Negative energy gap in HgTe-CdTe heterostructures with thick wells

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Magnetotransport measurements have been performed on one multiple quantum well and two superlattices with relatively thick wells (> 100 Å). Whereas both superlattices are semimetallic and display considerable electron-mass broadening, the multiple quantum well shows no broadening and is found to have an energy gap of 16 meV at low temperatures. This represents the first experimental confirmation of the recent theoretical prediction that HgTe-CdTe should have two semiconducting regimes, one in the thin-well limit and a second for much thicker wells. It is also unusual that, due to the negative temperature coefficient of the effective mass, the electron mobility for thick-well samples continues to increase with T well into the region where phonons dominate the scattering.

In this paper we discuss a magnetotransport investigation of HgTe-CdTe quantum structures with relatively large well thicknesses ($104 < d_W < 139$ Å). Of the three samples studied, two are superlattices while the third is a multiple quantum well. The results provide the first experimental demonstration that a thick-well HgTe-CdTe quantum structure can be semiconducting rather than semimetallic. This finding has the counterintuitive implication that increased quantum confinement (brought about by narrowing the well size) sometimes has the effect of decreasing the energy gap rather than increasing it. We also report the first experimental observation of electron-mass broadening in a HgTe-CdTe superlattice.

It is by now well documented that the energy gap E_g of a HgTe-CdTe superlattice depends strongly on the thickness of the quantum wells.[1,2] Although bulk HgTe is a semimetal, quantum confinement causes the superlattice to be a semiconductor whenever the wells are sufficiently thin. Band-structure theory[3,4] predicts that if d_W is gradually increased, E_g decreases until the lowest conduction band ($E1$) and the highest valence band (HH1) meet at the center of the Brillouin zone and the superlattice becomes semimetallic. If d_W is increased further, the two bands cross at some point k_{zc} along the growth-direction axis.[2] It has been verified experimentally that in this regime, the energy gap is at or very close to zero. From measurements of the temperature dependence of the intrinsic carrier density, energy gaps near zero have been observed previously for Hg-based superlattices with d_W as small as 78 Å and as large as 130 Å.[2,5] However, Johnson, Hui, and Ehrenreich[6] have recently pointed out that for still wider wells a second semiconducting regime may occur (the effect is also apparent from the analysis of Hoffman *et al.*[2]). This is because the $E1$-HH1 crossing at k_{zc} eventually reaches the zone boundary ($k_z = \pi/d$) and the two bands then separate, opening up an energy gap.[7] The range of well thicknesses over which the superlattice will be semimetallic is related to the k_z dispersion of the $E1$ band, which in turn depends primarily on the superlattice barrier thickness. For thin barriers the bandwidth of $E1$ is large, and there will be a considerable range of well thicknesses over which $E1$ and HH1 cross. However, for thick barriers there is little k_z dispersion and there will be only a small window of d_W for which the bands cross. In that case the structure passes almost directly from a positive-gap semiconducting region into a negative-gap semiconducting region, with virtually no semimetallic region in between. We conclude that the opportunity for observing the negative-gap semiconducting region is much greater in thick-barrier multiple quantum wells than in thin-barrier superlattices.

The materials studied in the present work were grown by molecular-beam epitaxy in a system which has been described in detail elsewhere.[8] Each sample consists of 100 periods of alternating layers of HgTe and $Hg_{1-x}Cd_xTe$ ($x \approx 0.85$) deposited directly onto a lattice-matched [100] $Cd_{1-x}Zn_xTe$ substrate, with no intervening buffer layer. Crystal perfection as determined from x-ray rocking curve measurements was found to be extremely good. A method which relies on the spacings between x-ray satellite peaks in conjunction with growth-rate data[2] has been employed to determine the well and barrier thicknesses listed in Table I. We note that sample 1 should be considered a multiple quantum well rather than a superlattice, since the 89 Å barriers are thick enough to prevent significant electron tunneling between neighboring wells. (The tight-binding formalism of Schulman and Chang[9] predicts that the bands in that sample should have almost no k_z dispersion, whereas the barriers in samples 2 and 3 are thin enough to give $E1$ a bandwidth on the order of 15 meV.)

Van der Pauw Hall and conductivity measurements were performed on each of the three samples as a function of magnetic field (0–70 kG) and temperature (4.2–300 K). Because multiple carrier species were almost always present, a mixed conduction analysis of the

TABLE I. Sample characteristics.

Sample	d_W (Å)	d_B (Å)	$n_{4.2\,K}$ (cm^{-3})	$\lvert E_g^0\rvert$ (meV)
1	128	89	≈ 0	16
2	104	55	7.5×10^{15}	<3
3	139	58	3.7×10^{15}	<3

field-dependent data at a given temperature was performed in order to extract the densities and mobilities for the various carrier types. The data acquisition and analysis procedures have been described in detail elsewhere.[2] Table I gives low-temperature electron concentrations for each of the samples. With increasing temperature, the electron densities increase in a manner consistent with the thermal generation of intrinsic carriers. From the temperature dependence of n_i we were able to determine accurate energy gaps, which are also listed in Table I.

Samples 2 and 3 are n type at low temperatures. In both cases the intrinsic densities follow the relation $n_i(T)\sim T^{3/2}$, implying that the energy gaps are approximately zero (≤ 3 meV). On the other hand, sample 1 is essentially insulating at 4.2 K, possibly because it is p type and the holes have frozen out at low T. However, the increase of n_i with T is much more rapid than $T^{3/2}$, indicating the presence of an energy gap in that sample. The law of mass action predicts that if n_i is normalized to $T^{3/2}$ and plotted versus T^{-1} on a semilog scale, the slope of the curve is proportional to the zero-temperature extrapolation of the gap, E_g^0. Although the derivation of that simple result assumes parabolic bands, the error introduced can be small compared to other factors when the gap is very narrow (e.g., $10<E_g<50$ meV) and the intrinsic density can be determined over a broad temperature range. The technique therefore provides an extremely useful characterization of E_g^0 in narrow-gap samples. It was shown previously that the agreement with gaps determined from magneto-optical and optical measurements is quite good in cases where a comparison could be made.[2] Data plotted in this manner for samples 1 and 3 are given in Fig. 1, along with results for three superlattices with thinner wells which were studied previously.[2] The samples labeled $d_W=51$, 58, and 78 Å were members of a series whose energy gaps decreased almost monotonically with increasing well thickness (there is naturally a dependence on barrier thickness as well, but it is much weaker). Sample 3 clearly has a gap near zero, as have a number of other previously studied samples with d_W between 78 and 130 Å.[2,5] However, sample 1, which is a multiple quantum well with $d_W=128$ Å, shows a slope corresponding to $E_g^0\approx 16$ meV. Note that whereas n_i for samples 1 and 3 are equal to within a factor of 2 at 300 K, they differ by nearly 2 orders of magnitude at $T=20$ K. Furthermore, the slope of the curve for sample 1 would be noticeably different for a gap of, say, 13 meV. This illustrates the high sensitivity to small energy gaps as long as n_i can be determined down to relatively low temperatures.

These results represent the first experimental confirmation that HgTe-CdTe quantum structures can be semiconducting with a sizable "negative" energy gap in the thick-well regime. We pointed out above that this phenomenon should be most readily observable in a multiple quantum well such as sample 1. For the appropriate well and barrier thicknesses, the tight-binding band-structure calculation[9] (with a valence-band offset of 350 meV) yields that the direct energy gap at $k_x=0$ should be ≈ -17.2 meV. However, since the valence-band maximum is predicted to be at $k_x\approx 0.03$, the more appropriate comparison is with the indirect gap of -9.5 meV. Considering the level of uncertainty in the calculations, the agreement of either value with the experimental result of -16 meV must be considered quite good.

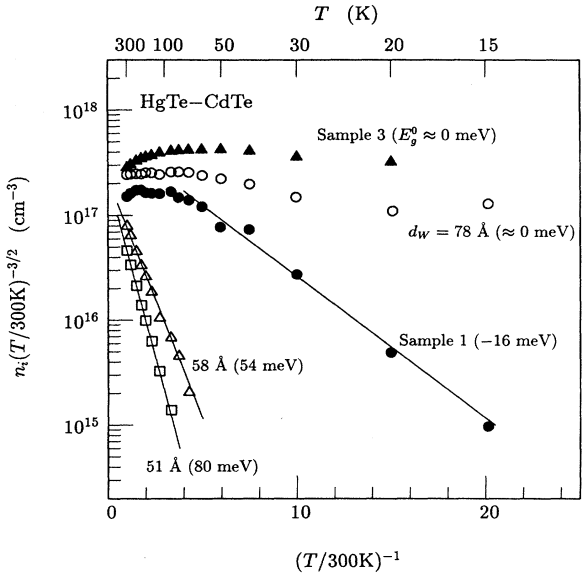

FIG. 1. Experimental intrinsic carrier density (normalized by $T^{3/2}$) vs inverse temperature for four superlattices and one multiple quantum well (sample 1). The samples with $d_W=51$, 58, and 78 Å are BMCCT21, 17, and 16, respectively, from Hoffman *et al.* (Ref. 2).

Figure 2 plots the temperature dependence of the electron mobility in sample 1, along with $\mu_n(T)$ for two thinner-well superlattices studied previously.[2] These three samples occupy all three of the regimes outlined above (semiconductor-semimetal-semiconductor). The main qualitative differences between the sets of data are easily understood in terms of the relation between in-plane effective mass and energy gap: $m_{nx}(T)\sim|E_g(T)|$ in conjunction with the positive temperature coefficient of $E_g(T)$. (The qualitative details will naturally also depend on such factors as the density of charged scattering centers, etc.) The triangles in Fig. 2 are electron mobilities for a superlattice with a positive energy gap of 56 meV at low temperatures. Due to the increase of the gap and hence the mass with temperature, μ_n monotically decreases with T. The open circles represent mobilities for a superlattice which is semimetallic at low temperatures ($E_g^0\approx 0$ meV). As long as the gap is near zero, which theory predicts should be the case for any T less than

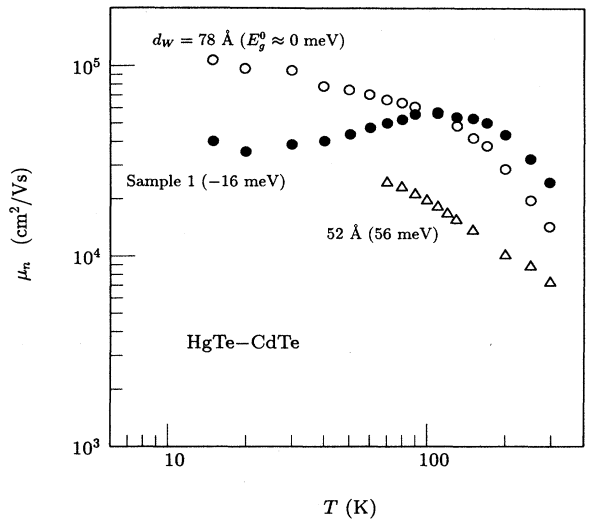

FIG. 2. Experimental electron mobility vs T for two superlattices and one multiple quantum well (sample 1). The samples with $d_W = 56$ and 78 Å are BMCCT3 and 16, respectively, from Hoffman *et al.* (Ref. 2).

≈ 60 K, the electron mass is very light ($\approx 0.002 m_0$) and the mobility remains quite high ($\approx 10^5$ cm^2/V s). Note that μ_n has only a mild dependence on temperature in that region. However, the superlattice finally becomes semiconducting, and the experimental mobility begins to decrease more rapidly at $T > 90$ K as the gap and mass increase. The solid circles represent data for sample 1, which is a multiple quantum well (we expect the near absence of the semimetallic region). At low temperatures, the sizable negative energy gap[10] causes the electron mass to be relatively large (the calculation predicts $\approx 0.017 m_0$). This probably accounts for the fact that in the low-temperature limit, μ_n for sample 1 is considerably lower than that for the semimetallic sample (open circles). However, with increasing temperature the magnitude of the negative energy gap decreases, the mass decreases, and μ_n increases. It is unusual that this continues well into the region where phonon scattering is expected to dominate the mobility. The experimental $\mu_n(T)$ has a broad peak above 110 K, and does not begin a strong decrease until $T > 170$ K. This is consistent with the theoretical prediction that $E_g = 0$ is not reached until $T \approx 170$ K. Note that even in the high-temperature region where μ_n steadily decreases with increasing T, the mobility in sample 1 is higher than that in the $d_W = 78$-Å sample (open circles). This is expected, since at high temperatures E_g and hence m_{nx} are predicted to be smaller in the sample which started with a negative gap (the opposite of their relative magnitudes at low temperatures). We are thus able to account for all of the main qualitative features of the data in Fig. 2 simply in terms of the variation of electron effective mass with well spacing and temperature.

We now discuss mobility results for the two thick-well superlattices, samples 2 and 3. Although both were n type at low temperatures, the magnetic-field-dependent Hall and conductivity data indicate the presence of more than one species of electron in each sample. A similar effect had been observed in zero-gap, p-type HgTe-CdTe and $Hg_{1-x}Zn_xTe$-CdTe superlattices studied previously.[2,11] There the field-dependent data showed clear evidence for more than one type of hole, with mobilities differing by about an order of magnitude. It was pointed out that such a result is actually an expected consequence of the band structure, since theory predicts the coexistence in the superlattice of holes with a wide range of effective masses. This "mass broadening" occurs because the in-plane mass at a given growth-direction wave vector is approximately proportional to the energy gap at that k_z, and $E_g(k_z)$ is a rapidly varying function when the $E1$ and HH1 bands are close or cross. It was further noted that in zero-gap samples, one should also have mass-broadening of electrons. That it was not observed in the previous study is probably due to two main factors. First, since all of the samples were p type, the low-temperature measurements were not as sensitive to the properties of minority electrons. Second, because the superlattices had a maximum well thickness of only 81 Å, the $E1$-HH1 crossing was always near $k_z = 0$. This gives the maximum amount of broadening for holes but the minimum amount for electrons.

A useful way of illustrating the broadening effect in samples 2 and 3 is to analyze the data by the "mobility spectrum" technique developed by Beck and Anderson.[12] In contrast to conventional mixed-conduction treatments[13] (such as that employed in the present study) which assume a fixed number of carrier species with discrete mobilities, the technique allows for a continuous spectrum of mobilities. Beginning with the field-dependent Hall coefficient and conductivity, a function $n_{\max}(\mu)$ is generated, which represents the maximum density of carries with a given mobility that can be assumed present if one is to maintain consistency with the data. Figure 3 illustrates the mobility spectra for samples 1 and 3, where the quantity plotted is $\sigma_{\max}(\mu_n) \equiv n_{\max}(\mu_n) e \mu_n$. We find that the spectrum for sample 1, whose temperature-dependent electron mobility was discussed above, contains a single, relatively narrow peak. This is as expected in a multiple quantum well, since mass broadening is directly related to the k_z dispersion. On the other hand, the maximum in the spectrum for sample 3 is very wide, which we interpret as being due to mass-broadening. Within the wide envelope are two peaks having mobilities about an order of magnitude apart. As has recently been demonstrated for cyclotron resonance in p type HgTe-CdTe superlattices,[14] one expects that within the broadened spectrum, there may be peaks corresponding to external positions of the energy bands (in the present case they would correspond to electrons at $k_z = 0$ and at $k_z = k_{zc}$, where k_{zc} is the $E1$-HH1 crossing point).

Figure 4 gives electron and hole mobilities as a function of temperature for sample 3. As was discussed above, the analysis at low temperatures yields two electrons with mobilities differing by an order of magnitude. The higher mobility, $\mu_{n1} \approx 1.7 \times 10^5$ cm^2/V s, is quite

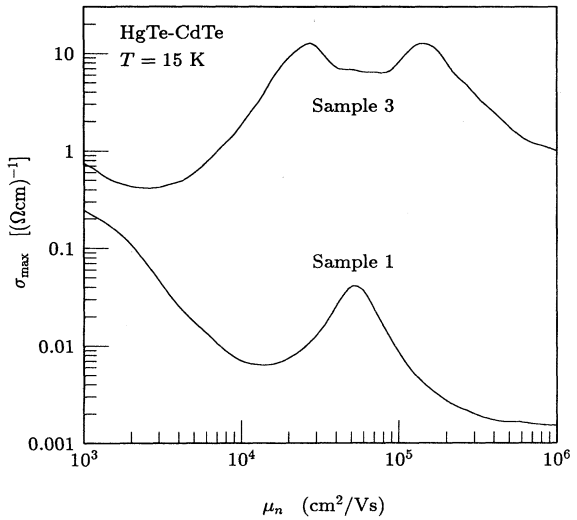

FIG. 3. Electron "mobility spectra" for samples 1 and 3 at 15 K. The double peak for sample 3 is attributed to mass broadening.

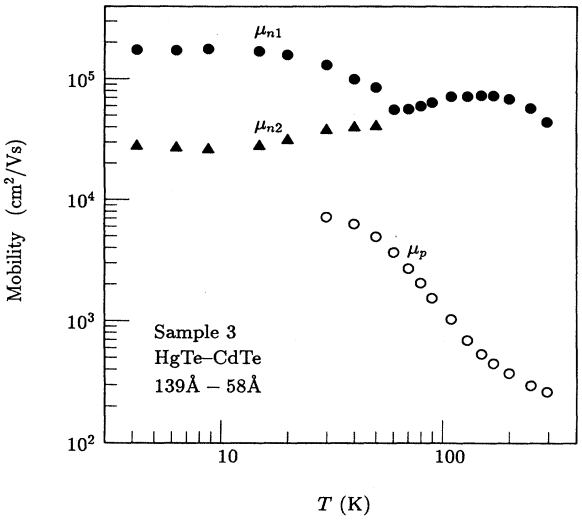

FIG. 4. Electron and hole mobilities vs T for sample 3.

similar to those for minority electrons in zero-gap p-type samples studied previously.[2,11] However, at temperatures above 50 K, only a single electron could be resolved. This is not surprising, since one expects much more mass broadening when the electrons populate only the states near the bottom of the band than when they become more energetic at higher temperatures (and are affected by band nonparabolicity). Although the lowest-temperature data were not sensitive to minority holes, μ_p could be determined for $T \geq 30$ K. Over this temperature range, the mobilities shown in the figure are comparable to those for majority holes in zero-gap p-type samples.[2] Electron and hole mobilities for sample 2 are similar to those shown in Fig. 4.

It should be pointed out that in disagreement with the data, the tight-binding band-structure formalism[9] (with a valence-band offset of 350 meV) does not yield zero-energy gaps at $k_x=0$ for the well and barrier thicknesses corresponding to samples 2 and 3. The d_W listed in Table I are large enough that a negative gap is predicted for sample 2 (as in sample 1) and an indirect (the valence-band maximum is at $k_z \approx 0.03$) gap near zero is predicted for sample 3. The experimental evidence for E_g $(k_x=0) \approx 0$ in samples 2 and 3 appears to be fairly conclusive. Not only is a net energy gap of $E_g^0=0\pm 3$ meV obtained for both samples (see Fig. 1), but the very high-electron mobilities and the observation of strong mass broadening both argue for a crossing of $E1$ and HH1. Neither mass broadening nor $\mu_n > 10^5$ cm^2/V s is observed in sample 1, which clearly does have a negative gap. The reason for this discrepancy between band-structure theory and the data is presently unclear. It can be argued that for sample 2, the uncertainty in the superlattice layer thicknesses as well as in the input parameters to the theory may be great enough to account for the disagreement (for example, decreasing the valence-band offset to 200 meV would yield much better consistency). However, the same cannot be said for sample 3, since $d_W=139$ Å is far greater than any well thickness for which a crossing of $E1$ and HH1 is expected. The simplest way to reconcile theory and experiment is to hypothesize that for some reason the theory has greatly underestimated the k_z dispersion of the $E1$ band. However, further study is required before this possibility can be tested. We emphasize that in most regards, there has been remarkable agreement between the dominant features of the calculated band structures and the main qualitative trends of the transport, magneto-optical, and optical data.

In summary, we have discussed a magneto-transport investigation of HgTe-CdTe heterostructures with thick quantum wells. The results confirm experimentally the recent theoretical prediction that thick-well HgTe-CdTe can be semiconducting with a "negative" energy gap. Since band-structure theory predicts that the indirect gap may shrink to zero for still-thicker wells, further study will be required to determine the extent of the large-d_W semiconducting region. Due to the temperature dependence of the effective mass, the electron mobility is observed to increase with T well into the region where phonons are the dominant scattering mechanism. We have also observed for the first time the effects of electron-mass broadening in zero-gap HgTe-CdTe superlattices. At low temperatures, the data indicate the coexistence of electrons with mobilities spanning a range of over an order of magnitude.

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[10]The experimental gap of 16 meV represents the separation between the lowest conduction band and the highest valence band, which are HH1 and HH2, respectively, according to the band-structure calculation. However, the in-plane electron mass is proportional to the absolute value of the $E1$-HH1 separation, for which the calculation gives -45 meV.

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[13]The mobility-spectrum technique should be viewed as a very useful complement to the conventional mixed-conduction analysis rather than as a replacement. While it provides valuable guidance in determining the types and approximate mobilities of carrier species present in a given sample, the conventional analysis appears to yield more precise quantitative results.

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