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Differences in optical properties of (111) and (100) CdTe/(Cd,Mn)Te superlattices

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Comparison of optical properties between (100) and (111) superlattices of CdTe/(Cd,Mn)Te of similar Mn concentrations ($x > 0.20$) shows pronounced differences near the exciton ground-state energies. This contrast can be observed particularly in the photoluminescence and its excitation spectra at low lattice temperatures. Its origin may be due to dependences on crystalline direction of microscopic, strain-driven details at the heterointerfaces.

I. INTRODUCTION

First studies of optical properties in CdTe/(Cd,Mn)Te superlattices have been reported recently, with emphasis on exciton characterization.[1-3] These have been carried out on structures grown on the [111] crystalline direction which is the normally preferred superlattice axis even though the substrate material (GaAs) itself is (100) oriented. However, by selectively perturbing the nucleation of CdTe on a clean (100) GaAs surface during the molecular-beam-epitaxial growth of the superlattice, (100)-oriented CdTe/(Cd,Mn)Te structures have now also been successfully produced.[4] The availability of semiconductor superlattices grown in a different crystalline orientation is not a common occurrence and offers, in principle, the opportunity to study explicitly possible differences in the electronic character of the heterointerfaces. In this paper we show how pronounced differences are found in strained-layer CdTe/(Cd,Mn)Te quantum wells for the (100) and (111) orientations, particularly manifested in photoluminescence and its excitation spectra near the lowest interband optical (exciton) resonances. We argue that at least part of these differences are due to the existence of strain-induced random potential wells near the heterointerfaces which are particularly effective in capturing heavy holes in the (111) case.

II. EXPERIMENTAL DETAILS

The superlattice structures investigated by us included several (100)- and (111)-oriented multiple-quantum-well (MQW) CdTe/(Cd,Mn)Te samples, grown on (100)-oriented GaAs substrates, with the Mn concentration exceeding $x > 0.20$. Details of their preparation are given elsewhere.[4,5] Excitonic properties were examined by photoluminescence and excitation spectroscopy at low temperatures by standard optical techniques. Incident dye-laser power was kept relatively low (about 1 mW), loosely focused onto the front surface of the samples. Figure 1 shows a comparison between the luminescence obtained at $T = 1.8$ K from a (100)- and a (111)-oriented MQW sample, both with the same Mn concentration $x = 0.24$ in the alloy layers. The layer thicknesses for the two structures were $L_w = 57$ and 71 Å for the CdTe layers, and $L_b = 96$ and 128 Å for the (Cd,Mn)Te layers, respectively. The superlattice structures were separated from the substrates by approximately 2-μm-thick buffer layers of (Cd,Mn)Te with a composition identical to that in the "barrier" layers. The spectral position of the bright luminescence emission in each superlattice is determined by a combination of quantum-well confinement effects, a strain contribution [different for the (100) and (111) orientations], exciton Coulomb binding, and additional localization energies. The spectrum for three different (100)-oriented samples showed the presence of a well-defined peak with a broader lower-energy contribution as shown in the left-hand panel of Fig. 1. This lower-energy feature saturated with increasing excitation (the case illustrated in Fig. 1) but became the dominant emission at low excitation levels ($P < 1$ mW). The higher-energy feature which we associate with an "intrinsic" exciton had a linewidth $\Delta E \sim 10$ meV in our best (100) sample. In strong contrast, the luminescence from the (111) samples generally showed only one broad feature ($\Delta E \sim 30$ meV) whose details were largely unaffected by the excitation levels. The observed

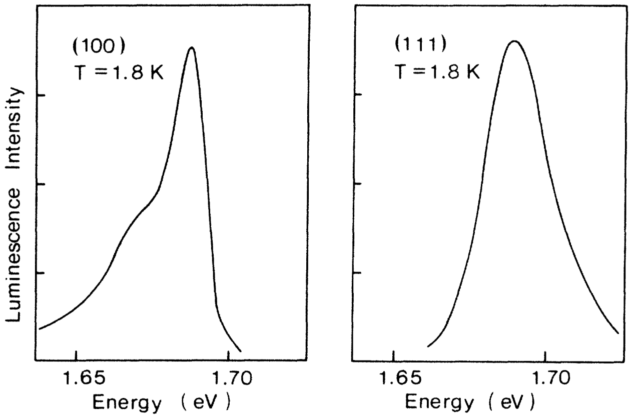

FIG. 1. Luminescence spectra of a (100)- and a (111)-oriented CdTe/(Cd,Mn)Te MQW sample ($x = 0.24$) at $T = 1.8$ K. The details of the structures are given in the text.

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large spectral red shifts of this emission in an external magnetic field and their anisotropy in the field orientation versus the superlattice axis have recently been used by us to argue that the luminescence for the (111) case originates from excitons which are preferentially bound to the heterointerfaces.[1-3] [The use of magnetic fields in probing the exciton states in the CdTe/(Cd,Mn)Te superlattices is useful since the spin-exchange interaction of the Bloch states of an exciton with the d electrons of the Mn ion can yield direct information about the penetration of the exciton envelope function into the (Cd,Mn)Te layers.] The observed spectral shifts of the luminescence in comparable magnetic fields were nearly a factor of 3 smaller for the peak of the (100) sample than for that of the (111) sample of Fig. 1,[6] implying less interface localization for the former. Finally, while the radiative efficiencies for the superlattices we studied were high at low temperatures, the efficiency decreased considerably more rapidly with increasing temperature for the (100)-oriented samples than for the (111) structures.

Whereas luminescence spectra include effects from exciton energy relaxation and localization effects, excitation spectra provide a more direct view of the "unrelaxed" exciton's absorption features. Here the differences between the (100)- and (111)-oriented CdTe/(Cd,Mn)Te superlattices of comparable Mn concentration are particularly striking, as illustrated in Figs. 2 and 3. Figure 2 shows the low-temperature excitation spectrum for a (100)-oriented MQW sample of $x=0.24$, $L_w=84$ Å, and $L_b=94$ Å (20-layer pairs). The spectrum consists of several well-defined features, the most notable of which is the lowest-energy peak at 1.627 eV with a half-width $\Delta E \sim 8$ meV. We associate this resonance with the exciton ground state in the strained CdTe quantum-well layers. The luminescence spectrum had features of the (100) sample in Fig. 1; the position of the main luminescence peak is indicated by the arrow in Fig. 2 and shows a Stokes shift of about 6.4 meV with respect to the adjacent peak in the excitation spectrum. A uniform biaxial strain from lattice mismatch contributes hydrostatic and uniaxial components; the latter splits the $m_j=\frac{3}{2},\frac{1}{2}$ valence-band degeneracy at $k=0$ in the zinc-blende CdTe. The exciton ground state is reached from the $|m_j|=\frac{3}{2}$ valence band if we assume a type-I superlattice. The two smaller peaks in the excitation spectrum at approximately 1.653 and 1.672 eV are associated with other strain-split valence-band structures of the superlattice (with a possible contribution from the excited states of the hole). Preliminary results from our magneto-optical experiments support the idea that the mean valence-band offset in the (100) case is quite small (<20 meV); thus the strain-split $|m_j|=\frac{1}{2}$ "light"-hole states would have little if any quantum-well confinement. Finally, the peak at 1.751 eV in Fig. 2 is due to the $n=2$ confined electron (exciton) transition. Details of our interpretation of the structure, linewidths, and amplitudes of the excitation spectra for the (100) case will be presented elsewhere; our purpose here is to highlight the differences in the overall optical signature between the (100)- and (111)-oriented superlattices.

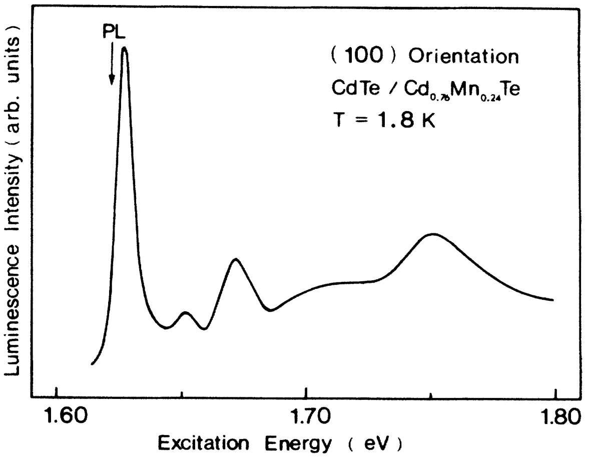

FIG. 2. Excitation spectrum of a (100)-oriented CdTe/(Cd,Mn)Te MQW sample ($x=0.24$) at $T=1.8$ K and $\hbar\Omega=1.606$ eV. The position of the photoluminescence (PL) peak is indicated by the arrow.

As seen from Fig. 3, the excitation spectra recorded for three (111)-oriented CdTe/(Cd,Mn)Te MQW samples (including one with a finite Mn concentration in the well layers) is in strong contrast with that obtained for the (100) samples of comparable Mn concentration. The concentrations are given in the figure; the CdTe and (Cd,Mn)Te layer thicknesses for the samples (from the bottom up) were $L_w=120$, 71, 70 Å, and $L_b=120$, 128, 130 Å, respectively. Typical for the three samples of dif-

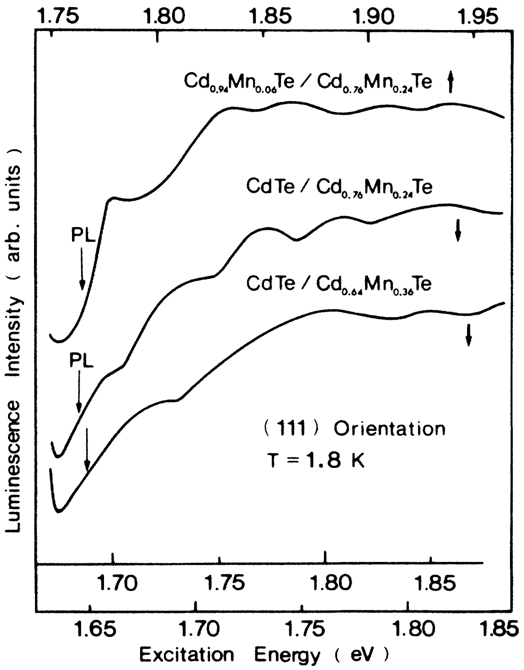

FIG. 3. Excitation spectra for three (111)-oriented MQW samples of different Mn concentration at $T=1.8$ K. The arrows on the right-hand side refer to the scales of energy from top to bottom, respectively. The peak positions of luminescence spectra are indicated by the longer set of arrows.

ferent x values is the lack of the pronounced exciton ground-state resonance seen in (100) orientation; rather, the unifying first-order feature for the (111) samples is the broad and gradual sloping of the "absorption edge." The degree of steepness of this edge increases distinctly with decreasing amount of contrast in the x values for the heterolayer pairs, and for the uppermost trace in Fig. 3 the emergence of an incipient peak (at about 1.780 eV) can be clearly seen. In the other two samples there is also a semblance of structure at low energy (shoulders at 1.697 and 1.685 eV, respectively). The additional structure at higher energies in all the samples is at least in part influenced by Fabry-Perot interference effects in our thin-film samples. At present the connection of this structure to any exciton excited-state resonances is unclear and a subject for further study. We also note that there is recent evidence that for a substantially lower Mn concentration ($x = 0.06$), a well-defined peak in the excitation spectrum emerges and has been interpreted as the lowest exciton resonance.[7]

III. DISCUSSION

We now consider possible origins for the observed differences in the excitation and luminescence spectra for the (100)- and (111)-oriented CdTe/(Cd,Mn)Te MQW samples of comparable Mn concentration. While the excitation spectra of the (100) samples shows a spectrally well-defined and relatively narrow exciton ground-state resonance expected for a type-I superlattice, the (111) case is considerably more ambiguous. For example, particularly for the lower two traces in Fig. 3 [$x = 0.24$ and 0.36 in the (Cd,Mn)Te layers], the excitation spectra might suggest an indirect optical transition. An indirect transition in real space corresponds to a type-II superlattice while an indirect transition in k space requires that the valence- (or conduction-) band extremum be shifted away from the Brillouin-zone center ($k = 0$). Another alternative is the presence of a sufficient amount of disorder or space charge in the quantum wells so that the exciton absorption is broadened to a virtual continuum.

In the CdTe/(Cd,Mn)Te structures discussed here, lattice-mismatch—generated strains are large, nearly 1%, for the range of x values in question ($x > 0.20$). Furthermore, the observed shifts in the exciton energies in external magnetic fields in both the (100) and (111) orientations[6] support the notion that the valence-band offsets are small and probably of the same order of magnitude as the bulk-exciton binding energy in CdTe (9 meV). This presents a difficulty in estimating the exciton binding energy in the quantum wells since available calculations only apply to the case of large carrier confinement.[8] Addition of the strain then produces a complicated situation with several interacting effects so that correlating experimental information (e.g., from Fig. 2) to deduce exciton binding with meaningful precision is not yet possible to us. Applying the usual deformation-potential formulation to these strained superlattices shows readily, however, that the uniaxial component of the tensional strain parallel to the growth axis (z) produces roughly twice the amount of the heavy-light—hole (HL) valence-band splitting E_{HL} ($k = 0$) in the (111) CdTe layers in comparison with the (100) case (this difference originating mainly from the respective values of shear deformation-potential constants). The absolute magnitude of strain (in linear approximation) in the superlattice layers can be estimated as usual if we assume uniform elastic deformation of the layers; however, the presence of a significant dislocation density at the GaAs-substrate/(Cd,Mn)Te-buffer-layer interface as well as the finite dislocation density in the superlattice makes such estimates somewhat uncertain. For simplicity, we have assumed that all of the strain is in the CdTe layers. It then follows immediately that a simple homogeneous strain picture cannot explain the difference in the excitation spectra for the (100) and (111) orientations by evoking a real-space indirect transition for the latter since the larger E_{HL} for the (111) case [$E_{\mathrm{HL}}(111) \sim 60$ meV versus $E_{\mathrm{HL}}(100) \sim 30$ meV] would make the (111) case less type II than the (100) case (the values are for $x = 0.24$).

The presence of large uniaxial strains can produce mixing of the Γ_8 (light-hole) and Γ_7 (spin-orbit) valence bands to shift the valence-band extremum away from $k = 0$ in a zinc-blende crystal.[9] For a spin-orbit splitting on the order of 1 eV in CdTe, however, this effect should be small up to the breaking stresses in bulk material. Additionally, in a quantum well loss of translational invariance leads to mixing of the "heavy"- and "light"-hole bands and may induce unusual dispersion for the in-plane motion of the carriers, further enhanced by the strain. These effects have been theoretically considered in the (unstrained) GaAs/(Ga,Al)As (Ref. 10) and the (strained) HgTe/CdTe superlattices (Ref. 11), but not to our knowledge in the presence of excitonic effects (which induce further mixing of states). In the absence of a more detailed theoretical analysis it remains unclear whether strain perturbation in the (111)-oriented CdTe/(Cd,Mn)Te quantum wells could induce k-space shifts of the valence-band extremum while the (100)-oriented structures present little or no such evidence. However, the range of energies in Fig. 3 for the slowly rising edges (particularly for the two lower traces) implies that for a phonon-assisted exciton transition the indirect modulation of the valence-band extremum is on the order of 50 meV, a value which would seem to require an extraordinary amount of state mixing.

An alternative consideration for the distinct differences in exciton characteristics for the (100) and (111) orientations focuses on the nature of the interfaces themselves. Specifically, this involves possible microscopic differences in the formation of the strained and polar heterointerfaces with possible directional dependences, and their influence on adjacent, thin (< 100 Å) semiconductor layers. Recent results from x-ray photoemission spectroscopy have been used to argue that the valence-band offset ΔE_v for the Ge/GaAs heterointerface varies over a range of more than 100 meV for the differently reconstructed polar and nonpolar orientations.[12] Here the shifts in $\Delta E_v(111)$ and $\Delta E_v(\bar{1}\bar{1}\bar{1})$ [relative to the nonpolar (110) orientation] are substantially larger than those for the (100) interfaces, presumably because of the larger interface (dipolar) charges in the former. For the CdTe/(Cd,Mn)Te heterointerface the "chemical contrast" (and accumulation of intrinsic interface charge) is likely to be much smaller, and we suggest that apart from space-charge effects, local interface strain could play a similar role in "pinning" the energy position of the valence-band maximum and influence the band-edge energies throughout the thin heterolayers. As a first-order departure from the virtual-crystal approximation, such local strains are randomly fluctuating due to the compositional fluctuations $\Delta x(r)$ inherent in a mixed crystal [(Cd,Mn)Te] and can provide a significant measure of strain-driven disorder, thereby directly influencing the exciton resonances. A small ΔE_v for an idealized unstrained CdTe/(Cd,Mn)Te heterojunction implies that relatively small modulation in the energy position of the valence-band maximum in the CdTe layers would have a large impact on the exciton states. In this scenario, the absence of a distinct exciton ground-state resonance in the excitation spectra of Fig. 3 shows the influence of such shifts and disorder broadening on the valence-band offsets as determined by the details near the heterointerface. With strain underlying these effects, it is not surprising that lowering the Mn concentration drastically would allow a well-defined exciton ground state to appear in the excitation spectra, even in the (111) orientation. Qualitative evidence that the (111) interface may be more "disordered" than the (100) interface is corroborated by observations of electron and x-ray-diffraction patterns in our structures which generally showed fewer diffracted orders for the (111) samples.

Several aspects in the luminescence spectra also appear to support the idea that fluctuations in the exciton potential are more pronounced near the (111) heterointerfaces than the (100) heterointerfaces. The recombining (energy-relaxed) excitons are clearly more localized in the (111) case; this can be seen directly by comparing the 6.4-meV Stokes shift between the excitation and (the intrinsic peak in) the luminescence spectra for a (100) sample (Fig. 2) and, similarly, an approximate value of 15 meV for the $Cd_{0.94}Mn_{0.06}Te/Cd_{0.76}Mn_{0.24}Te$ (111) sample of Fig. 3. This explains in part why the luminescence from the (111) quantum wells consistently persists at higher temperatures than for the (100) case (assuming that free excitons recombine nonradiatively at dislocations and other defects). Similarly, the broad luminescence linewidth in the (111) samples supports the notion of a larger amount of disorder broadening. According to recent evidence,[1-3] the exciton localization for the (111) orientation is interface related; further work has shown specifically that a substantially two-dimensional hole state exists at the heterointerface, Coulomb correlated with the electron.[13] We suggest here that initial hole localization occurs, at least in part, as a result of strain fluctuations in the interface region, these fluctuations originating from fluctuations in the Mn-ion concentration. (The complete localization clearly also includes magnetic polaron effects as discussed in Refs. 13 and 14.)

In a simple illustration of these arguments, we estimate the possibility for the existence of random potential wells for heavy-hole states near the CdTe/(Cd,Mn)Te heterointerfaces in a crude effective-mass model (as mentioned, exciton properties will be sensitive to the heavy-hole energies in the presence of small valence-band offsets in the strained quantum-well system). For simplicity, we assume that $\Delta E_v = 0$ and define a local volume ΔV about the geometrical interface such that $\Delta V = 2a \times a_B^2$, where $2a$ is its dimension perpendicular to the layer plane (a is the mean perpendicular lattice constant) and a_B is the Bohr radius of the heavy hole in the hydrogenic approximation. While the definition of this volume is somewhat arbitrary, we consider it to be physically relevant when considering the fluctuations in the strain near the interface. The mean variation in the fluctuating Mn-ion concentration in this volume is easy to evaluate by assuming a normal statistical distribution, and yields

$$\Delta x = 2[x(1-x)/N]^{1/2} , \qquad (1)$$

where $N = 2\Delta E/\Omega$ is the number of cation sites in the volume ΔV, and Ω is the volume of the unit cell. Then, if we specifically consider the uniaxial component of strain and the fluctuation in heavy-light—hole (HL) splitting ΔE_{HL},

$$\Delta E_{HL} = \frac{\partial E_{HL}}{\partial s} \frac{\partial s}{\partial x} (\Delta x) . \qquad (2)$$

In this expression $\partial E_{HL}/\partial s$ is directly proportional to the uniaxial deformation-potential constants appropriate for the rhombohedral (111) and tetragonal (100) cases. The quantity $\partial s/\partial x$ can be obtained from the known dependence of the lattice constant of (Cd,Mn)Te on the Mn concentration. In considering the fluctuations in the heavy-hole (HH) energy ΔE_{HH}, we further assume that a large fraction (~ 0.5) of ΔE_{HL} can directly be applied to ΔE_{HH}. Also, we have not included the contribution to ΔE_{HH} from the (smaller) hydrostatic component of strain since the corresponding deformation-potential constant for the valence band is not known. Then, for values appropriate to the (111) CdTe/(Cd,Mn)Te interface, we estimate for the average random heavy-hole potential well a depth of approximately 25 meV and a binding energy of some 4 meV (in a mean volume ΔV defined above). In low-temperature photoluminescence experiments, excitons will attempt to thermalize to the deeper wells of the distribution of random potentials thereby leading to larger effective localization energies. In absorption (excitation spectroscopy), the random potential wells influence the interband transition cross section by direct broadening of the absorption peaks. For the (100) case the estimated localization energies are about a factor of 2 smaller. We note that in Fig. 1 the low-energy shoulder of the luminescence spectrum is interpreted by us as being due to excitons localized at the interface; the relatively easy saturation of this feature with increasing excitation level implies also that the density of these states is substantially lower than that in the (111) case.

The above estimate presents very crudely ideas which may be of more general value in connection with strained-layer superlattices involving semiconductor alloys (and their inherently finite disorder). In particular, it seems to us that deviations from the virtual-crystal approximation near the interfaces should be expected to have a strong influence on the electronic and optical properties in these structures. For a better estimate of such effects, a tight-binding approach would clearly be more appropriate in a more realistic calculation. Furthermore, while the ideas expressed here do suggest the existence of random, strain-induced potential wells near the CdTe/(Cd,Mn)Te interface, it is more than likely that interface reconstruction and rearrangement in chemical bonding are distinctly different for the (100) and (111) orientations (with consequent influence on the heterojunction band lineup). In particular, for the (111) case we feel that the measured optical properties further suggest that this interface may be nonpseudomorphic. Finally, we note again that in the present quantum-well system, exciton localization effects inherently involve a magnetic component from the exchange effect, i.e., magnetic polaron effects, whose contributions have been recently estimated,[15] but which further complicate the comparison between experiment and theory in the present context.

In conclusion, we have presented initial results which show that the optical properties near the exciton ground state for (100)- and (111)-oriented strained-layer CdTe/(Cd,Mn)Te superlattices of comparable Mn concentration show large differences. Assuming that these differences are not due to extrinsic defects and impurities, we have suggested that they reflect varying degrees of microscopic, strain-related details (on the scale of the exciton Bohr radius) by the heterointerfaces. At the same time, further work is needed to correlate optical spectroscopy with electron and x-ray-diffraction measurements for a wider range of growth conditions and material parameters of these superlattices.

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