Observation of Localized Above-Barrier Excitons in Type-I Superlattices

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This Letter reports experimental evidence for the existence of *localized* excitons at above-barrier energies in type-I superlattices. By using magnetoabsorption measurement on a series of $Zn_{0.86}Cd_{0.14}Se/Zn_{0.75}Mn_{0.25}Se$ superlattices, where the subbands localized in nonmagnetic and magnetic layers undergo drastically different Zeeman splittings, we show conclusively that above-barrier excitons are localized in the *barrier* rather than in the well regions.

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In studies of semiconductor superlattices carried out so far, the focus of attention has generally been on energy states below the barriers, i.e., on conduction and valence subbands confined *in the wells* of the superlattice. Although the existence of above-barrier subbands in superlattices has been recognized for a long time [1], theoretical understanding of such subbands has been largely limited to numerical calculations of eigenstates and optical transition probabilities [2,3]. Optical transitions involving above-barrier states have also been observed experimentally in $GaAs/Ga_{1-x}Al_xAs$ superlattices, either by Raman spectroscopy [4] or by photoluminescence excitation spectroscopy [3]. While it was recognized that the above-barrier subbands can form excitons, it was assumed that such above-barrier excitons are delocalized [4].

In this Letter we present evidence that above-barrier excitons can in fact be *localized* (or confined), and that in type-I superlattices the regions of localization are the *barrier layers*. To accomplish this, we use magnetotransmission spectroscopy on superlattices formed from alternating nonmagnetic and diluted magnetic semiconductor (DMS) layers [5]. In such structures the Zeeman splitting of states localized in the DMS regions is considerably larger than in non-DMS regions (on the scale of tens of meV) [6,7]. This difference in behavior in different layers can be exploited to pinpoint the localization in space of subbands taking part in specific transitions.

The mechanism of localization of electrons at above-barrier energies can be physically understood as follows. A electron wave traveling in the barrier region experiences a reflection as it reaches the barrier-well interface, similarly to the case of below-barrier electrons traveling inside the well. Just as for electrons in the wells, the constructive interference condition will have a strong effect on the shape of the above-barrier electron wave function. A simple calculation using the Kronig-Penney model reveals that this condition in fact leads to a strong *localization* of the wave function in the *barrier* region, which can be as strong as (or even stronger than) that for the states at below-barrier energies, localized in the wells. Our analysis shows that the condition of localization corresponds to the constructive interference condition, i.e.,

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

where $k_b = 1/\hbar (2m^* E)^{1/2}$ is the wave vector in the barrier region, L_b the barrier width, and n an integer. The energy E (relative to the top of the barrier) that corresponds to the localized above-barrier states can be obtained from Eq. (1). Our numerical results show that the integrated probability of the lowest above-barrier state in the barrier (which provides measure of localization) can be as large as (or larger than) the integrated probability of the ground state in the wells. In a type-I superlattice, a localized exciton can therefore form between such a localized above-barrier electron in the conduction band and a localized above-barrier hole in the valence band, whose wave functions are schematically shown in Fig. 1. As is clear from the figure, such an exciton will be localized in the barriers.

We investigated three $Zn_{0.86}Cd_{0.14}Se/Zn_{0.75}Mn_{0.25}Se$ superlattices, with the concentrations of Cd and Mn so chosen as to give type-I band alignment (band offset being 210 meV for the conduction band and 40 meV for the valence band) [8]. This provided an opportunity to examine the behavior of above-barrier subbands in a type-I superlattice. The superlattices were grown by molecular beam epitaxy (MBE) on (100) GaAs substrates, after deposition of a ZnSe buffer layer. The details of the growth are given elsewhere [9]. The superlattices contained alternating ZnCdSe layers (wells) and ZnMnSe layers (barriers). The well widths in the three superlattices (referred to subsequently as SL1, SL2, and SL3) were 60, 85, and 130 Å, respectively, and the barrier width was kept the same ($L_b = 85$ Å) in all three cases. The number of periods in the three superlattices were 100, 85, and 65 in SL1, SL2, and SL3, respectively. We emphasize that the prediction of exciton localization in the barriers of type-I superlattices is universal, and our

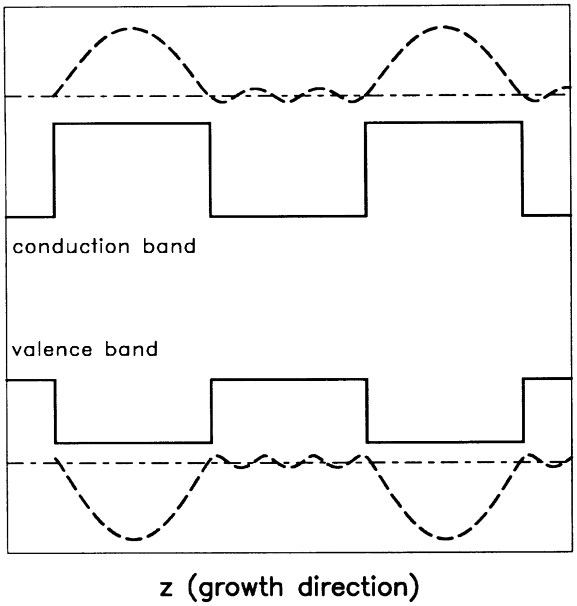

FIG. 1. The band structure of a type-I superlattice (solid lines) and the wave functions (dashed lines) of the first above-barrier subbands both in the conduction band and in the valence band are schematically plotted. The eigenenergies at the center of the superlattice Brillouin zone, which correspond to the wave functions shown, are plotted by the dash-dotted lines. The localization of the subbands shown results in the formation of above-barrier excitons localized in the barrier regions of the superlattice.

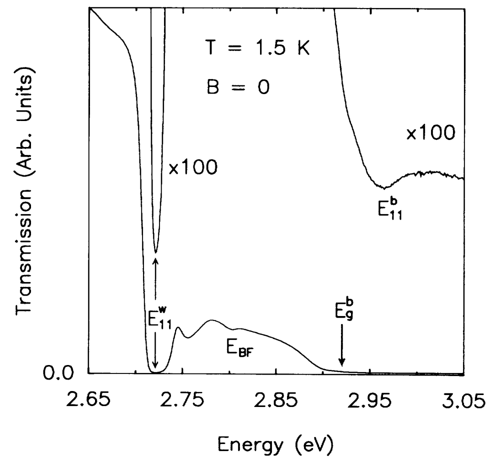

FIG. 2. Transmission spectrum of a $Zn_{0.86}Cd_{0.14}Se$/$Zn_{0.75}Mn_{0.25}Se$ superlattice (SL1) observed at 1.5 K and zero magnetic field. The peak labeled E^w_{11} is the excitonic transition associated with the lowest heavy-hole and electron subbands ($N=1$) confined in the wells; E_{BF} is the excitonic transition from the ZnSe buffer layer; and E^b_{11} is the excitonic transition associated with the lowest above-barrier heavy-hole and conduction electron subbands. The arrow labeled E^b_g indicates the energy gap of the barrier material, obtained from a $Zn_{0.75}$-$Mn_{0.25}Se$ epilayer.

choice of a DMS/non-DMS structure was dictated only by the possibility of identifying the layers in which specific optical transition actually take place.

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 the magnetic field and the wave vector of incident light both parallel to the growth axis of the sample. 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) transmission spectrum for SL1 in the absence of magnetic field. Several excitonic absorption peaks are observed. We identify the peak at 2.721 eV (labeled E^w_{11}) as the free exciton transition between the first heavy-hole subband and the first electron subband (the ground state below the barriers) of the superlattice, and the peak at 2.802 eV (labeled E_{BF}) as the free exciton transition from the ZnSe buffer layer. We also measured the transmission spectrum of an epitaxial film of $Zn_{0.75}Mn_{0.25}Se$ grown under exactly the same conditions as those for the barriers of the superlattices, which determines the band edge of the barriers as 2.920 eV (marked as E^b_g) [10]. In Fig. 2, the energy of the peak labeled E^b_{11} is 2.965 eV, which is larger than E^b_g. The shape and sharpness of this peak suggest that it is also an excitonic transition. Since $Zn_{0.75}Mn_{0.25}Se$ is present in the sample only in the barriers of the superlattice (i.e., not in the buffer layer, nor in the cap layer), all the states associated with $Zn_{0.75}$-$Mn_{0.25}Se$ are described by the subbands of the superlattice. Therefore we identify transition E^b_{11} as between the first above-barrier heavy-hole state and the first above-barrier electron state (the lowest-energy above-barrier transition). In the following we will focus on E^b_{11} and E^w_{11} peaks, and we will not concern ourselves with the other peaks in Fig. 2.

Magnetotransmission data on the ZnCdSe/ZnMnSe superlattices studied here fully verify the theoretical analysis already discussed, as argued below. When an external magnetic field is applied, the band edges of the ZnMnSe barrier will be Zeeman split, leading in turn to the splitting of optical transitions in the superlattice. Figure 3 shows the energies of the E^w_{11} and E^b_{11} transitions as a function of the magnetic field observed in SL3. Also shown in the figure is the splitting of the exciton line observed in the epilayer of $Zn_{0.75}Mn_{0.25}Se$ having the same Mn concentration as the barriers in SL3, and already used to determine E^b_g in Fig. 2. It is significant that the

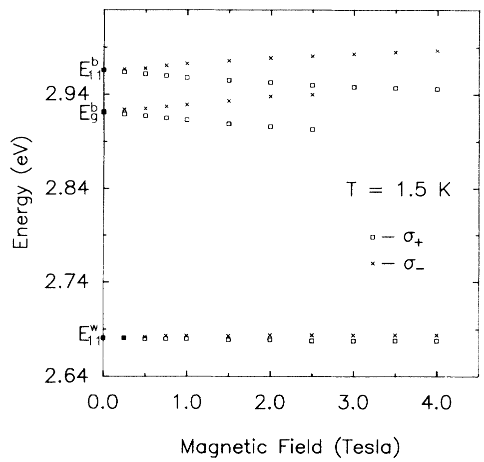

FIG. 3. Spin splittings of the excitonic transitions E_{11}^{w} and E_{11}^{b}, and of the E_g^b transition obtained from a $Zn_{0.75}Mn_{0.25}Se$ epilayer, as a function of magnetic field. The crosses are obtained with σ_- circular polarizations and represent transitions between spin-up states; the squares correspond to σ_+ polarizations and represent transitions between spin-down states.

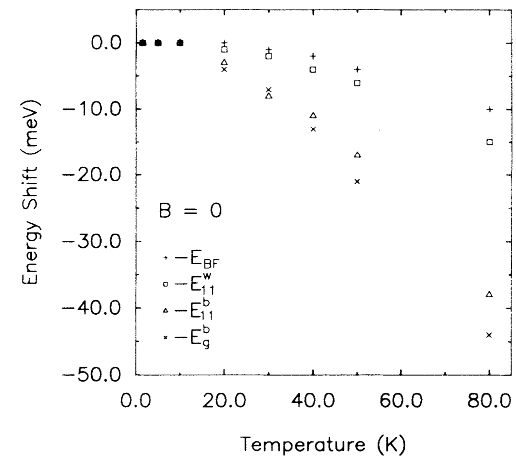

FIG. 4. Energy shifts of the excitonic transitions E_{BF} (ZnSe buffer), E_{11}^{w} (lowest well-to-well transition), E_{11}^{b} (lowest-energy above-barrier transition), and E_g^b ($Zn_{0.75}Mn_{0.25}Se$ epilayer) as a function of temperature. All shifts are measured relative to transition energy of the respective line observed at 1.5 K.

spin splitting of the above-barrier transition E_{11}^{b} is clearly larger than that of the below-barrier transition E_{11}^{w}, and almost (but not quite) as large as that in the ZnMnSe epilayer.

We recall that the structures investigated in this Letter are type-I superlattices, consisting of nonmagnetic wells and magnetic barriers. The relatively small (but observable) Zeeman splitting of the ground-state exciton transition E_{11}^{w} (which originates and terminates in the nonmagnetic wells) thus arises from the partial penetration of the wave functions of the initial and final states into the magnetic barriers [8]. By contrast, the much larger Zeeman splitting of E_{11}^{b} (almost the same as that for "bulk" $Zn_{0.75}Mn_{0.25}Se$ material) indicates that the E_{11}^{b} transition originates and terminates on states localized predominantly in the DMS (i.e., barrier) region. The fact that the splitting of E_{11}^{b} is slightly (about 15%) below that in the $Zn_{0.75}Mn_{0.25}Se$ epilayer indicates that a small part of the wave function extends into the non-DMS layers, again in accord with the picture shown in Fig. 1. The data shown in Fig. 3 are very similar to those observed on SL1 and SL2, and provide direct evidence that the above-barrier exciton in a type-I superlattice can be localized in the barrier layers.

Additional corroboration that the wave functions of the above-barrier states reside primarily in the barrier layers is obtained as follows. We recall that the energy gaps of wide gap II-VI semiconductors decrease as the temperature increases. Furthermore, the zero field energy gap of a II-VI–based DMS changes faster than that of non-DMS materials due to the exchange interaction [11]. The temperature dependences of the transitions E_{11}^{w}, E_{BF}, E_g^b, and E_{11}^{b} in SL1 in the absence of the magnetic field are shown in Fig. 4. The data clearly indicate that the energy shift with increasing temperature of the first above-barrier excitonic transition E_{11}^{b} is larger than that of the first below-barrier excitonic (ground-state) transition, and follows closely the temperature dependence of the energy gap E_g^b of the $Zn_{0.75}Mn_{0.25}Se$ epilayer, again showing that the behavior of E_{11}^{b} is more "barrierlike" as compared to E_{11}^{w}, which must necessarily reflect the properties of the (nonmagnetic) well material.

To confirm our arguments, we have calculated the wave functions and the energies of the ground states below the barriers and of the lowest states above the barriers in $Zn_{0.86}Cd_{0.14}Se/Zn_{0.75}Mn_{0.25}Se$ superlattices, using accurate band-structure calculation in the $\mathbf{k}\cdot\mathbf{p}$ approximation (with the conduction band, the valence bands, and the spin-orbit-split band included [12]) and parameters corresponding to our samples [8]. For the ground states, most of the wave function is confined in the well regions (as of course is expected). In contrast, for the lowest states above the barriers most of the wave function in the valence as well as in the conduction bands is confined in the barrier regions, resulting in the formation of the excitons localized in the barrier layers. The calculated energies are also in good agreement with the assignment of the transitions. The discussion of the numerical results, and detailed fitting of all the optical transitions shown in Fig. 2 with and without magnetic field, will be given in a more extensive paper.

In summary, we have compared the Zeeman splittings in $Zn_{0.86}Cd_{0.14}Se/Zn_{0.75}Mn_{0.25}Se$ superlattices for the above-barrier exciton transition with that for the ground-state exciton, and we compared the temperature dependence of the two transitions. Both observations show that the above-barrier transition is determined primarily by the barrier layer parameters, indicating that the wave functions of the above-barrier subbands are localized in the barriers, in excellent agreement with theoretical predictions.

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