# Electrical determination of the valence-band discontinuity in HgTe-CdTe heterojunctions

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Current-voltage behavior is studied experimentally in a $Hg_{0.78}Cd_{0.22}Te$-CdTe-$Hg_{0.78}Cd_{0.22}Te$ heterostructure grown by molecular beam epitaxy. At temperatures above 160 K, energy-band diagrams suggest that the dominant low-bias current is thermionic hole emission across the CdTe barrier layer. This interpretation yields a direct determination of $390 \pm 75$ meV for the HgTe-CdTe valence-band discontinuity at 300 K. Similar analyses of current-voltage data taken at 190–300 K suggest that the valence-band offset decreases at low temperatures in this heterojunction.

The HgTe-CdTe heterojunction is the building block for a number of interesting device structures which have been experimentally realized. These include the HgTe-CdTe superlattice,[1–7] the resonant tunneling HgTe-$Hg_{1-x}Cd_xTe$ double barrier heterostructure,[8,9] and the single barrier $Hg_{1-x}Cd_xTe$ negative differential resistance heterostructure.[10,11] In all of these structures, the valence-band offset, $\Delta E_v$ at the HgTe-CdTe interface is an important quantity in determining device behavior. Several theoretical and experimental values of $\Delta E_v$ have been reported.[12–20] Most recently, x-ray photoemission spectroscopy (XPS) experiments on HgTe-CdTe heterojunctions have yielded values of approximately 350 meV for $\Delta E_v$ at room temperature.[16–18] These results are in serious disagreement with most interpretations of published superlattice photoluminescence data, which indicate that $\Delta E_v$ must be nearly 0 meV to explain the observed high-energy luminescence.[5–7] The XPS results are also in apparent disagreement with earlier low-temperature magnetoabsorption experiments which yielded a value of 40 meV for $\Delta E_v$,[20] although it has been suggested that these two measurements could be consistent with each other if $\Delta E_v$ is temperature dependent.[21]

In this letter, we report a direct electrical measurement of the valence-band discontinuity at the HgTe-CdTe interface. The sample studied was grown on a semi-insulating GaAs substrate by molecular beam epitaxy (MBE) in a Riber 2300 system. The active region consisted of a CdTe barrier layer sandwiched between two $Hg_{0.78}Cd_{0.22}Te$ electrodes. Transmission electron microscopy (TEM) showed that the CdTe layer was 180 Å thick. The $Hg_{0.78}Cd_{0.22}Te$ electrodes were doped $n$ type with indium, to a carrier concentration of $3.6 \times 10^{16}$ cm$^{-3}$ at 30 K. The top (bottom) electrode was 0.5 $\mu$m (3 $\mu$m) thick. A 2.5-$\mu$m CdTe buffer layer preceded the growth of the active device region of the heterostructure. Mesas were fabricated in the sample by wet etching with $Br_2$:HBr:$H_2O$ in a 0.005:1:3 ratio. Au was used to make ohmic contacts to both the tops of the mesas and the etched $Hg_{0.78}Cd_{0.22}Te$ surface, forming a set of isolated two-terminal devices. The mesas were circular, with diameters ranging from 35 to 70 $\mu$m. Several distinct preparations of the sample were performed, with over 100 devices tested in total at room temperature. Roughly 25% of the devices were "short-circuits," with markedly higher currents and nearly linear current-voltage ($I$-$V$) curves. The remainder of the devices displayed uniform behavior, with overall current densities deviating by no more than 20%. Measured currents from the fabricated devices were found to be proportional to device area, indicating that edge transport mechanisms were not significant.

Figure 1 is an energy-band diagram for the heterostructure under an applied bias of 50 mV, calculated by solving Poisson's equation self-consistently via the method of Bonnefoi *et al.*[22] It should be noted that the calculated band diagram is independent of the values of the band offsets, except for an overall shift of the conduction- and valence-band edges in the CdTe layer. Figure 1 suggests that the dominant source of current at high temperatures is the thermionic emission of holes from the $Hg_{0.78}Cd_{0.22}Te$ cladding layers across the CdTe valence-band barrier. It is important to note that the $n$-type doping of the electrodes does not

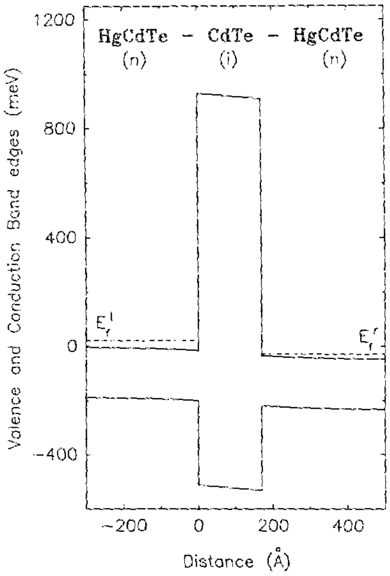

FIG. 1. Calculated band diagram for the $Hg_{0.78}Cd_{0.22}Te$-CdTe-$Hg_{0.78}Cd_{0.22}Te$ single barrier heterostructure, under an applied voltage of 50 mV. The upper (lower) solid line represents the conduction- (valence-) band edge as a function of distance in the direction of growth. The dashed line represents the Fermi energy in each of the electrodes, which are doped $n$ type at $3.6 \times 10^{16}$ cm$^{-3}$. The CdTe barrier is 180 Å thick.

prohibit this transport mechanism because the band gap in $Hg_{0.78}Cd_{0.22}Te$ is small ($\approx 200$ meV).[23] At zero applied bias, the size of the potential energy barrier which the holes cross is given by

$$\phi_{\text{hole}} = E_f + E_g^{(x=0.22)} + \Delta E_v^{(x=0.22)},$$

where $E_f$ is the Fermi energy relative to the conduction-band edge in the $Hg_{0.78}Cd_{0.22}Te$ electrodes, $E_g^{(x=0.22)}$ is the electrode band gap, and $\Delta E_v^{(x=0.22)}$ is the valence-band offset between $Hg_{0.78}Cd_{0.22}Te$ and CdTe. For all reported theoretical and experimental values of $\Delta E_v$, the potential energy barrier for thermionic emission of electrons is much larger than $\phi_{\text{hole}}$. It follows that thermionic electron currents can be ignored for this heterostructure.

A simple theoretical treatment, similar to the Bethe model for Schottky barriers,[24] can be employed to calculate thermionic hole current densities across the CdTe barrier as a function of applied voltage. The resulting expression is

$$J_{\text{therm}} = A^*T^2 \exp\left(\frac{-\phi_{\text{hole}} + cqV}{kT}\right)\left[1 - \exp\left(\frac{-qV}{kT}\right)\right],$$

where $A^*$ is the modified Richardson constant, $T$ is the temperature, $V$ is the applied voltage, $q$ is the hole charge, $k$ is the Boltzmann constant, and $c$ is the fraction of the total applied voltage which drops across the positively biased $Hg_{0.78}Cd_{0.22}Te$ electrode. For this single barrier heterostructure, $A^*$ is $120(m_h^*)$ in A/cm² K², where $m_h^*$ is the unitless hole mass. The contributions from the light- and heavy-hole bands are summed to give the total current from this mechanism. It is important to note that the factor $c$ is a function of the voltage applied across the heterostructure, and must therefore be calculated from the energy-band diagram for each individual bias condition. The value of $c$ generally is in the range 0.25–0.40 for the heterostructure studied here, as compared to the case of a Schottky barrier, where $c = 1$.

For applied voltages of approximately 50 mV and higher, tunneling of holes across the "triangular-shaped" CdTe barrier makes a contribution to the total current through the heterostructure. This transport mechanism can be treated theoretically in a manner which is analogous to the model for the thermionic hole current. The resulting expression for the hole tunneling current density, $J_{\text{htun}}$, differs from that for $J_{\text{therm}}$ by an integral term which replaces the factor $\exp(-\Delta E_v^{(x=0.22)}/kT)$:

$$J_{\text{htun}} = A^*T^2 \exp\left(\frac{-E_f - E_g^{(x=0.22)} + cqV}{kT}\right) \times\left[1 - \exp\left(\frac{-qV}{kT}\right)\right]\int_0^{u_0}(t^*t)u\exp\left(\frac{-u^2}{2}\right)du.$$

In this expression,

$$u^2/2 = m_h^* v_l^2/kT,$$

where $v_l$ is the group velocity of the holes in the growth direction, $u_0 = (2\Delta E_v^{(x=0.22)}/kT)^{1/2}$, and $t^*t$ is the transmission coefficient for holes tunneling through the CdTe barrier. In this study, we have calculated $t^*t$ via the Wentzel–Kramers–Brillouin (WKB) method. A two-band $k\cdot p$ theory formula[25] was used to find imaginary light-hole wave vectors in the CdTe barrier, while imaginary heavy-hole wave vectors were determined from the simple "one-band" formula.

The total current density $J$ is the sum of $J_{\text{therm}}$ and $J_{\text{htun}}$. In general, the thermionic current density is calculated more accurately than the tunneling current density because $t^*t$ is strongly dependent on many parameters, such as the barrier thickness, CdTe effective masses, and the applied voltage. It is therefore prudent to restrict analysis of experimental data to those voltages at which $J_{\text{therm}}$ is expected to dominate. For this heterostructure, it has been estimated that $J_{\text{htun}}$ becomes large (greater than 30% of the current) when $V \geqslant 100$ mV. At room temperature, $J_{\text{therm}}$ and $J_{\text{htun}}$ are much greater than the electron tunneling current $J_{\text{etun}}$. However, negative differential resistance regions have been observed in $I$-$V$ characteristics taken at $T = 4.2$ K, indicating that electron tunneling becomes an important transport mechanism at low temperatures. These results will be reported elsewhere.[11]

Figure 2 contains a typical experimental current density-voltage ($J$-$V$) characteristic, taken at room temperature. Also shown is a theoretical curve, which is obtained by setting $\Delta E_v^{(x=0.22)} = 285$ meV in our simple model of the $J$-$V$ behavior. $\Delta E_v^{(x=0.22)}$ was chosen by requiring the calculated and experimental currents to be the same at 50 mV, and was the only adjustable parameter used. Selecting different values of the applied bias results in variations of $\Delta E_v^{(x=0.22)}$ by roughly $\pm$ 10 meV over the voltage range 0–200 mV, well beyond the 100-mV limit discussed above. This supports the assertion that virtually all of the current in the heterostructure is due to $J_{\text{therm}}$ and $J_{\text{htun}}$. In fact, the shape of the theoretical $J$-$V$ curve is nearly independent of the choice of $\Delta E_v^{(x=0.22)}$, which enters the expression for $J_{\text{therm}}$ only in a voltage-independent multiplicative factor. Over 75 devices (those which were not shorted, as described previously) were tested at room temperature. In all cases, $\Delta E_v^{(x=0.22)}$ was found to be within 10 meV of the value obtained in Fig. 2. Due to the presence of Hg flux during the growth of CdTe layers, it is expected that the barrier material is actually $Hg_{0.05}Cd_{0.95}Te$.[26] Therefore, the experimentally obtained value of $\Delta E_v^{(x=0.22)}$ actually represents the valence-band discontinuity at a $Hg_{0.78}Cd_{0.22}Te$-$Hg_{0.05}Cd_{0.95}Te$ interface.

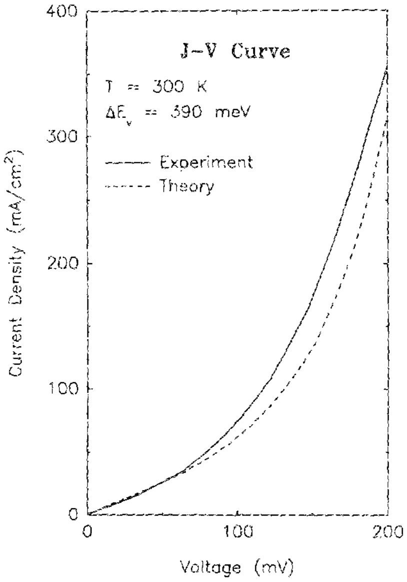

FIG. 2. Experimental $J$-$V$ curve (solid line) taken at room temperature. Also plotted is a best fit curve calculated for a HgTe-CdTe valence-band offset of 390 meV (dashed line). $\Delta E_v$ is the only adjustable parameter used to generate the best fit curve.

Assuming a linear variation of the valence-band edge in $Hg_{1-x}Cd_xTe$ with $x$, $\Delta E_v$ is then determined to be $390 \pm 75$ meV. The estimated error has been assigned by combining the previously discussed variation in $\Delta E_v^{(x=0.22)}$ with the following sources of uncertainty: (i) nonuniformity across the sample, (ii) uncertainty in cladding layer compositions and band gaps, (iii) the percentage of alloying of the CdTe barrier due to incorporation of Hg during growth, and (iv) errors made in determining the transmission coefficients for hole tunneling.

Further $I$-$V$ measurements were made on over 20 devices in a low-temperature microprobe station. Electron tunneling currents were found to be insignificant for temperatures above 160 K. Consequently, we report data here for 190 K and higher. Analysis of the low-temperature data was performed in the same manner as described previously for room-temperature measurements, producing theoretical $J$-$V$ curves which agreed within 5% of the experimental characteristics over the voltage range 0–100 meV.

Figure 3 is a plot of the values of $\Delta E_v$ which were determined as a function of temperature, along with a corresponding scale for $\Delta E_v^{(x=0.22)}$. Examination of Fig. 3 reveals that the band offset is found to vary strongly with temperature—an effect that has not been reported previously, to the best of the authors' knowledge. For example, it is found that $\Delta E_v = 245 \pm 70$ meV at $T = 190$ K. Band offset theories are at an early stage of development, with no temperature dependence yet estimated. It is possible that a transport mechanism which has not been considered may be contributing to the observed currents. This could lead to false determinations of the low-temperature band offsets. However, the observed agreement between the theoretical and experimental $J$-$V$ curves, without the use of any free parameters other than $\Delta E_v^{(x=0.22)}$, suggests that the correct current transport mechanisms have been included. It should be noted that the observed current decreases exponentially as the temperature decreases (as is expected for thermionic mechanisms), despite the decrease in $\Delta E_v$. This is reasonable because $\phi_{\text{hole}}$ includes terms which do not vanish at $T = 0$ K. Furthermore, the recent observation of negative differential resistance at $T = 4.2$ K is consistent with a valence-band offset which is much smaller than the room-temperature value.[11]

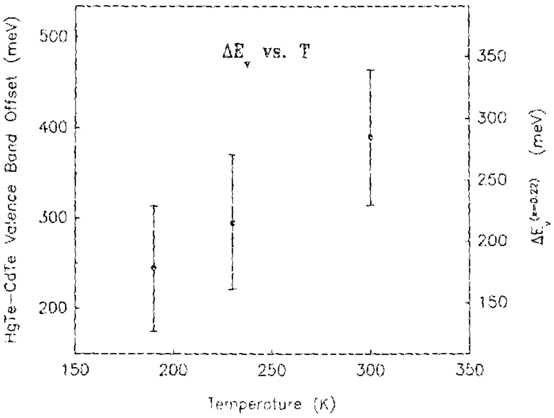

FIG. 3. Temperature dependence of HgTe-CdTe valence-band offset, as determined from experimental $J$-$V$ curves. Also plotted is the corresponding scale for the offset at the $Hg_{0.78}Cd_{0.22}Te$-$Hg_{0.05}Cd_{0.95}Te$ interface, $\Delta E_v^{(x=0.22)}$, assuming a linear dependence on composition, i.e., $\Delta E_v^{(x=0.22)} = 0.73\Delta E_v$.

In this letter, we have experimentally and theoretically studied the current-voltage behavior of a $Hg_{0.78}Cd_{0.22}Te$-CdTe-$Hg_{0.78}Cd_{0.22}Te$ heterostructure. Interpretation of the measured current as being dominated by thermionic and tunneling hole currents resulted in a determination of $\Delta E_v = 390 \pm 75$ meV at $T = 300$ K. This result is in reasonable agreement with recent XPS measurements. A similar analysis of low-temperature data indicates that the valence-band offset has a strong and previously unreported temperature dependence, with $\Delta E_v$ becoming smaller for low $T$. However, other transport mechanisms may have contributed to the low-temperature currents, leading to erroneously low values of $\Delta E_v$.

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[1] J. N. Schulman and T. C. McGill, Appl. Phys. Lett. **34**, 663 (1979).
[2] C. E. Jones, T. N. Casselman, J. P. Faurie, S. Perkowitz, and J. N. Schulman, Appl. Phys. Lett. **47**, 140 (1985).
[3] S. R. Hetzler, J. P. Baukus, A. T. Hunter, J. P. Faurie, P. P. Chow, and T. C. McGill, Appl. Phys. Lett. **47**, 260 (1985).
[4] J. P. Faurie, J. Reno, and M. Boukerche, J. Cryst. Growth **72**, 111 (1985).
[5] J. P. Baukus, A. T. Hunter, O. J. Marsh, C. E. Jones, G. Y. Wu, S. R. Hetzler, T. C. McGill, and J. P. Faurie, J. Vac. Sci. Technol. A **4**, 2110 (1986).
[6] D. J. Leopold, M. L. Wroge, and J. G. Broerman, Appl. Phys. Lett. **50**, 924 (1987).
[7] J. P. Baukus, A. T. Hunter, J. N. Schulman, and J. P. Faurie (unpublished).
[8] J. N. Schulman and C. L. Anderson, Appl. Phys. Lett. **48**, 1684 (1986).
[9] M. A. Reed, R. J. Koestner, and M. W. Goodwin, Appl. Phys. Lett. **49**, 1293 (1986).
[10] D. H. Chow and T. C. McGill, Appl. Phys. Lett. **48**, 1485 (1986).
[11] D. H. Chow, T. C. McGill, I. K. Sou, J. P. Faurie, and C. W. Nieh (unpublished).
[12] J. O. McCaldin, T. C. McGill, and C. A. Mead, Phys. Rev. Lett. **36**, 56 (1976).
[13] W. A. Harrison, *Electronic Structure and The Properties of Solids* (Freeman, San Francisco, 1980).
[14] J. Tersoff, J. Vac. Sci. Technol. B **4**, 1066 (1986).
[15] T. F. Kuech and J. O. McCaldin, J. Appl. Phys. **53**, 3121 (1982).
[16] S. P. Kowalczyk, J. T. Cheung, E. A. Kraut, and R. W. Grant, Phys. Rev. Lett. **56**, 1605 (1986).
[17] T. M. Duc, C. Hsu, and J. P. Faurie, Phys. Rev. Lett. **58**, 1127 (1987).
[18] C. K. Shih and W. E. Spicer, Phys. Rev. Lett. **58**, 2594 (1987).
[19] A. Zoryk and M. Jaros, Appl. Phys. Lett. **50**, 1191 (1987).
[20] Y. Guldner, G. Bastard, J. P. Vieren, M. Voos, J. P. Faurie, and A. Million, Phys. Rev. Lett. **51**, 907 (1983).
[21] J. P. Faurie, C. Hsu, and T. M. Duc, J. Vac. Sci. Technol. A **5**, 3074 (1987).
[22] A. R. Bonnefoi, D. H. Chow, and T. C. McGill, to be published in J. Appl. Phys.
[23] R. Dornhaus, G. Nimtz, and B. Schlicht, *Narrow-Gap Semiconductors* (Springer, Berlin, 1983), pp. 158–160.
[24] S.M. Sze, *Physics of Semiconductor Devices* (Wiley, New York, 1981), pp. 255–259.
[25] E. O. Kane, *Physics of III-V Compounds* (Academic, New York, 1966), Vol. 1, Chap. 3, pp. 75–100.
[26] J. Reno, R. Sporken, Y. J. Kim, C. Hsu, and J. P. Faurie (unpublished).