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The orientation independence of the CdTe–HgTe valence band offset as determined by x-ray photoelectron spectroscopy

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Abstract. We have investigated the valence band offset (ΔE_V) of the CdTe–HgTe heterojunction for three orientations, (100), (110) and (111)B, using *in situ* x-ray photoelectron spectroscopy. The difference in energy between the Cd 4d and Hg $5d_{5/2}$ core levels, ΔE_{CL}, and consequently ΔE_V was found to be independent of surface orientation and the surface structure immediately prior to growth of the uppermost layer. ΔE_V was found to be 0.37 ± 0.07 eV.

1. Introduction

The valence band offset (ΔE_V) of an abrupt CdTe–HgTe heterojunction is an important parameter for the fabrication of devices as well as having a large effect on the band structure of quantum wells and superlattices (see, for example, Meyer *et al* [1]). ΔE_V for the CdTe–HgTe interface has recently been the subject of a certain amount of controversy. The common anion rule predicts a small valence band offset which was initially corroborated by a magneto-optical investigation by Guldner *et al* [2], i.e. their measurements were consistent with a valence band offset of 40 meV, However, a much larger value of 350 meV was reported later by two separate x-ray photoelectron spectroscopy (XPS) investigations [3, 4]. The valence band offset was also found to be independent of growth sequence and the thickness of the uppermost layer from 5 to 35 Å [4]. In addition, XPS and ultraviolet photoemission spectroscopy (UPS) measurements by Sporken *et al* [5] have shown that the valence band offset is temperature independent and therefore the discrepancy between these two values can not be explained as the result of a temperature dependence. The ensuing controversy, which has been extensively reviewed by Meyer *et al* [1], appears to be resolved in favour of the larger value.

Self-consistent tight-binding (SCTB) calculations by Muñoz *et al* [6] have predicted a large dependence on orientation, 180 meV between the (100) and (110) surfaces ($\Delta E_V = 0.46$ and 0.28 eV, respectively). In contrast, Van de Walle *et al* [7], using self-consistent local density functional methods, predict no surface dependence, i.e. $\Delta E_V = 0.27$ and 0.28 eV, respectively. In fact a more general study by the latter authors suggests that this independence is a characteristic of a number of important interfaces, e.g. CdTe–HgTe, AlAs–GaAs and Si–Ge. Indeed this has been shown to be the case for the GaAs–AlAs heterojunction [8]. More recent calculations by Muñoz *et al* [9] resulted in a much smaller dependence on orientation, 90 meV between the (100) and (110) surfaces ($\Delta E_V = 0.46$ and 0.37 eV, respectively). In order to determine which is correct for the CdTe–HgTe heterojunction we have investigated the effect of surface orientation as well as the effect of interface structure on the valence band offset.

2. Experimental details

Epitaxial growth was carried out in a four-chamber RIBER 2300, molecular beam epitaxial (MBE) system which has been modified to permit the growth of Hg-based materials. The vacuum in the growth chamber is better than 6×10^{-10} Torr when no Hg has recently been admitted. Three MBE cells were employed, two of which were commercial cells and which contained high-purity CdTe and Te. The third cell, designed by us, is a stainless steel cell for Hg which can be refilled without breaking the vacuum. The flux of the latter cell is stable to within ±1.5 and ±3% over a period of 2 and 30 h, respectively. The growth chamber is connected with the XPS chamber (3×10^{-10} Torr) with a transfer system whose vacuum was better than 1×10^{-9} Torr.

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The CdTe-HgTe heterojunctions were grown on (110) CdTe and on (100)- and (111)B-oriented CdTe and CdZnTe substrates which had been degreased, chemo-mechanically polished for several minutes, etched in a weak solution of bromine in methanol and rinsed in methanol. Immediately prior to loading the substrates into the MBE system, they were rinsed in de-ionized water, briefly dipped in hydrochloric acid and then rinsed in de-ionized water so as to remove all of the original oxide and carbon from the substrate surface. We have found that, as a result of this previous step, the newly formed oxide, is much more easily evaporated from the surface. This is accomplished by heating the substrates at temperatures up to about 350 °C while being monitored by reflection high-energy electron diffraction (RHEED) as described elsewhere [10]. Throughout this paper we consistently use the convention of referring to the direction of the incident electrons when referring to reconstruction in a particular azimuth.

Approximately 0.1 and 2 μm of CdTe were grown on CdTe and CdZnTe substrates, respectively. This growth was initiated at 300 and 340 °C, respectively and continued while lowering the temperature to 230 °C where the growth was completed. Then a thin layer, 6-40 Å, of HgTe was grown at 180 °C. For the (100) and (111)B orientations, this thin layer of HgTe was on a Te-stabilized surface as well as a surface displaying attributes of both Te and Cd stabilization. The former surface structure was established by exposing the CdTe film to a Te flux of 3×10^{-7} Torr at 210 °C. The latter surface structure was established by evaporating Te from the surface at about 340 °C for several minutes while maintaining a smooth surface as evidenced by the presence of uniform streaks and the absence of spots in the RHEED pattern. In the (100) case this mixture of Te and Cd stabilization of this surface is characterized by half-order reconstruction in the [011] and [010] azimuths. The (111)B surface is more complicated. Here the Te (1×1) stabilized surface undergoes a transition to $(2\sqrt{3} \times 2\sqrt{3})R30°$ reconstruction upon evaporation of Te from the surface. The as-grown surface structure in the (110) orientation could not be changed either with excess Te flux or with an increase in temperature up to 340 °C, and therefore HgTe was grown only on the as-grown CdTe surface.

The resulting heterojunctions were transferred via an ultra-high-vacuum transfer system and investigated by XPS under nearly *in situ* conditions. XPS experiments were preformed with a RIBER MAC 2 electron spectrometer using an Mg Kα x-ray source (1253.6 eV) with an acceleration voltage of 10 kV, a current of 10 mA and without a monochromator. The energy scans were repeated for at least 12 h in order to achieve an acceptable signal-to-noise ratio.

3. Results and discussion

The valence band offset ΔE_V is schematically shown in figure 1 and is given by

$$\Delta E_V = (E^{HgTe}_{Hg5d5/2} - E_V^{HgTe}) - (E^{CdTe}_{Cd4d} - E_V^{CdTe}) + \Delta E_{CL}. \quad (1)$$

Therefore, in order to determine ΔE_V, we have to measure these three binding energy differences for HgTe, CdTe and the CdTe-HgTe heterojunction. Where $E^{HgTe}_{Hg5d5/2}$ and E^{CdTe}_{Cd4d} are binding energies of the Hg $5d_{5/2}$ and Cd 4d core levels in HgTe and CdTe, respectively. E_V^{HgTe} and E_V^{CdTe} are the energies of the valence band maxima in HgTe and CdTe, respectively, and ΔE_{CL} is the binding energy difference between the Hg $5d_{5/2}$ and Cd 4d core levels in the HgTe-CdTe heterojunction. This procedure results in a value of 0.37 ± 0.07 eV for ΔE_V for the (100) orientation. The large uncertainty is due primarily to the difficulty in determining the position of the valence band maximum (see figure 2). As can be seen by comparing the XPS spectra for (100) and (110) CdTe in figure 2, the energy difference between the Cd 4d core level and valence band maximum in CdTe is independent of these two surface orientations. The same is true for

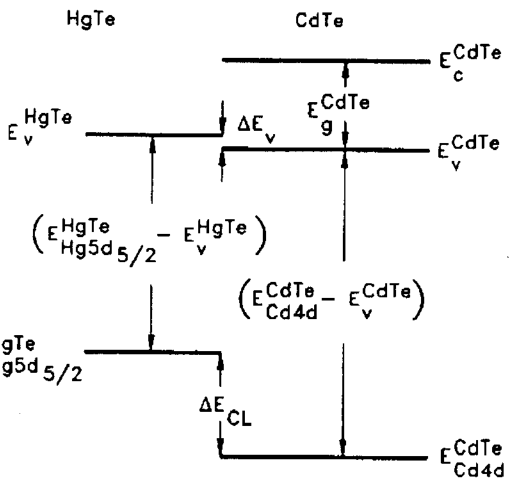

Figure 1. A schematic diagram of the relevant energy levels of an abrupt CdTe–HgTe heterojunction.

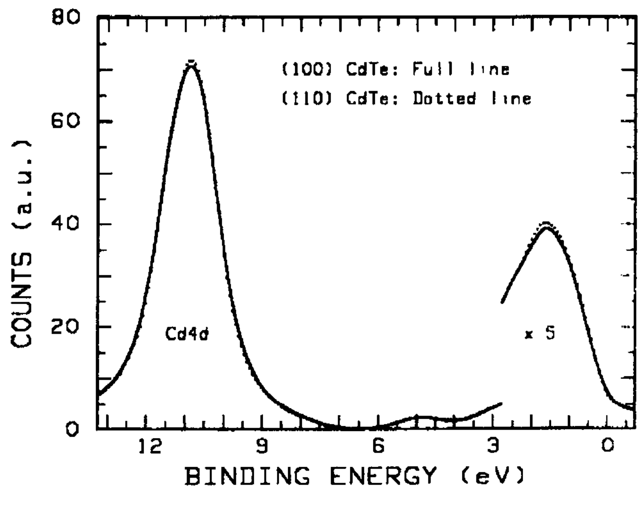

Figure 2. XPS spectra of (100) and (110) CdTe, showing the Cd 4d core level peak and the CdTe valence band maximum.

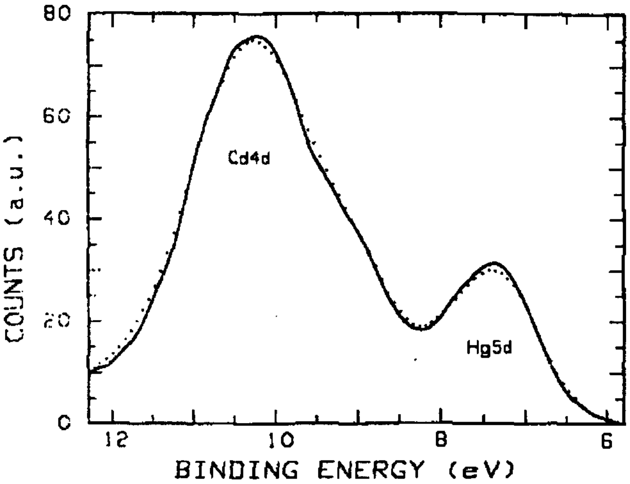

Figure 3. An XPS spectrum of a (110) CdTe–HgTe heterojunction (full curve) and a least-squares fit of the XPS spectra of a (110) CdTe and (110) HgTe film (dotted curve) in the vicinity of the Cd 4d and Hg 5d core levels.

Table 1. The energy difference between the Cd 4d and Hg $5d_{5/2}$ core levels for the (100), (110) and (111)B orientations.

Orientation	ΔE_{CL} (eV)
(100)	2.96 ± 0.03
(110)	3.01 ± 0.03
(111)B	2.98 ± 0.03

(111)B. This demonstrates that this energy difference is a bulk property and is independent of orientation as is usually assumed. Consequently all orientation or interface effects on ΔE_V are contained in ΔE_{CL} which can be determined with greater precision than the position of the valence band.

An XPS spectrum for a (110) CdTe–HgTe heterojunction is shown in figure 3 and the corresponding spectra for CdTe and HgTe epitaxial films in the region of the Cd 4d and Hg 5d core levels can be seen in figure 4. ΔE_{CL} cannot be determined directly for the heterojunction due to the overlapping of the Cd 4d, Hg $5d_{3/2}$ and Hg $5d_{5/2}$ core levels. First the HgTe and CdTe spectra were combined and fitted to the heterojunction spectrum by means of a least-square procedure. This least-square fit as well as the heterojunction spectrum are plotted in figure 3. In order to more accurately determine the position of the peak due to the Hg $5d_{5/2}$ core level it was resolved from the HgTe spectrum as depicted by the dotted curve in figure 4. This was accomplished by assuming that this peak is symmetrical, i.e. that the high-energy flank is a mirror image of the low-energy flank. This should be a good assumption because only minimal inelastic scattering is expected under the low-energy flank. ΔE_{CL} was then determined by measuring the energy difference between the peak centres at half maximum of the Cd 4d and Hg $5d_{5/2}$ core levels.

The results for the (100), (110) and (111)B orientations are tabulated in table 1. Two different interface structures were investigated for the (100) and (111)B orientations. In the first case HgTe was grown on (100)-(2 × 1) and (111)B-(1 × 1) Te-stabilized CdTe surfaces respectively, whereas in the second case HgTe was grown on a mixed surface with half-order reconstruction in both the [011] and [010] azimuths for the (100) orientation and $(2\sqrt{3} \times 2\sqrt{3})R30°$ reconstruction for (111)B. In each case the two corresponding values are the same within the experimental uncertainities given in table 1. As can be seen in table 1, ΔE_{CL} and therefore ΔE_V for the CdTe-HgTe heterojunction is, within experimental uncertainty (± 0.03 eV), independent of orientation and interface structure.

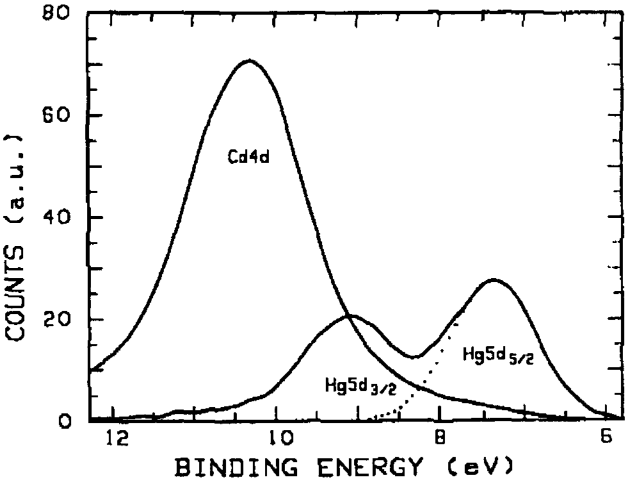

Figure 4. XPS spectra of (110) CdTe and (110) HgTe films in the vicinity of the Cd 4d and Hg 5d core levels.

4. Conclusions

In conclusion, by means of *in situ* XPS experiments we have shown that ΔE_{CL} (and therefore that ΔE_V) for the CdTe–HgTe heterojunction is independent of the surface orientation and the surface reconstruction immediately prior to the growth of HgTe, whether Te-stabilized or a mixture of Cd and Te stabilization. These results agree with the self-consistent local density predictions of Van de Walle *et al* [7] but not with the SCTB calculations of Muñoz *et al* [6, 9]. Furthermore, ΔE_V has been determined to be 0.37 ± 0.07 eV, in good agreement with the literature [3–5].

Acknowledgments

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