at B_{xc} demonstrates that the intrawell relaxation runs on a time scale much shorter than the characteristic tunneling times.

A study on nonmagnetic (Zn,Cd)Se/ZnSe ADQW's has revealed that tunneling of excitons by the emission of two LO phonons is a very efficient process with characteristic times below 1 ps.[4] Recent theoretical work[5] has shown that exciton tunneling by the emission of only one LO phonon requires barriers much thinner than investigated here, ensuring sufficiently strong mixing of direct and indirect exciton states. For sample (b), the energy separation between the tunneling levels is even below the 1-LO-phonon threshold. Acoustic-phonon scattering yields orders of magnitudes smaller tunneling efficiencies than polar coupling. Our data below the 1-LO-phonon threshold are consistent with radiationless resonance energy transfer (RRET),[18–21] caused, e.g., by dipole-dipole interaction. A characteristic feature of this mechanism is that the tunneling rate[22] is independent of the barrier height, a tendency most clearly seen for sample (a) in Fig. 5. Instead, this rate is governed by the emission-absorption overlap factor between initial and final states, accounting for the finite broadening of these states, required to fulfill energy conservation. In sample (a), as in a similar study on GaAs/(GaAl)As ADQW's,[20] the initial exciton is always resonant to states from the electron-hole continuum of the NMW, enabling direct transfer with virtually no change of energy. This is followed by rapid intrawell relaxation and subsequent photon emission from the exciton ground state. In this case, which is different from the classical RRET scenario, the tunneling rate is almost independent of the energy separation between initial and final states, as discussed in Ref. 20. On the contrary, as a result of the large exciton binding energy in our structures (30–35 meV), the SMW exciton of sample (b) is located energetically below the NMW continuum edge already at zero-field. This brings ultimately the emission-absorption overlap of Dexter-type[21] into play, yielding a resonance enhancement of the tunneling rate as observed experimentally (see Fig. 5).

In summary, we have designed and fabricated (Zn,Cd)Se/ZnSe/(Zn,Mn,Cd)Se ADQW structures. They are distinguished from other semimagnetic ADQW's by the fact that only the semimagnetic well is affected by the external magnetic-field, providing a much better control of the tunneling conditions. We have found convincing evidence for the importance of Coulomb effects and the tunneling of excitons as an entity, as well as a reverse of the tunneling direction. Our data indicate that, below the 2-LO-phonon threshold, RRET is responsible for the exciton transfer. It will be interesting to study this process in more detail, e.g., by time-resolved measurements.

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[22] Though being questionable in a strict sense, we maintain the term ''tunneling'' for the RRET, because it bridges also a region of classically forbidden energy.