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Interface localization of excitons in CdTe/$Cd_{1-x}Mn_xTe$ multiple quantum wells

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Photoluminescence in undoped CdTe/$Cd_{1-x}Mn_xTe$ multiple quantum wells at low temperatures shows highly efficient excitonic emission. By studying the emission spectra as a function of temperature, external magnetic field, and its dependence on well thickness, we have obtained strong evidence for the importance of the heterointerface in providing centers of localization for excitons in these strained-layer structures.

Recently, the growth of good quality $Cd_{1-x}Mn_xTe$/$Cd_{1-y}Mn_yTe$ multiple quantum wells (MQW) has been realized by molecular-beam epitaxy (MBE) techniques, and strong near-band-gap photoluminescence has been observed in these structures.[1-3] The $Cd_{1-x}Mn_xTe/Cd_{1-y}Mn_yTe$ quantum wells are examples of strained-layer superlattices with low dislocation densities, but with additional magnetic properties anticipated from the presence of the magnetic ion Mn^{2+}. The observed high quantum efficiency of radiative recombination in these structures poses a question about the origin of this emission, and the role of enhancement possibly provided by quantum-well confinement effects similar to those influencing exciton recombination, e.g., in $GaAs/Ga_{1-x}Al_xAs$ superlattices. In this Rapid Communication, we present results of spectroscopic studies which strongly suggest that, apart from any confinement effects, localization of excitons at interfaces of the $Cd_{1-x}Mn_xTe$/$Cd_{1-y}Mn_yTe$ heterojunction provides a strong mechanism for predominantly radiative recombination. We conjecture that the localization takes place in potential wells caused by random strain and compositional fluctuations at the heterointerfaces, and that it may be a general feature in strained-layer superlattices.

We have performed standard photoluminescence, reflectance, and some excitation spectroscopy on a number of undoped $Cd_{1-x}Mn_xTe/Cd_{1-y}Mn_yTe$ MQW samples, grown at Purdue University. The structures were fabricated on [100]-oriented GaAs substrates with the direction of growth in the [111] direction.[1] The quantum-well samples contained typically 100 heterolayer pairs on an approximately 2-μm-thick buffer layer. Electron microscopy shows that sharp and well-defined interfaces on the scale of a lattice parameter were obtained, with low dislocation densities, in the strained-layer MQW's.[4] In this Rapid Communication we present explicit results for those samples where the Mn concentration was zero in the wells. This choice is useful as it permits a simpler and clearer interpretation of the influence of an externally applied magnetic field, as shown below.

Figure 1 shows photoluminescence spectra at $T=1.8$ K for two CdTe/$Cd_{0.70}Mn_{0.30}Te$ MQW samples, together with a reference spectrum obtained from high-quality bulk CdTe. Low-intensity excitation (<1 mW) was applied at a photon energy of 2.110 eV. The samples denoted as SL-9 and SL-8 had approximate CdTe well widths of 650 and 57 Å, respectively. The barrier width for SL-9 was about 650 Å and that for SL-8 about 114 Å. The bulk CdTe sample shows, under moderate spectral resolution, a free-exciton peak (correlated also through reflectance spectra) and a dominating impurity bound exciton line. In the MQW sample SL-9, reflectance spectra showed a free-exciton-like feature coinciding with the higher-energy luminescence peak centered at 1.594 eV, very near the value for the transverse free-exciton energy in bulk CdTe. The ratio of the free-exciton amplitude to that of the broader lower-energy feature, as well as the energy position of the latter, was found to depend on the beam spot location on the sample. We note that for the rather thick layers in SL-9, the probability of elastic accommodation of the lattice constant mismatch (approximately 0.6%) over the entire structure decreases, thus leading to expected [confirmed by transmission electron microscopy (TEM)] formation of dislocations. It was considerably more difficult

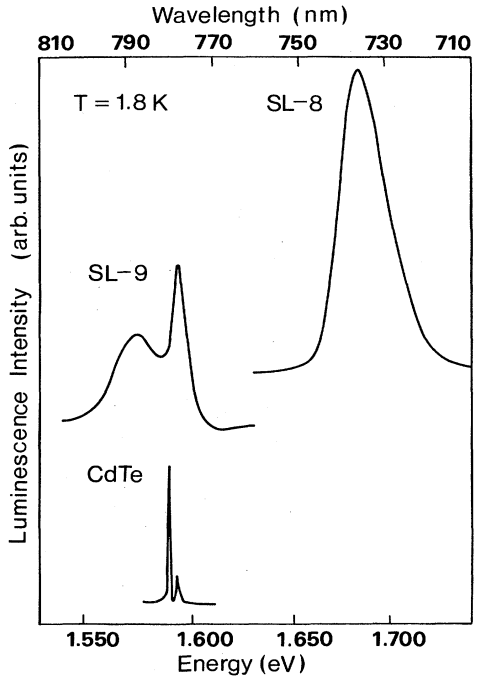

FIG. 1. Photoluminescence spectra at 1.8 K for two CdTe/$Cd_{0.70}Mn_{0.30}Te$ MQW samples (well widths 57 Å for SL-8 and 650 Å for SL-9) in comparison with high-quality bulk CdTe.

to obtain the free-exciton edge for SL-8 from reflectance data which now showed an appreciably broadened resonance at roughly 1.73 eV. Excitation spectra on other narrow well samples ($d < 100$ Å) also showed a rather broad free-exciton edge. From such measurements we have deduced that the high-energy tail of the emission spectrum of SL-8 merges gradually into the free-exciton region. The amplitudes of the three spectra in Fig. 1 are in the same relative units, and clearly show the large enhancement of radiative efficiency (integrated area) in the MQW samples, particularly for SL-8. Other narrow well samples showed similar, high-efficiency emission from a comparably dominant 25–30-meV-wide feature below a broadened free-exciton edge.

To elucidate further the origin of the observed photoluminescence, we have studied spectra such as those in Fig. 1 as a function of temperature and external magnetic field. Figure 2 shows the temperature dependence of the spectrum of the 650-Å-wide well sample SL-9, taken at a location on the sample where the free-exciton emission at the lowest temperature was weaker than that originating from the broader low-energy peak. The lower-energy peak shows rapid quenching with temperature in the range 1.8–40 K, with an associated and clearly discernible red shift much in excess of the band-gap shrinkage. In contrast, the free-exciton amplitude (and spectral position) is only moderately affected in the same temperature regime, consistent with the binding energy of approximately 11 meV in bulk CdTe. Similar examination of the dominant emission in sample SL-8 (57-Å well) and other narrow well samples showed only a weak temperature dependence of the amplitude and line shape up to 100 K, suggesting thus a much more effective "binding" in this excitonic emission than that for the lower-energy peak in SL-9.

The influence of an external magnetic field is shown in Fig. 3, where the positions of the luminescence peaks are shown for sample SL-9 (on left) and SL-8 (on right) at 1.8 K. The luminescence was collected in a direction perpendicular to the MQW layer planes and was analyzed for its polarization content. The free-exciton peak in SL-9 showed little shift up to 40 kG, consistent with the known electron and hole g factors in bulk CdTe. In striking contrast, a much larger red shift occurred for the lower-energy peak with the field perpendicular to the layer plane. The degree of preferred circular polarization (σ_+) at 40 kG was approximately 0.30 (Faraday configuration). With the field oriented parallel to the layer plane the shifts were much smaller with a mixture of σ_- and π polarization (Voigt configuration). In the case of sample SL-8, even larger field-induced red shifts were observed in Faraday configuration, with the degree of circular polarization about 0.84 at 40 kG. Again, with the field in the layer plane, the shifts were significantly smaller. It is noteworthy that very little change was observed in the emission line shapes throughout the field experiments at 1.8 K.

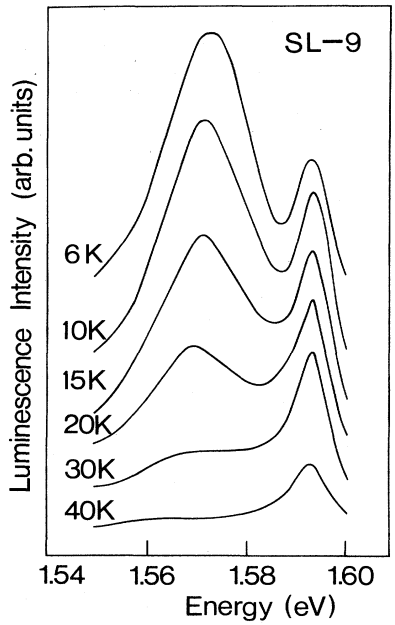

FIG. 2. Temperature dependence of luminescence of the wide well sample SL-9.

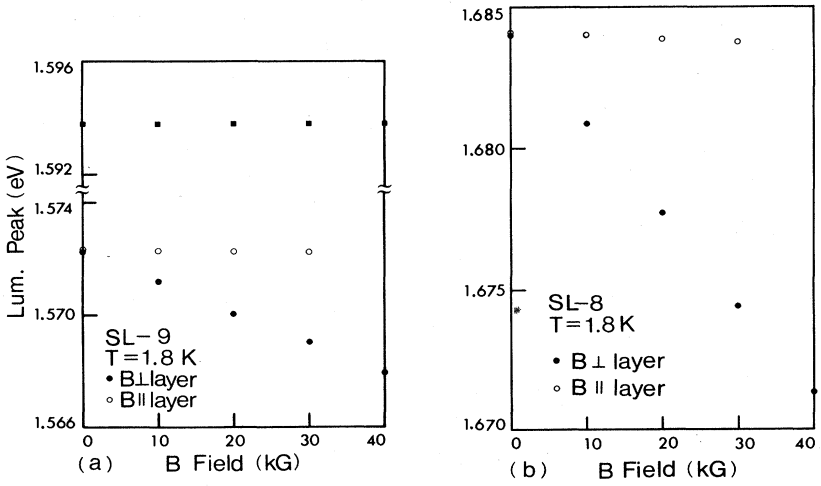

FIG. 3. Effect of the magnetic field on the position of the luminescence peaks (a) in sample SL-9, and (b) in sample SL-8 at 1.8 K. Field orientation with respect to the MQW layer plane is indicated. In (a) the free-exciton peak is shown as black squares.

The experimental results outlined above display a range of physical attributes of interband excitations in the $CdTe/Cd_{1-x}Mn_xTe$ quantum wells. In this Rapid Communication, however, we wish to limit the discussion mainly to those aspects which are of importance in supporting our arguments of the role of the heterointerfaces in possible localization of excitons.

At present there is no conclusive data to indicate what the precise relative conduction- and valence-band offsets are in the $CdTe/Cd_{1-x}Mn_xTe$ structures. However, there is no apparent reason to doubt that these superlattices are not of type I. Part of the quantitative problem is due to the contribution of strain from lattice constant mismatch between the successive layers as well as from the GaAs-substrate–buffer-layer interface. The [111] growth direction makes strain estimates cumbersome and we have had only mediocre success in matching energies obtained from unstrained free-exciton quantum-well calculations (e.g., along the lines of Ref. 5) with crude estimates made for strain corrections. Following the removal of the GaAs substrate by selective etching, we have observed energy shifts and linewidth narrowing of the spectra in the narrow well samples (such as SL-8 in Fig. 1) by a few meV. The substrate appears thus not to be the dominant factor in determining the quantum-well electronic energies. We also note the apparent success with which the absorption and luminescence spectra of the $GaAs/GaAs_{1-x}P_{1-x}$ strained-layer superlattice has been theoretically analyzed,[6] although on an energy scale coarser than one considered here.

The spectra for sample SL-9 in Fig. 1 unambiguously shows the presence of a free exciton as well as strong emission immediately below it. The pronounced amplitude decay with increasing temperature and the associated spectral red shift (Fig. 2) suggest some form of exciton localization within a range of continuous states below the free-exciton edge. Apart from impurity effects, notably similar behavior has been observed in several mixed (bulk) crystals, interpreted as exciton localization by weak crystalline disorder.[7] Alloy potential fluctuations, originating from compositional fluctuations can trap an exciton as a whole in an appropriately sized local energy minimum, or selectively capture the hole (or electron) with the electron (hole) maintaining the Coulomb correlation.[8] In our case of CdTe quantum wells, such fluctuations in composition would not be expected to be of importance unless an exciton were sufficiently near the $Cd_{0.70}Mn_{0.30}Te$ interface. Of course, trapping of the free excitons (approximately 60 Å Bohr radius) at defects somewhere else within the well would still appear to be a very likely alternative at this point or our argument. By considering a multiple trapping process as the mechanism for thermally activated amplitude decay, we have made a simple model calculation along the lines of Sasaki, Serizawa, and Nishino[7] with an assumed effective mobility edge in sample SL-9 at about 1.59 eV. A rough agreement (limited by uncertainties about strain effects) can be reached with the temperature-dependent spectra of Fig. 2 for an exponential density of states with 5-meV half-width, if an average additional energy loss of some 5 meV during energy relaxation within a set of localized states is assumed to take place by a mechanism such as tunneling by acoustic phonons. Tunneling is, however, by no means the only mechanism for the additional energy adjustment which appears to be required by our model; in particular, polaronic effects may well play an important role. We extend these arguments to the narrow well samples such as SL-8 where our data suggest excitonic localization which is further enhanced by quantum-well confinement effects. While the linewidth of emission in SL-8 is broader than of what we consider to be a corresponding feature in SL-9, its occurrence farther down on the free-exciton tail and a considerably higher threshold for thermal quenching implies a greater degree of localization and/or self-energy adjustment. The high radiative efficiency and the lack of a sharp free-exciton edge further suggest that the localization is not associated with a defect center such as a impurity, again bringing up the possibility of the fluctuating potentials in the region of the heterointerface.

These suggestions about the role of the interface in localizing excitons are considerably strengthened when we consider the magnetic-field-dependent data in Fig. 3. In the Faraday geometry, the observed shifts at 1.8 K are much in excess of those expected for the exciton spin splitting in bulk CdTe. At the same time, the large magneto-optical effects in bulk $Cd_{1-x}Mn_xTe$ have been thoroughly studied, their strength often expressed through the "giant" effective g factor. We can make a simple estimate about the expected magnitude of the spin splitting for an exciton whose wave function is symmetrically distributed in the CdTe well while considering the extent of its evanescent tails into the $Cd_{0.70}Mn_{0.30}Te$ barrier (assuming sharp interfaces and that the electron and the hole occupy the lowest $n=1$ quantum-well levels). Ignoring the electron-hole exchange, we write schematically for the exciton-Mn-ion exchange part of the Hamiltonian in the $|j,m_j\rangle$ electron-hole representation

$$H_{\text{exch}}=-\alpha\sum_i(\mathbf{s}_e\cdot\mathbf{S}_i)|F_e(\mathbf{R}_i)|^2+\frac{\beta}{3}\sum_i(\mathbf{j}_h\cdot\mathbf{S}_i)|F_h(\mathbf{R}_i)|^2, \quad (1)$$

where α and β refer to the conduction- and valence-band exchange constants in $Cd_{0.70}Mn_{0.30}Te$, $\mathbf{s}_e$ and $\mathbf{j}_h$ the electron spin and hole angular momentum operators, $\mathbf{S}_i$ the Mn-ion spin moments, and $F_e(\mathbf{R}_i)$ and $F_h(\mathbf{R}_i)$ the envelope parts of the electron and hole wave functions, respectively. Here, the summation over i implies that only the evanescant tails of the envelope functions are contributing. For purposes of estimating the maximum shift we further assume that at 40 kG and 1.8 K the spin splitting leads to dominantly σ_+ recombination at the $|\frac{1}{2},-\frac{1}{2}\rangle$ to $|\frac{3}{2},-\frac{3}{2}\rangle$ transition, with $N_0\alpha=220$ meV and $-N_0\beta=880$ meV, respectively.[9] In this way we find that the experimentally observed shifts are more than two orders of magnitude larger for SL-9 and about one order of magnitude larger for SL-8 than estimates based on symmetrical electron-hole wave functions in the wells. We thus have strong evidence that significant portions of the exciton wave function must reside preferentially within the interface region. While the spin splitting is numerically smaller for sample SL-9 than it is for SL-8, it is particularly dramatic for the former considering the ratio of the well width to the free-exciton radius of approximately 10. In the estimate we have somewhat arbitrarily assumed that the 477-meV band-gap difference between CdTe and $Cd_{0.70}Mn_{0.30}Te$ is accommodated between conduction and valence bands in the ratio of 3 to 1. Our conclusion, however, is not altered by this specific assumption in any significant way. The less than complete circular polarization observed in the Faraday geometry is probably due to the fact that the emission linewidths in samples SL-8 and SL-9 are substantial in comparison with the magnetic-field-induced shifts and thus imply the admixture of other (j,m_j) transitions to the luminescence. We have also ignored the

heavy-hole–light-hole exciton and the possible strain-induced splitting of the $J=\frac{3}{2}$ valence band which may be of importance as well.

We now briefly consider the possible origins for preferred localization of excitons at the heterointerfaces in the $CdTe/Cd_{1-x}Mn_xTe$ quantum wells. The remarkably high quantum efficiency in our narrow well samples does not suggest that impurity effects at interfaces are likely because of the usually rather strong internal Auger recombination usually associated with such bound excitons in the bulk. An isoelectronic impurity could be important but there is little evidence of preferred impurity aggregation at the interfaces in the $CdTe/Cd_{1-x}Mn_xTe$ structures. On the other hand, localization in narrow $GaAs/Ga_{1-x}Al_xAs$ quantum wells has been recently shown to occur from well width fluctuations.[10] We can readily estimate that well width fluctuations are not a primary mechanism for the kind of interface localization our data imply. Bastard and collaborators have made recent calculations where specific model geometries of structural imperfections at $GaAs/Ga_{1-x}Al_xAs$ interfaces have been used to estimate exciton localization energies.[11] Since the origin of most such imperfections are the compositional fluctuations, the question here concerns their role in the specific case of the $CdTe/Cd_{1-x}Mn_xTe$ strained-layer superlattice, namely, the variations in the Mn-ion density near the interface. Studies through transmission electron microscopy by Otsuka *et al.* show an abrupt interface (with a change in the perpendicular component of the lattice constant) on the scale of a lattice constant.[4] We are thus concerned with an interface region of approximately this thickness, and the fluctuations in its electronic potentials along the plane of the interface. If we look for localization of the exciton center-of-mass motion, the Fourier components in the fluctuation spectrum which are comparable to the exciton Bohr volume are usually the most important in the bulk case.[7] Presently, however, the quasi-two-dimensional aspect will be important and a modified set of criteria needs to be developed for localization.[10] Furthermore, at the $CdTe/Cd_{1-x}Mn_xTe$ interface, preferred initial localization of either the hole or the electron could take place, while the Coulomb correlation remained to maintain an excitonlike entity.

In a mixed crystal, the first-order correction by concentration fluctuations $\delta x(\mathbf{r})$ to the virtual-crystal approximation can be simply expressed for lowest interband transitions through $dE_g(\mathbf{r})=(dE_g/dx)dx(\mathbf{r})$, from which an average spread in, e.g., the free-exciton resonance can be trivially estimated for a statistially distributed cation concentration in the bulk case.[12] In the present case, a rough range of the density of states in the low-energy tail of a free exciton can be similarly estimated, but the criteria for localization would critically depend on the details of the exciton wave function. Furthermore, we conjecture that the local fluctuations in interface strain which accompany concentration fluctuations in a strained-layer superlattice, can provide the exciton or single-particle (hole) attractive potentials in question. The details of such strain fluctuations are expected to be closely related to any reconstruction which may occur at the $CdTe(111)/Cd_{1-x}Mn_xTe$ interface. At the same time, such characteristics may be common to many strained-layer superlattices involving mixed crystals.

We only list here some of the other issues associated with the observed excitonic luminescence in $CdTe/Cd_{1-x}Mn_xTe$ which will be addressed elsewhere and which require further experimental study. The rather broad linewidths show at least a partially inhomogeneous character as determined from real time spectral diffusion.[13] Nevertheless, we cannot rule out polaronic effects which can originate either from enhanced exciton-phonon coupling or exchange effects similar to those leading to magnetic polarons in bulk semimagnetic semiconductors.[14] The observed anisotropy in the magnetic field-induced shifts (Fig. 3) appears to be well in excess of that expected from the simple difference in Faraday and Voigt configurations. This implies, for example, an unusually configured exciton or that the effective magnetic susceptibility near the interface is strongly anisotropic.

In conclusion, we have presented experimental evidence which strongly suggests that localization of excitons takes place at the interfaces of $CdTe/Cd_{1-x}Mn_xTe$ multiple quantum wells. The useful aspect of exciton spectroscopy which this work amplifies is that it can provide a relatively interface specific probe on the scale of a few lattice constants. At the same time, further work and analysis is required to bring about a more detailed understanding of the attractive interface potentials and the orbital asymmetries of the exciton wave function.

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