Observation of type-I excitons and related confinement effects in type-II superlattices

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CdSe/$Zn_{1-x}Mn_xTe$ superlattices are characterized by type-II band alignment. We have used these structures to demonstrate that type-II superlattices can exhibit type-I excitons, i.e., excitons which are confined in the *same* semiconductor layer (either in CdSe or in $Zn_{1-x}Mn_xTe$ in the present example). Such spatially direct excitons form in a type-II structure when one of the carriers (electron *or* hole) originates from a well, while the other (hole *or* electron) originates from a state localized in the barrier, which is typical for subbands at above-barrier energies.

Semiconductor superlattices are usually classified according to their band alignment at the interfaces between constituent materials. A type-I superlattice is characterized by band offsets such that the same semiconductor layers serve as quantum wells for both conduction electrons and valence-band holes. For example, ZnCdSe/ZnSe is a type-I superlattice, ZnCdSe layers being the quantum wells and ZnSe layers the confining barriers. The intensity of excitonic transitions in such a system is enhanced by the localization of the wave functions of both electrons and holes in the same layer.[1] If the quantum wells for the electrons and the holes exist in different (i.e., adjacent) layers, such a system is referred to as a type-II superlattice. CdSe/ZnTe is an example of such a type-II system, in which the conduction electrons at energies below the barriers are localized in the CdSe layer and the valence-band holes in the ZnTe layers. Excitonic transitions are considered unimportant in such a system, because the wave functions of the electrons and the holes are then spatially separated,[1,2] resulting in extremely weak Coulomb attraction.

In optical studies carried out so far, attention has been focused primarily on excitons involving electron and hole states at energies below the barriers, which are necessarily localized in their respective quantum well regions. Excitons can, however, also be formed from above-barrier states, and can in fact be *localized in the barrier regions.* This has been recently observed by us in type-I ZnCdSe/ZnMnSe superlattices, where at above-barrier energies both the electron and the hole subbands were shown to be confined in the barriers.[3] The objective of this work is to present experimental evidence that in type-II superlattices the same process of localization of above-barrier subbands in barriers leads to the formation of spatially direct (type-I-like) excitons. For reasons to be discussed below, we have chosen CdSe/$Zn_{1-x}Mn_xTe$ (type-II) superlattices to demonstrate this effect.[4]

Figure 1 shows the energy band alignment of CdSe/$Zn_{1-x}Mn_xTe$ superlattices. The valence-band offset for the closely related CdSe/ZnTe system is $\Delta E_v = 0.64 \pm 0.07$ eV at room temperature, as determined by x-ray photoelectron spectroscopy.[5] For the CdSe/$Zn_{1-x}Mn_xTe$ system, for a small value of x ($0.03 < x < 0.10$ in our study), the band alignment should not differ significantly from that of CdSe/ZnTe, and we shall use the value 0.64 eV as the valence-band offset for our system as well, as shown in the figure. Two types of excitonic transitions are possible in such type-II superlattices. One takes place between electron states localized in CdSe wells and hole states in $Zn_{1-x}Mn_xTe$ wells, as shown by the arrow marked II in Fig. 1. We shall refer to this process, involving spatially separated states, as a type-II excitonic transition. The other occurs between electron (or hole) subbands confined in the wells and hole (or electron) subbands at above-barrier energies, confined in the barriers. In that case both the electron and the hole states involved in the transition are localized *in the same layer,* as shown by the arrows marked I in Fig. 1. We shall refer to these spatially direct processes as type-I excitonic transitions. Our choice of the specific material used in this study is based on the fact that the type-I excitons confined in the nonmagnetic layer CdSe exhibit very different magneto-optical properties from those in the diluted magnetic semiconductor (DMS) layer $Zn_{1-x}Mn_xTe$. This difference can be exploited for identifying the type-I excitons in a type-II structure, and for

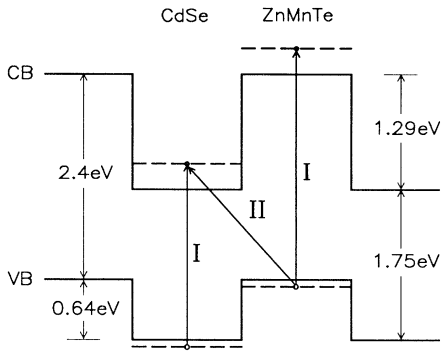

FIG. 1. Schematic diagram of the band alignment for CdSe/$Zn_{1-x}Mn_xTe$ superlattices. Dashed lines represent electron (hole) states confined in CdSe ($Zn_{1-x}Mn_xTe$) well layers, and electron (hole) states confined in $Zn_{1-x}Mn_xTe$ (CdSe) barrier layers at above-barrier energies. Arrows marked I and II represent possible lowest-energy transitions described in the text.

pinpointing the specific layers in which they are physically localized.

The samples involved in this work were grown by molecular-beam epitaxy (MBE) on (100) GaAs substrates. The CdSe/$Zn_{1-x}Mn_xTe$ superlattices were grown after depositing a 2-μm ZnTe buffer layer. The growth conditions were similar to those used for the growth of CdSe/ZnTe superlattices, described elsewhere.[6] The relevant sample parameters are summarized in Table I. All superlattices used here contain 20 periods of alternating CdSe and $Zn_{1-x}Mn_xTe$ layers. We have also grown two epilayers (EL1 and EL2) with the same Mn concentration as the $Zn_{1-x}Mn_xTe$ layers in two of the superlattices (SL1 and SL2, respectively) for determining the band gap of the $Zn_{1-x}Mn_xTe$ layers in those superlattices. Superlattices SL3 and SL4 were grown in one sample, separated by a 1800-Å ZnTe layer, with $Zn_{1-x}Mn_xTe$ layers having the same value of x but different thickness. The different layer thicknesses in the later two superlattices allow us to study the effect of quasi-2D confinement on states which are localized in the barrier layers.

In order to carry out transmission experiments, the GaAs substrates were removed from the samples by mechanical polishing, followed by selective etching using a 20:1 H_2O_2:NH_4OH solution at room temperature. All absorption experiments were carried out using circularly polarized light in the Faraday configuration, i.e, with both the magnetic field and the wave vector of the incident light parallel to the growth axis of the samples. The samples were placed in a temperature-variable (from 1.5 to 300 K) optical cryostat equipped with a 6-T superconducting magnet. The light source consisted of a halogen lamp and a monochromator. The monochromatic light was mechanically chopped, and standard lock-in detection was used to reduce the noise.

Figure 2 shows a low-temperature (1.5 K) absorption spectrum in the energy range of interest for SL1, observed in the absence and in the presence of an external magnetic field for both circular polarizations (σ_+ and σ_-). In zero magnetic field three clear excitonic absorption peaks were observed: at 1.807 eV [labeled E_1 in Fig. 2(a)], at 2.382 eV [labeled E_b in Fig. 2(b)], and at 2.441 eV [labeled E_2 in Fig. 2(b)]. The absorption coefficients of peaks E_1 and E_2 are estimated to be 3.7×10^4/cm and 2.2×10^4/cm, respectively, which are comparable with those of quantum-well exciton transitions from typical

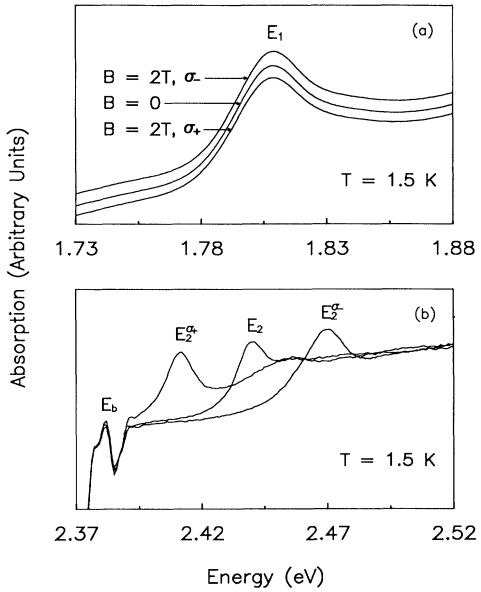

FIG. 2. The absorption spectrum of SL1 taken at 1.5 K with and without an external magnetic field (2 T) for two opposite circular polarizations. Type-I excitonic transitions confined in (a) CdSe layers and in (b) $Zn_{1-x}Mn_xTe$ layers are clearly seen. Spectra observed for the σ_+ and σ_- circular polarizations are slightly displaced vertically in (a), for clarity.

type-I II-VI superlattices [for example, the exciton absorption coefficient for ZnCdSe/ZnSe superlattice with comparable well thickness is about 1×10^5/cm (Ref. 7)]. We recall that CdSe/$Zn_{1-x}Mn_xTe$ is a type-II superlattice, with a valence-band offset of about 0.64 eV. From the bulk parameters of the constituent materials we estimate the lowest-energy type-II transition, i.e., the transition shown by line II in Fig. 1, to be around 1 eV. Unfortunately, we were not able to detect this transition because it is out of the range of our detector, but this will not affect the subsequent discussion. We can exclude the possibility that peak E_1 is an excited type-II transition, i.e., a transition between an excited (or ground) electron state confined in CdSe wells and a ground (or excited) hole state confined in $Zn_{1-x}Mn_xTe$ wells, because E_1 does not shift when an external magnetic field is applied, as shown in Fig. 2(a). At the same time we note that the energy of E_1 is higher than the band gap of cubic CdSe

TABLE I. Description of samples used in experiments.

Sample name	CdSe layer thickness (Å)	$Zn_{1-x}Mn_xTe$ layer thickness (Å)	x	Experiment E_1 (eV)	Experiment E_2 (eV)	Theory E_1 (eV)	Theory E_2 (eV)	Structure
SL1	80	130	0.06	1.807	2.441	1.806	2.440	Superlattice
SL2	200	130	0.10	1.760	2.465	1.761	2.465	Superlattice
SL3	55	160	0.03	1.861	2.415	1.861	2.415	Superlattice
SL4	55	90	0.03	1.861	2.434	1.861	2.433	Superlattice
EL1		19 000	0.06		2.426			Epilayer
EL2		8000	0.10		2.449			Epilayer

(1.75 eV). We thus assign E_1 to the lowest-energy type-I excitonic transition, i.e., a transition between the lowest electron state confined in the CdSe conduction-band well and the lowest above-barrier hole state confined in the CdSe valence-band barrier layer. Using similar arguments, the peak E_2 (whose energy is higher than the measured band gap of the companion epilayer $Zn_{0.94}Mn_{0.06}Te$, 2.426 eV) is attributed to the lowest-energy type-I (spatially direct) excitonic transition between the above-barrier electron state confined in the $Zn_{1-x}Mn_xTe$ barrier and the hole state confined in the ZnMnTe well. The peak E_b is the free exciton transition from the ZnTe buffer layer.

The difference between the magneto-optical behavior of the excitonic transitions E_1 and E_2 shown in Fig. 2 fully verifies the conclusion that E_1 occurs between states localized in CdSe, while E_2 originates and terminates on states localized in the DMS layers $Zn_{1-x}Mn_xTe$. When an external magnetic field is applied, the Zeeman splitting of the band edges in the DMS layers is much larger (typically by about 100 times at low temperatures) than that in the non-DMS layers, due to the *sp-d* exchange interaction between the band electrons and the *d* electrons associated with the Mn ions.[8] As can be seen in Fig. 2(b), when an external magnetic field (2 T) is applied, the type-I excitonic transition E_2 localized in the $Zn_{1-x}Mn_xTe$ layers shifts to higher energy (marked $E_2^{\sigma-}$, 29 meV above E_2) for incident right-circular polarization (σ_-), and to lower energy (marked $E_2^{\sigma+}$, 29 meV below E_2) for left-circular polarization (σ_+). In contrast, there is no observable shift for either of the circular polarizations in Fig. 2(a)—hence our conclusion that the E_1 transition takes place between states strongly localized in the nonmagnetic CdSe layer.

The low-temperature (1.5 K) absorption spectra observed for superlattices SL2, SL3, and SL4 are very similar to those already described for SL1. The lowest-energy excitonic transitions in zero magnetic field are summarized in Table I for all samples studied in this work. As in Fig. 2, E_1 in Table I represents the energy of the type-I excitonic transitions which take place in the CdSe layers, and E_2 represents the transition occurring in $Zn_{1-x}Mn_xTe$ layers. The thicknesses of $Zn_{1-x}Mn_xTe$ layers are the same in SL1 and SL2. Note that the energy of peak E_2 at zero magnetic field increases when the band gap of $Zn_{1-x}Mn_xTe$ layers is increased (by increasing the Mn content), again indicating that the E_2 transitions are indeed confined in the $Zn_{1-x}Mn_xTe$ layers. Furthermore, the Zeeman splittings of the E_2 transitions for both SL1 and SL2 are (within experimental error) the same as the band-edge splittings observed for the companion epilayers EL1 and EL2. This further confirms that the electron and the hole wave functions are almost entirely localized in $Zn_{1-x}Mn_xTe$ layers, demonstrating the formation of spatially direct (type-I) excitons in type-II superlattices.

Superlattices SL3 and SL4 were grown for the purpose of investigating the effect of varying the thickness of $Zn_{1-x}Mn_xTe$ layers of identical composition. Since the actual concentration of Mn in a ternary alloy can differ slightly from the nominal when prepared in different growths, we grew SL3 and SL4 in a single sample with different $Zn_{1-x}Mn_xTe$ thicknesses but the same value of x, in order to eliminate the uncertainty in the Mn concentration in the two specimens being compared. We see a single type-I excitonic transition at 1.861 eV from the CdSe layer (the thickness of CdSe is the same in both SL's) and, as we expected, two type-I excitonic transitions from the $Zn_{1-x}Mn_xTe$ layers (at 2.415 and 2.434 eV, respectively). To identify the origin of the individual $Zn_{1-x}Mn_xTe$ transitions, we etched away one of the superlattices. After etching, we observed only a single excitonic $Zn_{1-x}Mn_xTe$ transition, either from SL3 or from SL4, depending on which one was etched away. The Zeeman splittings of the two transitions are shown as a function of magnetic field in Fig. 3 by crosses and squares for the right- and left-circular polarizations, respectively. The behavior of the splittings originating from the two superlattices is the same, within experimental error, indicating that they take place in layers consisting of the identical $Zn_{1-x}Mn_xTe$ alloy.

The energy difference between the transitions observed in SL3 and SL4 is 19 meV. Before presenting exact numerical analysis of the data, we discuss this shift of E_2 in approximate terms, in order to identify the physical mechanism behind the observed dependence of E_2 on the $Zn_{1-x}Mn_xTe$ layer thickness. We recall that the E_2 transitions associated with the $Zn_{1-x}Mn_xTe$ layer are between hole states confined in the valence-band wells and electron states at above-barrier energies, confined in the conduction-band barrier. For a rough estimate of the confinement energy in the well, we use the infinitely deep well approximation, with the effective masses of bulk ZnTe,[9] and the thickness of the $Zn_{1-x}Mn_xTe$ layers. The estimated difference between the ground-state energies for the heavy holes in SL3 and SL4 is 5 meV. We attribute the remaining 14 meV of the total observed energy shift to the difference in the confinement energies for

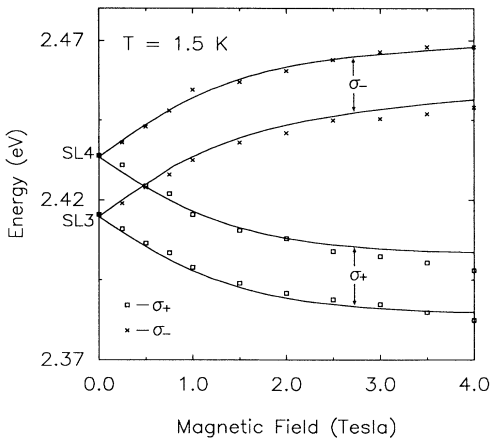

FIG. 3. Magnetic field dependence of the photon energies of the E_2 excitonic transitions confined in the $Zn_{1-x}Mn_xTe$ layers of SL3 and SL4. The squares and crosses represent experimental data for transitions observed with σ_+ and σ_- circular polarizations, respectively. Solid lines show theoretical fits calculated numerically, as discussed in the text.

the above-barrier electron states in the two superlattices.

Confinement of subbands at above-barrier has been shown to arise from the constructive interference condition given by[3,10]

$$k_b L_b = n\pi \ , \tag{1}$$

which is identical in form to the confinement condition of below-barrier (i.e., quantum-well) states, except that k_b and L_b represent the wave vector and width of the barrier instead of the well. Using the relation $k=\sqrt{2mE}/\hbar$, we then obtain the energy above the barrier of the subband localized in the barrier layer,

$$E_n = (\hbar^2/2m_b^*)(n\pi/L_b)^2 \ , \tag{2}$$

where m_b is the effective mass of the barrier material and n is an integer. By using the ZnTe effective mass for $Zn_{1-x}Mn_xTe$ (Ref. 9) and the thicknesses of SL3 and SL4, we estimate from Eq. (2) that the difference between the electron confining energies for SL3 and SL4 is about 18 meV. This value is 4 meV larger than the 14 meV estimated from the experimentally observed shift discussed above. The physical reason for the difference arises in part from the assumption made in deriving Eq. (1) that the electrons experience total reflections at the interfaces,[3,10] which is an idealization. From rigorous calculation that will be described below, the energy difference between the hole states for SL3 and SL4 is 4.4 meV, and between the above-barrier electron states is 14.2 meV, yielding a total shift of 18.6 meV, in excellent agreement with experimental data.

The mechanism of localization just discussed for the above-barrier electron states also applies to hole states at above-barrier energies. Localization of such hole subbands in valence-band barriers is again confirmed by the observation of type-I excitons confined in CdSe layers in all superlattices listed in Table I at room temperature and below [recall Fig. 2(a)]. It is interesting that for SL1 the full width at half maximum of peak E_1 is increased only slightly as the temperature increases (from 38 meV at 1.5 K to 52 meV at room temperature). We note that the observation of a room-temperature excitonic absorption peak in another system, ZnCdSe/ZnSe type-I multiple quantum wells, has been attributed to the enhancement of confinement by two-dimensional (2D) effects (reduction of exciton radius in the confining wells).[7] Similarly, for the case of $CdSe/Zn_{1-x}Mn_xTe$ type-II superlattices we argue that the 2D effect increases the electron-hole Coulomb interaction due to the strong confinement of both the electrons in the CdSe well, and of the above-barrier holes in the CdSe barriers. This in turn results in the survival of the spatially direct type-I exciton up to room temperature. The excitonic features confined in $Zn_{1-x}Mn_xTe$ layers, on the other hand, disappear above about 200 K, most likely due to the weaker confinement, because the exciton is more three- than two-dimensional in character due to the greater thickness of the $Zn_{1-x}Mn_xTe$ layers (130 Å).

We have performed theoretical fits to the experimental data for all superlattices involved in this work, using accurate band-structure calculations in the $\mathbf{k}\cdot\mathbf{p}$ approximation (with the conduction, valence, and spin-orbit bands included[11]). In our calculations we have employed the experimentally determined energy gaps for $Zn_{1-x}Mn_xTe$ and cubic CdSe, with the remaining parameters of the model (E_p, Δ, γ_1, γ_2, γ_3, κ) estimated for these materials from literature bulk values.[9,12] In calculating the transition energies corresponding to E_1 and E_2, we used the layer thicknesses as adjustable parameters. Note that the transition energy E_1 is predominantly determined by the CdSe thickness, being relatively insensitive to the thickness of the $Zn_{1-x}Mn_xTe$ layers, while the reverse is true for E_2. The theoretical values of E_1 and E_2 for zero magnetic field are summarized in Table I.

In order to calculate the behavior of the transition energies in an external magnetic field, including the effect of exchange interaction between the band electrons and the localized Mn spins in the $Zn_{1-x}Mn_xTe$ layers, the $\mathbf{k}\cdot\mathbf{p}$ program was modified to include the exchange Hamiltonian,

$$H_{ex} = x_{eff} N_0 J \sigma_z \langle S_z \rangle \ , \tag{3}$$

where x_{eff} is the effective Mn concentration, N_0J is the exchange integral appropriate either for the conduction or for the valence band, σ_z is the electron spin, and $\langle S_z \rangle$ is the thermally averaged Mn spin given by

$$\langle S_z \rangle = -\tfrac{5}{2} B_{5/2}[5\mu_B B/k_B(T+T_0)] \ . \tag{4}$$

Here $B_{5/2}$ is the Brillouin function of the argument in square brackets, μ_B the Bohr magneton, B the applied magnetic field, k_B the Boltzmann constant, T the temperature, and T_0 a parameter representing antiferromagnetic interactions between the Mn ions.[13] In calculating the Zeeman shift of the observed transitions, we have used the literature values of the exchange integrals for the conduction and the valence bands,[8] and have treated x_{eff} and T_0 as adjustable parameters. It should be noted that x_{eff} determines primarily the magnitude of the Zeeman shift, and T_0 the curvature of its magnetic field dependence due to saturation of the Mn spin system. The theoretical fits for SL3 and SL4 transition energies in an external magnetic field for both circular polarizations are shown as solid curves in Fig. 3.

In summary, we have observed two distinct type-I (spatially direct) excitons in $CdSe/Zn_{1-x}Mn_xTe$ type-II superlattices, localized either in the CdSe or in the $Zn_{1-x}Mn_xTe$ layers. The $Zn_{1-x}Mn_xTe$ exciton shows a very large Zeeman shift, while the CdSe exciton is unaffected by the applied magnetic field, providing a direct indication of where the respective excitons are localized in space. By changing the thicknesses of the $Zn_{1-x}Mn_xTe$ layers, we observe the resulting shift of the confinement energy for the hole state localized in the well and for the electron state localized in the barrier, both of which comprise the type-I exciton associated with the $Zn_{1-x}Mn_xTe$ layer. We have also calculated the type-I transition energies and their Zeeman splittings, and find them to be in remarkably good agreement with the experimental data.

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