Ideal CdTe/HgTe superlattices

J. N. Schulman and T. C. McGill

California Institute of Technology, Pasadena, California 91125

(Received 13 March 1979; accepted 19 April 1979)

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.

PACS numbers: 73.40.Lq, 73.60.Fw, 71.25.Tn

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 and InAs/GaSb, 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%).

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. HgTe is a zero band gap semiconductor. Its band structure is similar to CdTe except that relativistic effects have pulled down the \( \Gamma_9 \) symmetry s-like conduction band minimum of CdTe below the \( \Gamma_9 \) 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. Hamiltonian matrix element parameters were determined for bulk CdTe and HgTe separately by reproducing the pseudopotential band structures of Katsuki and Kunimune. 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 the \( d \) states in our calculations. In both these compounds there are \( d \)-derived bands which hybridize with and cross the bottommost valence bands shown here. However, the precise character of these bottom valence bands is 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/GaAs and InAs/GaSb. 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. 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, \( \Delta E_V \), is then just the difference between the electron affinity plus band gap (ionization potential, \( \Phi \)) of the two:

\[
\Delta E_V = \Phi_{\text{CdTe}} - \Phi_{\text{HgTe}}
\]

The HgTe ionization potential has been measured by Shevchik et al. to be 5.9 eV. Both Shevchik and Swank have measured this quantity for CdTe and report 6.2 eV and 5.8 eV, respectively. These values of \( \Phi \) yield values of \( \Delta E_V \).
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 Purohit\textsuperscript{13} (including Swank's CdTe value) except for the HgTe number, which is from Shevchik.\textsuperscript{8} It can be seen that the ionization potential is more heavily dependent on the anion than the cation,\textsuperscript{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 Hg\textsubscript{1-x}Cd\textsubscript{x}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 Hg\textsubscript{1-x}Cd\textsubscript{x}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

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Bulk band structures calculated by tight-binding for CdTe and HgTe. The valence band maximum is set to 0 eV.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{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.}
\end{figure}
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 $\Gamma_6$ symmetry conduction band minimum state goes below the $\Gamma_8$ symmetry valence band maximum state as the mercury concentration is increased for the Hg$_{1-x}$Cd$_x$Te 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 $\Gamma_6$, $\Gamma_9$, and $\Gamma_8$ are modified when the periodic perturbation in the $z$ direction is superimposed. (The superscript $B$ indicates the irreducible representation of the bulk point group $T_d$. Only two group representations, which we call $\Gamma_6^B$ and $\Gamma_9^B$, are possible. (The superscript $S$ indicates the irreducible representation of the superlattice point group $D_{zd}$. The $\Gamma_6$ conduction band state becomes a state with $\Gamma_6^S$ symmetry in the superlattice case. The split off $\Gamma_8^S$ valence band state becomes a $\Gamma_9^S$ symmetry state. The fourfold degenerate $\Gamma_6^S$ state at the valence band maximum splits into two spin doubly degenerate superlattice states, one of $\Gamma_6^S$ symmetry and one of $\Gamma_9^S$ symmetry. 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
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 $\Gamma^0$ energy higher than $\Gamma^8$. The $\Gamma^0$, $\Gamma^8$ ordering should switch for layers thick enough to reconstitute bulk HgTe. This is what is shown in Fig. 4 if the top-lying $\Gamma^5$ state is interpreted in terms of bulk states correctly. It is derived from bulk $\Gamma^8$ or $\Gamma^8$. For thin layers it is derived from the conduction band minimum $\Gamma^5$ state. Its energy relative to the valence band maximum is close to that of the $\Gamma^5$ state and the $\Gamma^5$ state is at an energy which may make it more accessible to experiments sensitive to interfacial properties.

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.

ACKNOWLEDGMENTS

The authors are grateful to D. L. Smith and J. S. Best for many useful discussions. We would like to acknowledge the support of the Army Research Office under Contract No. DAAG29-77-C-0015.