

Ideal CdTe/HgTe superlattices

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In this paper we consider a new superlattice system consisting of alternating layers of CdTe and HgTe constructed parallel to the (001) zincblende plane. The tight-binding method is used to calculate the electronic properties of this system, in particular, band edge and interface properties. The energy gap as a function of layer thickness is determined. It is found to decrease monotonically with increasing HgTe layer thickness for a fixed ratio of CdTe to HgTe layer thicknesses. The symmetry of the valence band maximum state is found to change at certain HgTe layer thicknesses. This is explained by relating the superlattice states to bulk CdTe and HgTe states. The existence of interface states is investigated for the superlattice with 12 layers of CdTe alternating with 12 of HgTe. Interface states are found near the boundaries of the Brillouin zone, but none are found in the band gap.

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I. INTRODUCTION

The study of superlattice systems made from alternating layers of two semiconductors has been a fruitful source of new knowledge about interfaces, band structures and novel quantum effects on a submicron scale. In this paper we present the results of a theoretical study of the CdTe/HgTe superlattice, the third such system to be considered. The other two, AlAs/GaAs^{1,2} and InAs/GaSb,³ have been successfully fabricated using the molecular beam epitaxy (MBE) technique. The CdTe/HgTe superlattice is also a likely candidate for fabrication using MBE because of their common zincblende form and close lattice match (within 0.3%).⁴

The distinctive features of this superlattice are the bulk band structures of the HgTe and CdTe, and the value of the offset between the valence band edges. CdTe is direct with a low temperature band gap of about 1.6 eV.⁴ HgTe is a zero band gap semiconductor.⁴ Its band structure is similar to CdTe except that relativistic effects have pulled down the Γ_6 symmetry *s*-like conduction band minimum of CdTe below the Γ_8 symmetry valence band maximum. The light hole valence band acquires a positive effective mass and is thus empty. Empirical arguments, given in Sec. II of this paper, suggest the offset between the valence band edges is small, if not zero. Hence, CdTe/HgTe superlattices consist of alternating layers of a large band gap semiconductor with a small band gap semiconductor.

We investigate several aspects of the electronic structure of the superlattice. Section II briefly discusses the tight-binding method and its application to the CdTe/HgTe superlattice. The problem of band edge discontinuities is also dealt with. Section III describes the properties of the superlattice near the band gap edges including the value and nature of the band gap as a function of superlattice parameters. Section IV discusses the existence of interface states.

II. CALCULATION

The tight-binding method used in this calculation is similar to that used previously by the authors.⁵ Hamiltonian matrix

element parameters were determined for bulk CdTe and HgTe separately by reproducing the pseudopotential band structures of Katsuki and Kunimune.⁶ Spin-orbit splitting was incorporated by the inclusion of additional special parameters. The parameters are listed in Ref. 7. The resulting bulk band structures are shown in Fig. 1. In common with other tight-binding calculations, the valence bands closely resemble the pseudopotential bands. The conduction bands are somewhat flatter than in the pseudopotential case. We have not included *d* states in our calculations. In both these compounds there are *d*-derived bands which hybridize with and cross the bottommost valence bands⁸ shown here. However, the precise character of these bottom valence bands are unimportant to our results, and hence, for simplicity, we have excluded the *d* bands.

One additional parameter must be determined before the bulk parameters can be incorporated in the superlattice Hamiltonian matrix, the value of the valence band edge discontinuity between the two materials. It is this offset parameter which establishes the way in which the bands line up when the heterojunction is formed. Its effect on the band structure of superlattices has been explored for the two previous cases, AlAs/GaAs⁹ and InAs/GaSb.¹⁰ Its effect in the CdTe/HgTe case will be discussed in Sec. III.

We have chosen this parameter to be zero for the following reasons: One model of heterojunction band line-ups uses the electron affinities of the two materials to locate the conduction band edges.¹¹ It is assumed in this model that putting the materials into a heterojunction does not change the relative conduction band position at the interface. The valence band discontinuity, ΔE_V , is then just the difference between the electron affinity plus band gap (ionization potential, Φ) of the two:

$$\Delta E_V = \Phi_{\text{CdTe}} - \Phi_{\text{HgTe}}.$$

The HgTe ionization potential has been measured by Shevchik *et al.*⁸ to be 5.9 eV. Both Shevchik⁸ and Swank¹² have measured this quantity for CdTe and report 6.2 eV and 5.8 eV, respectively. These values of Φ yield values of ΔE_V

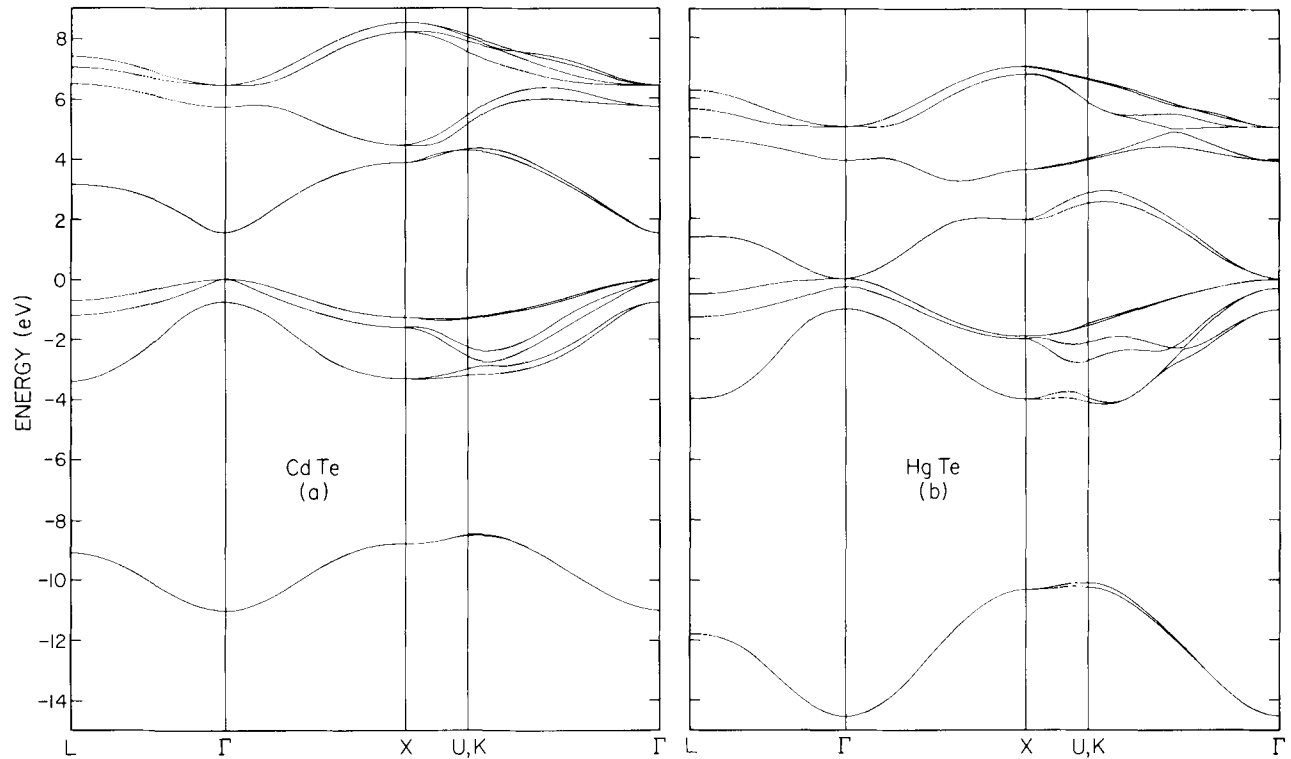


FIG. 1. Bulk band structures calculated by tight-binding for CdTe and HgTe. The valence band maximum is set to 0 eV.

of 0.3 and -0.1 eV, respectively. Further evidence that the discontinuity is small is given in Fig. 2. The band gap plus electron affinity of several III-V and II-VI compounds are shown there. The values are from a book by Sharma and Purohit¹³ (including Swank's CdTe value) except for the HgTe number, which is from Shevchik.⁸ It can be seen that the ionization potential is more heavily dependent on the anion than the cation,¹⁴ and that differences between compounds with the same anion (especially for the tellurium case) are small. We use a value of zero for the discontinuity, although a small value similar to that for the AlAs/GaAs heterojunction would not be unexpected.

III. CHARACTERISTICS OF THE BAND GAP

The band gap of the CdTe/HgTe superlattice differs from that of the random $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ alloy in two ways. First, the value of the gap for a fixed cadmium-to-mercury ratio varies as a function of the CdTe and HgTe repeated slab thicknesses. Second, the symmetry of the state at the valence band maximum exhibits a crossover between two symmetry types as the thickness is varied. This section discusses these features of the band gap.

Figure 3 shows the variation in the band gap versus HgTe layer thickness for superlattices with three ratios of CdTe layer thickness to total repeated slab thickness (x). The three horizontal line segments indicate the random $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ alloy band gaps calculated with our tight binding parameters in the virtual crystal approximation with the same values of x . It can be seen that for thin layers the band gap differs only slightly from the random alloy value. As the HgTe layer thickness increases, the gap decreases monotonically and approaches the bulk HgTe zero band gap limit. In common with the alloy, higher cadmium concentrations produce larger band gaps.

This band gap variation can be understood intuitively using a simple model. The zero band gap HgTe is envisioned as forming wells for the conduction electrons with the CdTe/HgTe conduction band discontinuity forming the sides of the wells. As the HgTe well width is increased, the energy of the

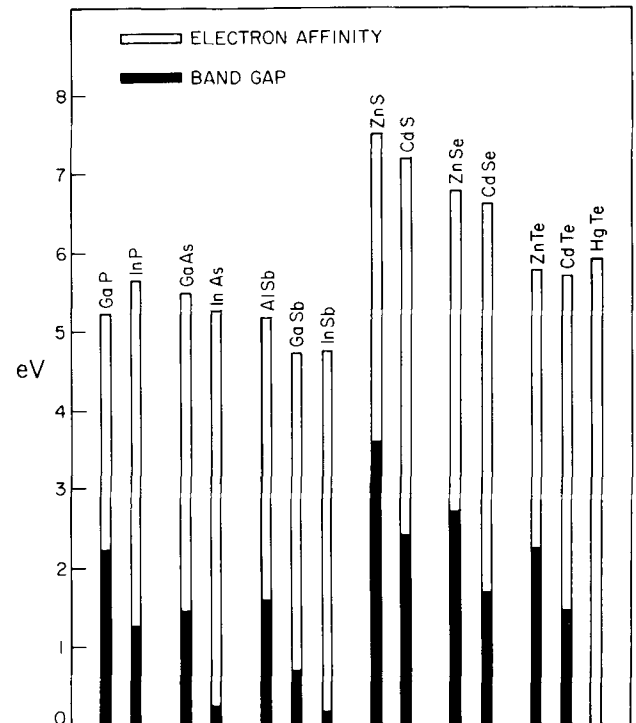


FIG. 2. Band gap plus electron affinity for several III-V and II-VI compounds. This is an approximation to the energy difference between the vacuum and the top of the valence band. The HgTe value is from Ref. 8. All others are from Ref. 13.

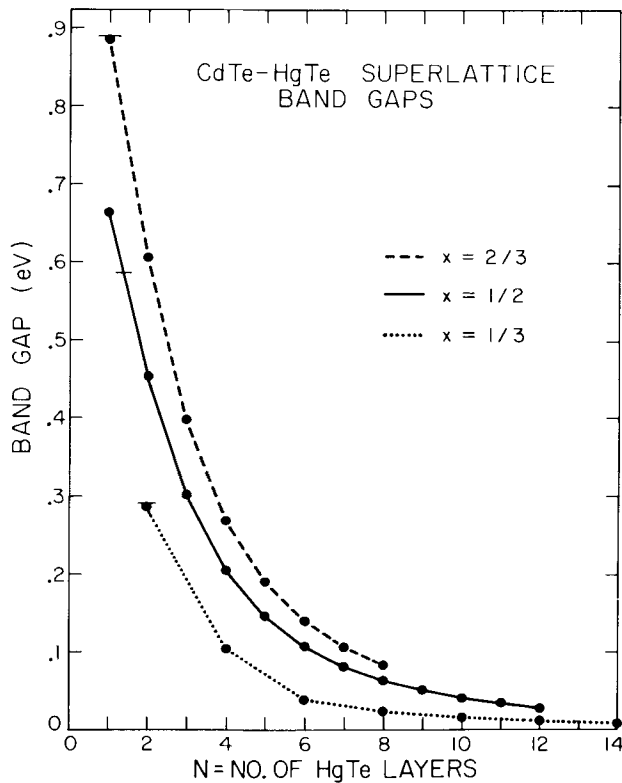


FIG. 3. Superlattice band gaps versus number of atomic layers of HgTe in a repeated superlattice slab. The dashed line represents superlattices with a CdTe to HgTe ratio of 2:1; the solid line, 1:1; and the dotted line, 1:2 ($x = \frac{2}{3}$, $\frac{1}{2}$, and $\frac{1}{3}$). The random alloy values are indicated by the three long horizontal dashes.

lowest well state decreases and thus the band gap decreases. Because of the zero valence band discontinuity, the hole states are not confined in either the CdTe or HgTe layers in this way.

The switch in symmetry of the valence band maximum as the thicknesses are varied will now be discussed. CdTe and HgTe have a different ordering of states at $k = 0$. The Γ_6

symmetry conduction band minimum state goes below the Γ_8 symmetry valence band maximum state as the mercury concentration is increased for the $Hg_{1-x}Cd_xTe$ alloy. An interesting feature of the superlattice system is that this same behavior can occur with the superlattice for a given cadmium concentration as slab thickness is varied. This is demonstrated in Fig. 4. It shows the change in energy levels for states near the band gap as a function of layer thickness. Panels (a), (b), and (c) are for superlattices with three ratios of CdTe to HgTe layer thickness. In Fig. 4(a) the HgTe layers are twice as thick as the CdTe layers; in Fig. 4(b) the layers are of equal thickness, and in Fig. 4(c) the CdTe layers are twice as thick as the HgTe layers. The three curves in each panel represent the energies at the bottom of the conduction band, the top of the valence band, and the next state in energy below the top of the valence band. All states have k vectors at the center of the Brillouin zone. The horizontal axis gives the number of atomic layers of HgTe per repeated superlattice slab.

The crossing of the curves in panels (a) and (b) (and thus the change in symmetry of the valence band maximum) can be interpreted in terms of the bulk zincblende states from which they are derived, but first the relationship between the bulk and superlattice state symmetries must be described. The three bulk zincblende symmetries Γ_6^B , Γ_7^B , and Γ_8^B are modified when the periodic perturbation in the z direction is superimposed. (The superscript B indicates the irreducible representation of the bulk point group T_d .¹⁵) Only two group representations, which we call Γ_6^S and Γ_7^S , are possible. (The superscript S indicates the irreducible representation of the superlattice point group D_{2d} .¹⁵) The Γ_6^B conduction band state becomes a state with Γ_6^B symmetry in the superlattice case. The split off Γ_7^B valence band state becomes a Γ_7^S symmetry state. The fourfold degenerate Γ_8 state at the valence band maximum splits into two spin doubly degenerate superlattice states, one of Γ_6^S symmetry and one of Γ_7^S symmetry.¹⁵

The different order of these states in energy as a function of layer thickness produces the crossover. Intuitively what might be expected to happen is that for thin alternating layers

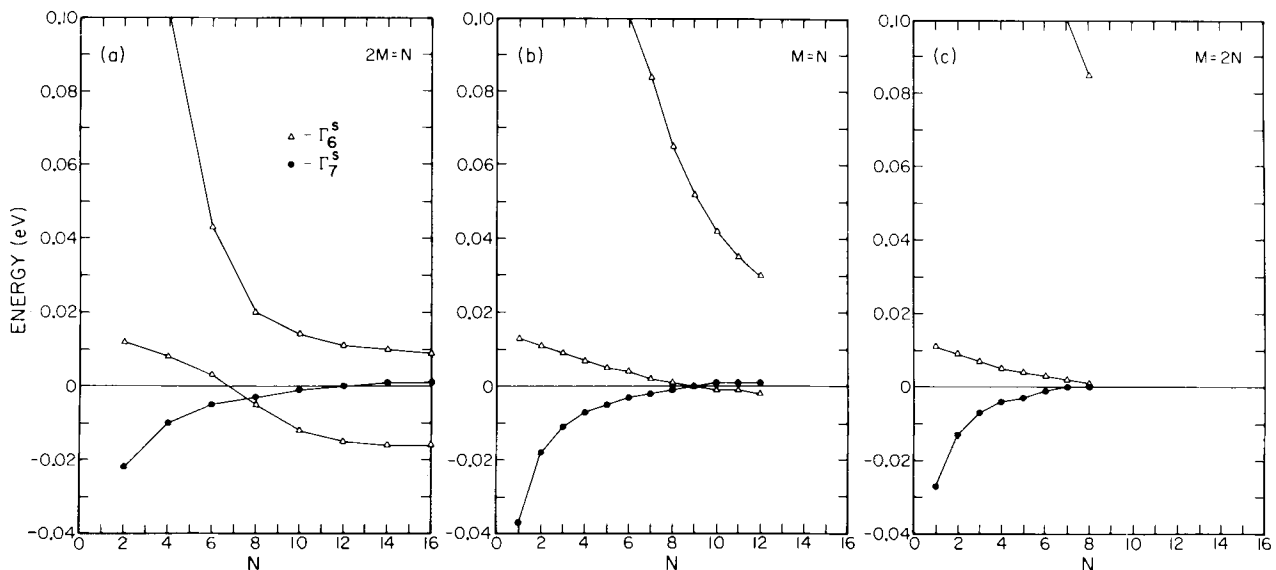


FIG. 4. Three superlattice energies at the band gap edges. The band gap is between the two higher energy states. Γ_6^S states are indicated by open triangles, and Γ_7^S states by filled circles. M and N are the number of CdTe and HgTe atomic layers per slab.

the ordering of the states would be similar to that for the random alloy with the same cadmium concentration. All three cadmium concentrations dealt with in Fig. 4 produce random alloy band structures with the Γ_6^B energy higher than Γ_8^B . The Γ_6^B, Γ_8^B ordering should switch for layers thick enough to reconstitute bulk HgTe. This is what is shown in Fig. 4 if the top-lying Γ_6^S state is interpreted in terms of bulk states correctly. It is derived from bulk Γ_6^B or Γ_8^B . For thin layers it is derived from the conduction band minimum Γ_6^S state. Its energy relative to the valence band maximum is close to that for the $Hg_{1-x}Cd_xTe$ random alloy of the same cadmium to mercury ratio as shown in Fig. 3. For thick layers it becomes the higher energy state of the pair of states which the bulk Γ_8^B level splits into. The higher energy Γ_6^S state does not actually pass through the other states. Only the lower energy Γ_6^S state crosses the Γ_7^S state as shown in (a) and (b). The HgTe layers in Fig. 4(c) are not thick enough to exhibit the crossing. The degree to which the HgTe layers are approaching bulk HgTe is measured by the energy difference between the higher energy Γ_6^S state and the Γ_7^S state. The thickest layer consists of 16 atomic HgTe layers alternating with eight of CdTe shown in Fig. 4(a). The states are still about 10 meV apart at this thickness.

IV. INTERFACE PROPERTIES

In the limit in which the superlattice layers are made large, the series of interfaces become isolated from each other. The thickest superlattices investigated by us have a total of twelve CdTe and HgTe layers each per repeated slab. As indicated in the previous section the single heterojunction limit has not yet been reached at this thickness. A comprehensive search for interface states cannot be accomplished for this reason. Interface states which die off very abruptly within two or three atomic layers from the interface can, however, be identified. Two states of this type have been found at the CdTe/HgTe interface near and at the Brillouin zone boundary. One has an energy approximately 2.6 eV below the valence band maximum. It has significant amplitude on about six layers surrounding the interface. The other interface state is at an energy which may make it more accessible to experimental methods. Its energy is 0.45 eV below the valence band maximum, but it is the topmost state at that particular point in reciprocal space. It is very localized within three layers of the interface. Both of these states have an interface nature only near a particular point on the Brillouin zone boundary, the

J point. Away from this point the state acquires a bulk-like character. There are no interface states at the center of the Brillouin zone. Results concerning interface states are more sensitive to the particular tight-binding parameters used than band structure results.

V. SUMMARY

A tight-binding calculation was used to investigate the band structure of a new superlattice consisting of CdTe and HgTe. The band gaps and the nature of the band gap edge states were found as a function of the superlattice thickness parameters. Novel features including the crossing of bands for increasing thickness but fixed alloy concentration were studied. Interface states were found in a range which might be susceptible to experiments sensitive to interfacial properties.

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- ¹L. L. Chang, L. Esaki, W. Howard, R. Ludeke, and G. Schul, *J. Vac. Sci. Technol.* **10**, 655 (1973).
- ²R. Dingle, A. C. Gossard, and W. Wiegmann, *Phys. Rev. Lett.* **34**, 1327 (1975).
- ³H. Sakaki, L. L. Chang, G. A. Sai-Halasz, C. A. Chang, and L. Esaki, *Solid State Commun.* **26**, 589 (1978).
- ⁴R. Dornhaus and G. Nimtz, *Springer Tracts in Modern Physics* **78** (1976).
- ⁵J. N. Schulman and T. C. McGill, *Phys. Rev. B* **20**, June 15, 1979.
- ⁶S. Katsuki and M. Kunimune, *J. Phys. Soc. Japan* **31**, 415 (1971).
- ⁷J. N. Schulman and T. C. McGill, *Appl. Phys. Lett.* **34**, 663 (1979).
- ⁸N. J. Shevchik, J. Tejada, M. Cardona, and D. W. Langer, *Phys. Status Solidi(b)* **59**, 87 (1973).
- ⁹R. Dingle, W. Wiegmann, and C. H. Henry, *Phys. Rev. Lett.* **33**, 827 (1974).
- ¹⁰G. A. Sai-Halasz, R. Tsu, and L. Esaki, *App. Phys. Lett.* **30**, 651 (1977).
- ¹¹A. G. Milnes and D. L. Feucht, *Heterojunctions and Metal-Semiconductor Junctions* (Academic, New York, 1972) pp. 3-13.
- ¹²R. K. Swank, *Phys. Rev.* **153**, 844 (1967).
- ¹³B. L. Sharma and R. K. Purohit, *Semiconductor Heterojunctions* (Pergamon, Oxford, 1974).
- ¹⁴J. O. McCaldin, T. C. McGill, and C. A. Mead, *J. Vac. Sci. Technol.* **13**, 802 (1976).
- ¹⁵G. F. Koster, J. O. Dimmock, R. G. Wheeler, H. Statz, *Properties of the Thirty-two Point Groups* (M.I.T., Cambridge, MA, 1963).