Determination of a Natural Valence-Band Offset: The Case of HgTe and CdTe

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We propose a method to determine a natural valence-band offset (NVBO), i.e., the change in the valence-band maximum energy which is intrinsic to the bulk band structures of semiconductors. We use the HgTe-CdTe system as an example in which we find that the valence-band maximum of HgTe lies 0.35 ± 0.06 eV above that of CdTe. The NVBO of 0.35 eV is in good agreement with the x-ray photoemission spectroscopy measurement of the heterojunction offset. The procedure to determine the NVBO between semiconductors, and its implication on the heterojunction band lineup and the electronic structures of semiconductor alloys, are discussed.

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Band lineup at heterojunction interfaces, the critical parameter for novel devices utilizing heterostructures, has attracted considerable interest both theoretically and experimentally. Many theories have attempted to put the bulk band structures on a common reference energy scale, thus establishing the so-called natural band lineups automatically. In Harrison's tight-binding (TB) theory,[1] a common reference can be established since the bulk bands are derived directly from the atomic term values. Through a Mattheiss construction,[2] Van de Walle and Martin use a model solid approach[3] where a common reference scale is also derived from atomic information. In Andersen's linear muffin-tin-orbital (LMTO) method,[4] the zero of the energy reference is defined within the atomic-sphere approximation (ASA). While the above theories are spiritually in common, they yield fairly different results. For example, for HgTe-CdTe Harrison's model gives <0.1-eV valence-band offset (VBO) where the other two models give fairly large VBO's: 0.28 eV by Van de Walle and Martin,[3] and 0.45 eV by Christensen and Andersen.[5]

The purpose of this Letter is to propose a method of experimentally establishing such intrinsic band lineups and of giving the relative energies of the valence-band maximum (VBM) as a function of alloy composition. Besides providing comparison with the above theoretical models of band lineups, it also has the following very appealing features. First, such quantities are associated with the bulk properties only, thus avoiding any ambiguity involved in determining the heterojunction valence-band offset (HVBO) due to the orientation or imperfection of the prepared interfaces. Moreover, they also provide a crucial parameter allowing the proper positioning of constituent bands in determining the electronic structures of pseudobinary semiconductor alloys. Such quantities are not available in any of the present coherent-potential approximation theories utilizing the TB method (while the first-principles self-consistent Korringa-Kohn-Rostoker coherent-potential approximation is available for metal alloys, it is almost impossible to apply it to semiconductor alloys because of the computational complexity). In addition, determining the relative position of the VBM as a function of alloy composition should be helpful for device modeling.

We use the HgTe-CdTe system as an example to demonstrate this method, in which we find a natural VBO (NVBO) of 0.35 eV, in agreement with the HVBO determined by Kowalczyk *et al.*[6] and Duc, Hsu, and Faurie.[7]

The key to our approach lies in the measurement of the core-level binding energies of semiconductor alloys, for example, $Hg_{1-x}Cd_xTe$, relative to the VBM as a function of the alloy composition. These quantities are defined as

$$E_c^v = E^{\mathrm{VBM}} - E^{\mathrm{core}}.$$

If one considers that there is an absolute energy scale, then the changes in these core-level binding energies (relative to the VBM) come from two contributions: the changes in the position of the VBM and the changes in the core-level energy positions on the absolute energy scale. To separate the two contributions, we calculate the core-level binding energies of $Hg_{1-x}Cd_xTe$ on an absolute energy scale, using a Born-Haber cycle in the context of the TB theory. The absolute energy scale here is defined in the same way as that of Harrison.[1] As we will show, on this absolute energy scale the compositional dependence of the cation binding energies (Hg 5*d* and Cd 4*d*) is nearly constant. Thus the measured changes in E_c^v of cations reflect the movement of the VBM with alloy composition, and the NVBO can be deduced.

The inset in Fig. 1(a) shows the valence-band spectra near the VBM, taken at normal-emission geometry with photon energy of 21 eV, of cleaved crystals of HgTe, $Hg_{0.7}Cd_{0.3}Te$, and CdTe, respectively. This choice of normal-emission geometry with 21-eV photon energy greatly enhances the emission of the electronic states near the VBM. By alignment of the VBM's of these three materials, the relative changes in the core-level binding energies referred to the VBM can be determined

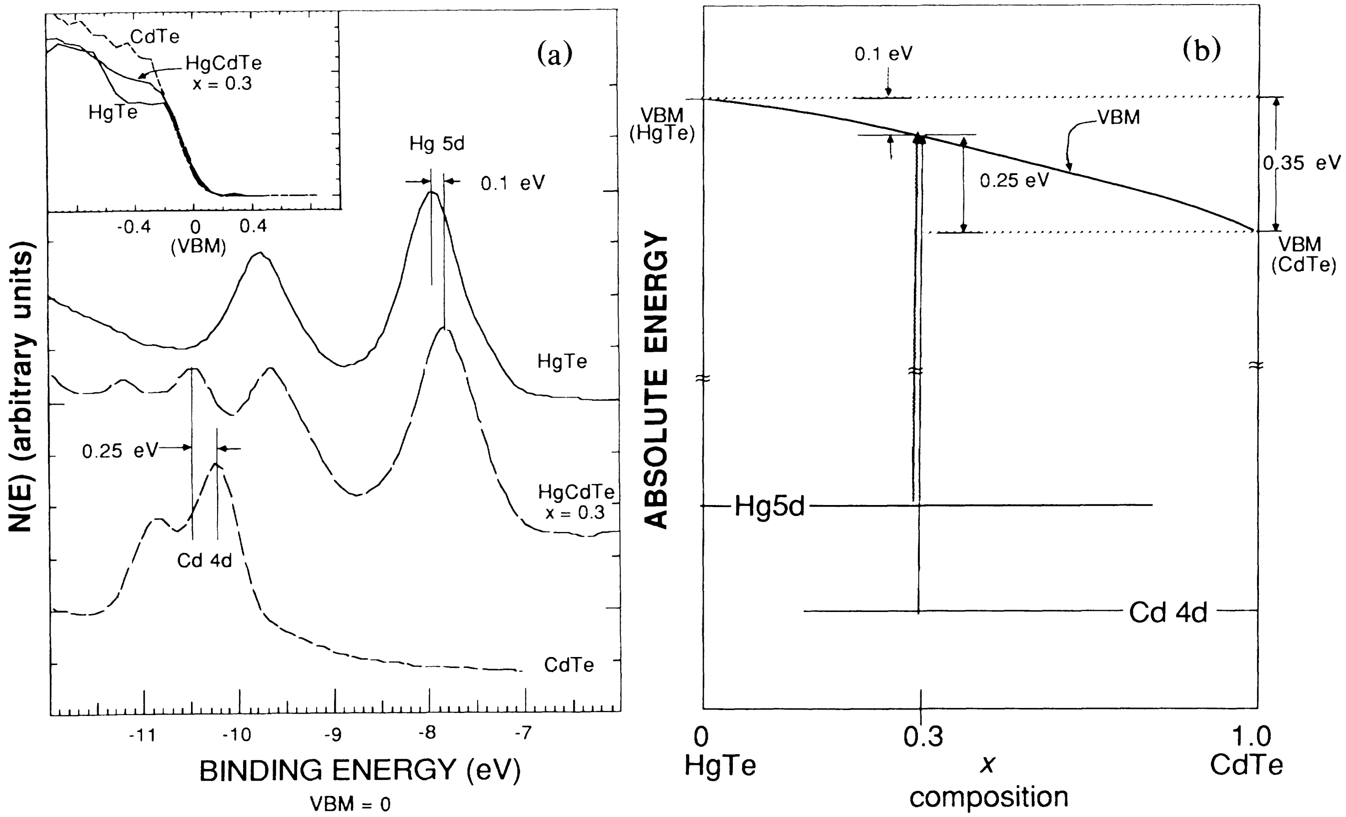

FIG. 1. (a) The Hg 5*d* and Cd 4*d* core levels of HgTe, HgCdTe, and CdTe with the valence-band maxima taken as zero binding energy. Inset: Accuracy of the alignment of the VBM's. (b) The schematic diagram showing the movement of the VBM as a function of composition. With the assumption that the core levels of cations stay constant on the absolute energy scale and that the VBM of HgTe lies 0.35 eV above that of CdTe, the measured core-level shift upon alloying can be fully explained.

very precisely to within 0.03 eV (systematic errors in determining the position of the VBM's are canceled). In Fig. 1(a), Hg 5*d* and Cd 4*d* of HgTe, $Hg_{0.7}Cd_{0.3}Te$, and CdTe are displayed together with the VBM's taken as the zero binding energy. Let us define

$$\Delta E_c^v(\text{Hg }5d,x)=E_c^v(\text{Hg }5d,\text{Hg}_{1-x}\text{Cd}_x\text{Te})-E_c^v(\text{Hg }5d,\text{HgTe}),$$

$$\Delta E_c^v(\text{Cd }4d,x)=E_c^v(\text{Cd }4d,\text{Hg}_{1-x}\text{Cd}_x\text{Te})-E_c^v(\text{Cd }4d,\text{CdTe});$$

then the experimental result is expressed as

$$\Delta E_c^v(\text{Hg }5d,x=0.3)=-0.1\pm 0.03\text{ eV},$$

$$\Delta E_c^v(\text{Cd }4d,x=0.3)=0.25\pm 0.03\text{ eV}.$$

Similar results have been reported[8] for a range of alloy composition (from $x=0.2$ to $x=0.39$) with slightly worse accuracy in determining ΔE_c^v: The Hg 5*d* (relative to the VBM) in the alloy shifts to lower binding energy than that of HgTe, and the Cd 4*d* does the opposite. Also noticeable is that the Hg $5d_{5/2}$ and Cd $5d_{5/2}$ separation is a constant, 2.70 ± 0.1 eV (which is similar to that of this work, 2.65 ± 0.03 eV), over the compositional range from $x=0.2$ to $x=0.39$.

As mentioned earlier, there are two contributions to these shifts: the shift of the VBM, and the shift of the core level, on the absolute scale. This relation is expressed as

$$\Delta E_c^v=\Delta E^{\text{VBM}}-\Delta E^{\text{core}}.$$

Our calculation which will be discussed below shows that on an absolute energy scale the cation core levels stay nearly constant. Thus the measured cation core-level shifts ΔE_c^v must result from the movement of the VBM. Assuming $\Delta E^{\text{core}}=0$, we can deduce the NVBO as

$$E^{\text{VBM,HgTe}}-E^{\text{VBM,CdTe}}=\Delta E_c^v(\text{Cd},x)-\Delta E_c^v(\text{Hg},x)=0.35\text{ eV}.$$

Figure 1(b) shows pictorially how the natural valence-band offset can account for the measured core-level shifts relative to the VBM. The VBM of HgTe is chosen to lie above that of CdTe by 0.35 eV. The Hg 5*d* and Cd 4*d* are chosen to stay constant on an absolute energy scale. The VBM of the alloys lies somewhere between those of HgTe and CdTe. Thus, for this alloy, the Hg 5*d* level relative to the VBM turns out to be shifted to lower binding energy compared to that in HgTe. Similarly, the Cd 4*d* level shifts to higher binding energy. The sum of these two shifts gives the NVBO. The NVBO of 0.35 eV in this work is in good agreement with the HVBO of 0.35 and 0.36 eV measured by Kowalczyk *et al.*[6] and Duc, Hsu, and Faurie[7], respectively. This indicates that the NVBO accounts for the HVBO in HgTe-CdTe; no extra dipole (referenced to our absolute scale) is needed.

Our approach to the calculation of the core-level binding energies of semiconductor alloys on an absolute energy scale is an extension of the work of Enderlein and Harrison.[9] The Born-Haber cycle is used because the initial-state and the final-state effects in the photoemission process are treated simultaneously. However, because the TB evaluation of E^{VBM} involves some degree of uncertainty, here we refer the binding energy to the zero of the absolute energy scale directly. Although the $z+1$ approximation[10] and the TB evaluation of the bond energy will limit the absolute accuracy of the theory, when we concentrate on the alloying effect, for example, the difference between the binding energy of Hg 5*d* in HgTe and that in HgCdTe, systematic errors introduced by the $z+1$ approximation and TB theory are mostly canceled.[11] The input parameters for the calculation are the bond lengths of the two binaries, and the atomic term values of the constituents and their $z+1$ atoms (e.g., Tl as the $z+1$ atom of Hg).

The accuracy of the calculation depends on how well the atomic term values are chosen. We use that of Chen and Sher[12] in which the relativistic effect causing the Hg 6*s* to be deeper than Cd 5*s* has been included. We obtain the following result:

$$E_B^{\mathrm{abz}}(\mathrm{Hg},\mathrm{Hg}_{1-x}\mathrm{Cd}_x\mathrm{Te}) = E_B^{\mathrm{abz}}(\mathrm{Hg},\mathrm{HgTe}) - (0.06\pm0.02)x\ \mathrm{eV},$$

$$E_B^{\mathrm{abz}}(\mathrm{Cd},\mathrm{Hg}_{1-x}\mathrm{Cd}_x\mathrm{Te}) = E_B^{\mathrm{abz}}(\mathrm{Cd},\mathrm{CdTe}) + (0.07\pm0.02)(1-x)\ \mathrm{eV},$$

$$E_B^{\mathrm{abz}}(\mathrm{Te},\mathrm{Hg}_{1-x}\mathrm{Cd}_x\mathrm{Te}) = E_B^{\mathrm{abz}}(\mathrm{Te},\mathrm{HgTe}) - (0.31\pm0.06)x\ \mathrm{eV}.$$

The superscript "abz" denotes the binding energies are referenced to the zero of the absolute energy scale. The accuracy of our calculation is estimated by our varying the atomic term values over a wide range (>3 eV) while keeping the difference of the cation term values constant (any alloying effect is caused by the difference in the cations). As one can see from the above expression, the cation binding energies on the absolute energy scale stay nearly constant with alloy composition. This supports the validity of lining up the cation core levels in HgCdTe to obtain the NVBO. Moreover, experimentally the Te 4*d* binding energy relative to the VBM in HgTe lies 0.6 ± 0.15 eV deeper than that in CdTe; in comparison with the calculation of the binding-energy difference of Te on the absolute energy scale, the result is certainly consistent with the existence of the NVBO of 0.35 eV.

Our calculation on the AlGaAs system leads to a similar result as on the HgCdTe system: On the absolute energy scale, the Al and Ga core levels stay constant to within 0.06 eV throughout the alloy compositional range. Thus, measurement of cation core levels relative to the VBM in AlGaAs alloys should give the NVBO of GaAs-AlAs.

Up to this point, we have used the TB absolute energy scale to define our NVBO. However, it may not be necessary as discussed in the following. Consider a common-anion alloy system, say $A_{1-x}B_xC$, where the ionicities of the two binaries AC and BC are very different. When the alloy is formed, the charge distribution associated with the anion site will be just the weighted superposition of that of the two binaries; however, the charge distributions associated with A and B sites could be very different from those in the binaries. What is gained (or lost) by cation A will come from (or go to) cation B. If such charge redistribution causes cation A to shift to lower (higher) binding energy on the absolute energy scale going from AC to BC, cation B will shift to higher (lower) binding energy going from BC to AC. Thus the compositional dependence of the cation binding energies will not be constant on the absolute energy scale; instead it gives two inclined lines with the same slope, i.e., the separation between the two cation core levels in the alloy stays constant. It is conceivable that such charge redistribution is similar to that at the ideal heterojunction interface.[13] If this is true, then by measuring the separation between the cation core levels, and comparing to the binding energy (referred to the VBM) difference of these two cation cores in the two binaries, we can get the correct VBO without doing the interface measurement. The VBO determined this way should also give the proper positioning of the constituent bands in the alloy. Similar arguments will also apply to common-cation systems. Thus the idea of the NVBO can exist without the need of referring to an absolute energy scale. Note that at a perfect heterojunction interface, there would be no necessity to add an additional dipole contribution with this approach. A direct test of this generalization is to examine whether the cation core-level separation in the common-anion alloys predicts that at the heterojunction interface of the two binaries.[14]

There appears to be an inconsistency between our results of NVBO of 0.35 eV for HgTe-CdTe and Harrison's result of <0.1 eV, although the same convention of common reference scale is applied. Actually, there is not! A recent TB calculation with the inclusion of the cation *d* orbitals gives a NVBO of 0.3 eV,[15] whereas including cation *d* states into the calculation of the bond energy does not change our result of alloying effect.

It is especially illuminating to compare our result with the NVBO of 0.45 eV obtained by LMTO within ASA since LMTO can be transformed to a first-principles TB formalism.[16] In fact, the application of LMTO within ASA to calculate the electronic structures of many metal alloy systems has been found in excellent agreement with the self-consistent Korringa-Kohn-Rostoker method,[17] since the proper positioning of the constituent bands is built in within ASA. It is our opinion that our method of using the pseudobinary alloy as the reference system for the determination of the natural band lineup is an ideal choice, since it appears that both the heterojunction and alloy problems are treated simultaneously.

We hope that this work will stimulate more research activities testing our method of deducing natural band lineups in other systems. These quantities are not only important for the heterojunction problem but also have very important implications for the electronic properties of semiconductor alloys. For example, the existence of the NVBO of 0.35 eV in HgTe-CdTe indicates that in HgCdTe alloys the electronic states near the VBM are subjected to strong alloy scattering. The anomalously low hole mobilities observed in HgCdTe alloys at low temperature[18] seem to support this prediction. We therefore also urge similar measurements to be done on AlGaAs alloys since the NVBO of AlAs-GaAs is probably large on the basis of the large HVBO reported.

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[1] W. A. Harrison, J. Vac. Sci. Technol. B **3**, 1231 (1985).

[2] L. F. Mattheiss, Phys. Rev. **134**, A970 (1964).

[3] C. G. Van de Walle and R. M. Martin, J. Vac. Sci. Technol. B **4**, 1055 (1986); C. G. Van de Walle, Ph.D thesis, Stanford University, 1986 (unpublished).

[4] O. K. Andersen, Phys. Rev. B **12**, 3060 (1975).

[5] N. E. Christensen and O. K. Andersen, private communication via M. van Schilfgaarde.

[6] S. P. Kowalczyk, J. T. Cheung, E. A. Kraut, and R. W. Grant, Phys. Rev. Lett. **56**, 1605 (1986).

[7] T. M. Duc, H. Hsu, and J. P. Faurie, Phys. Rev. Lett. **58**, 1127 (1987).

[8] W. E. Spicer, J. A. Silberman, I. Lindau, A.-B. Chen, A. Sher, and J. Wilson, J. Vac. Sci. Technol. A **1**, 1735 (1983); J. A. Silberman, Ph.D. thesis, Stanford University, 1986 (unpublished).

[9] R. Enderlein and W. A. Harrison, Phys. Rev. B **30**, 1867 (1984).

[10] The valence states of an atom X (atomic number z) with a core hole is approximated as that of an atom with atomic number $z+1$.

[11] This cancellation is similar to the cancellation of $z+1$ approximation discussed by P. Steiner, H. Hufner, N. Mårtensson, and B. Johansson, Solid State Commun. **37**, 73 (1981).

[12] A.-B. Chen and A. Sher, Phys. Rev. B **31**, 6490 (1985).

[13] This interface charge redistribution has been termed atomic dipole by J. Tersoff, Phys. Rev. Lett. **56**, 2755 (1986).

[14] The separation between Hg 5*d* and Cd 4*d* of 2.65 ± 0.03 eV in the alloy agrees very well with that of 2.696 ± 0.03 eV at a HgTe-CdTe heterojunction obtained in Ref. 7.

[15] The inclusion of cation *d* orbitals into tight-binding calculation has been brought up by A. Zunger, in Proceedings of the Fourteenth Annual Conference on Physics and Chemistry of Semiconductor Interfaces, Salt Lake City, UT, 1987 (to be published); see S.-H. Wei and A. Zunger, to be published. The calculation result is via W. A. Harrison, private communication.

[16] O. K. Andersen and O. Jepsen, Phys. Rev. Lett. **53**, 2571 (1984).

[17] J. Kudrnovský, V. Drchal, and J. Mãsek, Phys. Rev. B **35**, 2487 (1987), and the references therein.

[18] J. R. Meyer, F. J. Bartoli, and C. A. Hoffman, in Proceedings of the U.S. Workshop on Mercury Cadmium Telluride, Dallas, TX, 1986, edited by G. Lucovsky, J. Vac. Sci. Technol. A (to be published).