Energy band alignment of PbTe/CdTe(111) interface determined by ultraviolet photoelectron spectra using synchrotron radiation*

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The energy band structure with type-I alignment at the PbTe/CdTe(111) heterojunction interface is determined by the ultraviolet photoelectron spectrum using synchrotron radiation. The valence band and conduction band offsets are obtained to be 0.09±0.12 and 1.19±0.12 eV, respectively. These results are in agreement with theoretically predicted ones. The accurate determination of the valence band and conduction band offsets is useful for the fundamental understanding of the mid-infrared light emission from the PbTe/CdTe heterostructures and its application in devices.

Keywords: valence band offset, ultraviolet photoelectron spectra, synchrotron radiation
PACC: 7300, 7335, 7360P, 7960

1. Introduction

Lattice-matched new PbTe/CdTe heterostructures including quantum wells (QWs) and quantum dots (QDs), have received much attention due to their unique optical and electronic properties[1−3] and the promise to the fabrication of novel mid-infrared optoelectronic devices.[4,5] Recently, the large Rashba spin effect was found in the $Pb_{1-y}Sr_yTe/PbTe/Pb_{1-x}Sr_xTe$, and $Pb_{1-x}Sr_xTe/PbTe/CdTe$ asymmetric QWs, which may make these asymmetric QW structures a candidate material for spintronic devices.[6,7] The electronic properties of the PbTe/CdTe heterojunction, however, were rarely studied and discrepancy between theoretical prediction and experimental determination was in existence. The theoretical calculation by Leitsmann and Bechstedt provided an asymmetric band alignment with zero valence band offset (VBO) of PbTe/CdTe(100) and (110) interfaces using an *ab initio* pseudopotential method and slab approximations.[8] The only experimental measurement of the VBO for the PbTe/CdTe (111) interface by Si *et al.* using x-ray photoelectron spectroscopy (XPS) has given a type-I band alignment with the VBO value of $\Delta E_V = 0.135$ eV.[9] In experimental determination of the VBO for a semiconductor heterojunction using XPS, the main uncertainty comes from the difficulty in exactly determining the position of valence band maximum (VBM) due to the inferior signal to noise characteristics in XPS. To determine the VBM position in an XPS spectrum, it is a common way to use a Kraut method by fitting the measured VB spectrum with Gaussian broadened VB density of states (VBDOS) due to weak observed VB spectral signals. The calculated VBDOS by density functional theory (DFT) was convoluted by the XPS spectrometer resolution function to least square fit the VB data near VBM.[10,11] The obtained results, consequently, could be often semi-experimental. Obviously, for the essential energy band alignment parameters at the PbTe/CdTe (111) heterojunction interface more experimental data are needed.

In this paper, we report the measurement of ultraviolet photoelectron spectroscopy (UPS) for the determination of the VBO at the PbTe/CdTe (111) interface using synchrotron radiation as the excitation source. With changeable excitation energy (10–200 eV), synchrotron radiation photoelectron spectrum (SRPES) can provide with large absorption cross

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sections on both VBM and core levels (CLs). Large values of the absorption cross section and intense beam line can provide good sensitivity in both VBM and CL spectra, and consequently it is possible to determine the valence band offsets with higher accuracy.

2. Theoretical and experimental procedures

The principle in determination of VBO ($\Delta E_{\rm V}$) for a heterojunction by using photoelectron spectrum technique has been fully described in Ref. [8]. The VBO for the PbTe/CdTe interface can be acquired from the following formula

$$\Delta E_{\rm V} = \Delta E_{\rm CL}+(E^{\rm PbTe}_{\rm Pb5d_{5/2}}-E^{\rm PbTe}_{\rm VBM}) -(E^{\rm CdTe}_{\rm Cd4d}-E^{\rm CdTe}_{\rm VBM}), \quad (1)$$

where $\Delta E_{\rm CL}= E^{\rm CdTe}_{\rm Cd4d}-E^{\rm PbTe}_{\rm Pb5d_{5/2}}$ is the binding-energy difference between the Pb $5d_{5/2}$ core level (CL) of PbTe and the Cd 4d CL measured from the thin PbTe epilayer sample. The differences $(E^{\rm PbTe}_{\rm Pb5d_{5/2}}-E^{\rm PbTe}_{\rm VBM})$ and $(E^{\rm CdTe}_{\rm Cd4d}-E^{\rm CdTe}_{\rm VBM})$ are the binding-energy difference between CLs and VBM measured from PbTe and CdTe bulk samples, respectively. A schematic energy-band diagram for the PbTe/CdTe heterojunction is given in Fig. 1

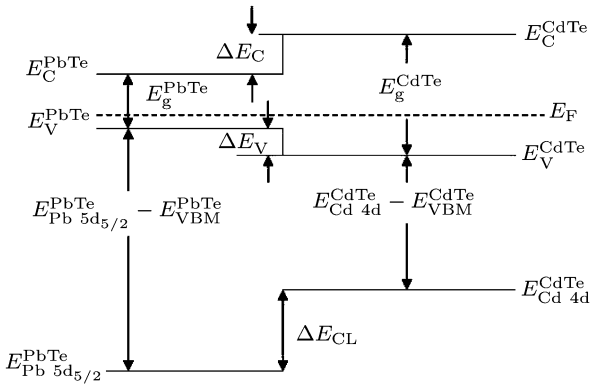


Fig. 1. The schematic energy-band diagram for PbTe/CdTe (111) heterojunction system, showing the quantities necessary for this method to determine the $\Delta E_{\rm V}$ and $\Delta E_{\rm C}$.

The measurements of UPS were performed at the surface physics station of Hefei National Synchrotron Radiation Laboratory in China. The experimental station is composed of a three-chamber VG multi-technique ultra high vacuum (UHV) system. The analysis chamber with a base pressure better than 2×10^{-8} Pa is equipped with an ARUPS10 hemispherical analyser, low energy electron diffraction (LEED), an x-ray source of magnesium (Mg) Kα target (1253.6 eV) for XPS measurements and an argon-ion gun for the pre-treatment of the samples. The incident beam line covers the energy range from 10 to 200 eV and the energy resolution ($E/\Delta E$) is higher than 1000. The details of the experimental station and the related beam line were described previously.[12]

Samples analysed in the UPS experiments were grown by a solid source molecular beam epitaxy system. Lattice-matched CdTe (111) B substrates were used to grow CdTe and PbTe overlayers. The growth of PbTe on CdTe (111) proceeded in a two-dimensional growth model. An $\sim$1.0 μm thick PbTe epilayer grown on CdTe(111) displayed high crystalline quality with a typical line width smaller than 150 arc sec as measured by high resolution x-ray diffraction and smooth morphology with easily observed atomic monolayer steps on PbTe surfaces as measured by an atomic force microscope. For the UPS analysis of the PbTe/CdTe (111) interfaces, thin PbTe overlayers of $\sim$5 nm were grown on CdTe. Once the samples were transferred to the analysis chamber, clean ordered PbTe (111) and CdTe (111) surfaces were obtained by argon ion (Ar^+) sputtering (1000 eV) at a low sputtering rate. The cleanliness and the orientation of the samples were checked by LEED and subsequent XPS scans for the removal of oxygen by observing the O 5s and C 1s peaks. The UPS measurements were carried out by excitation with a beam line energy of 75 eV, at which the absorption cross sections for the Pb5d and Cd4d CLs reached their maximum values. Large values of the absorption cross section and intense beam line provided good sensitivity in the VBM and CL spectra measurements. All the spectra were measured with an incident angle of 45° to the normal of the surface and the normal emission geometry. The analyser pass energy was set at 20 eV. To minimize the measurement error from the UPS system, the measured binding energies for all the samples were carefully calibrated by the gold (Au) work function and the binding energy of the Au $4f_{7/2}$ CL level that is 84.0 eV with respect to the Au Fermi level. In UPS measurements a large amount of electrons may be excited and emitted from the measured samples, and consequently the samples are often positively charged. An electric field caused by the charges could affect the measured absolute kinetic energies of photoelectrons by a shift of the whole spectrum. Calibration to a universal energy reference

is not necessary as it is the relative energy separation of spectral features that is used in the determination of VBO.

3. Results and discussions

Figure 2 shows the Pb 5d CL and the valence band (VB) spectra of the PbTe bulk sample. To accurately determine the CL peak positions, the CL peaks have been fitted using a Shirley background (in which a linear component is incorporated) and Voigt (mixed Lorentzian–Gaussian) profile. The position of VBM was determined by linear extrapolation of the leading edge of the valence-band. The energy difference between the Pb $5d_{5/2}$ CL peak and VBM is determined to be 18.47±0.05 eV. The experimental error was given by multiple measurements. This VBM value is slightly larger than the data obtained using XPS, 18.29 eV by Si *et al.*,[9] and 18.33 eV by Mcfeely *et al.*[13] Since the CL position can be determined with small uncertainty, the main discrepancy arises from the determination of the VBM. In the XPS measurements, the Kraut method with the VBDOS calculated by DFT was used to fit the leading edge of the VB spectrum.

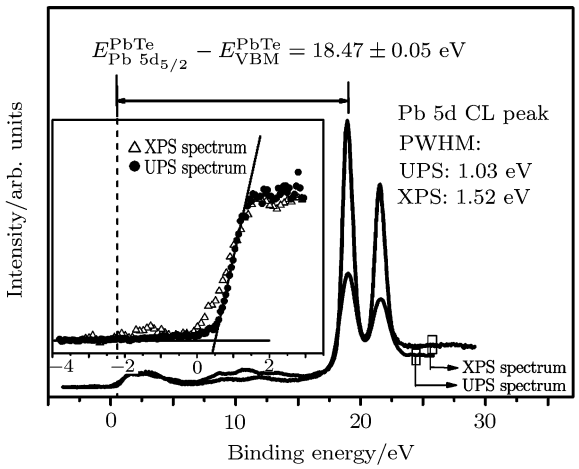


Fig. 2. A UPS spectrum of Pb 5d CL and VBM region for a PbTe bulk sample. Inset: the VBM is determined by two straight lines fitting the leading edge of the VB and the background. For the comparison the XPS data are also plotted.

To show the superiority of UPS using synchrotron radiation as the excitation source, a comparison of the measured UPS data with XPS ones for the same PbTe sample is shown in Fig. 2. The XPS data was obtained with excitation of a magnesium (Mg) $K\alpha$ target (1253.6 eV) that was installed in the analysis chamber. It is seen that UPS signal for the $Pb5d_{5/2}$ CL peak is much stronger than the XPS one. The full width at half maximum (FWHM) of the $Pb5d_{5/2}$ peak in the UPS spectrum is 1.03 eV, much smaller than the value of 1.52 eV for the XPS spectrum. The comparison of the VB spectra is plotted in the inset of Fig. 2, showing that the VB spectra measured by UPS has much sharper band edge than that measured by XPS. These results validate the hypothesis that in the UPS measurement the high absorption cross section and intense beam line provide high sensitivity for both the VB and CL spectra. As a result, the UPS spectra demonstrate better performance at the low energy side than the XPS spectrum, which indicates that the obtained energy difference of $(E^{PbTe}_{Pb5d_{5/2}} - E^{PbTe}_{VBM})$, 18.47±0.05 eV, is more reliable.

Figure 3 shows the Cd 4d CL peak and the VB spectrum of a CdTe (111) bulk sample. Since CdTe is semi-insulating, the surface charge will be accumulated significantly, and will shift the whole spectrum to the higher binding energy. But with the stable incident light beam, multiple scans (7 times), the fluctuation of the spectrum induced by surface charge is small. The energy difference between Cd 4d CL peak and the VBM, $(E^{CdTe}_{Cd4d} - E^{CdTe}_{VBM})$, is determined to be 10.84±0.05 eV. This result is slightly larger than the reported values of 10.69 eV for CdTe(111) by Waag *et al.*[14] and 10.70 eV by Si *et al.*[9]

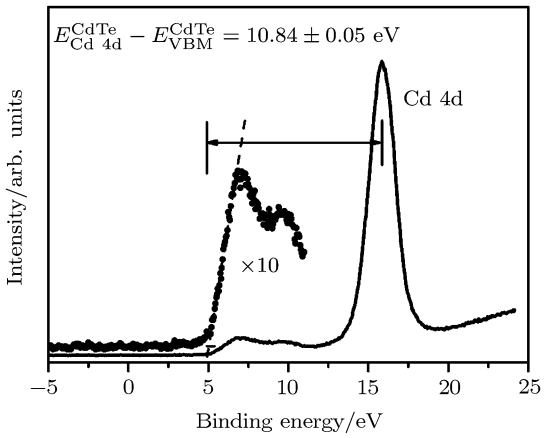


Fig. 3. A UPS spectrum of Cd 4d CL and VBM region for a CdTe bulk sample. Inset: the VBM is determined by two straight lines fitting the leading edge of the VB and the background.

Figure 4 shows a UPS spectrum for the PbTe/CdTe (111) heterojunction sample. The Pb5d CL peaks from the PbTe overlayer and the Cd4d CL peak from the underlying CdTe can be clearly distinguished. The energy difference between Cd4d CL and $Pb5d_{5/2}$ CL, ($\Delta E_{\rm CL} = E^{\rm CdTe}_{\rm Cd4d} - E^{\rm PbTe}_{\rm Pb5d_{5/2}}$), is obtained to -7.54 ± 0.02 eV. Note that the effect of the strain-induced piezoelectric field on the measured $\Delta E_{\rm CL}$ for the PbTe/CdTe interface can be neglected due to the good lattice match between PbTe ($a = 6.462$ Å, 1 Å=0.1 nm)) and CdTe ($a = 6.477$ Å), and that PbTe has a high dielectric value (ε) of 400.[15]

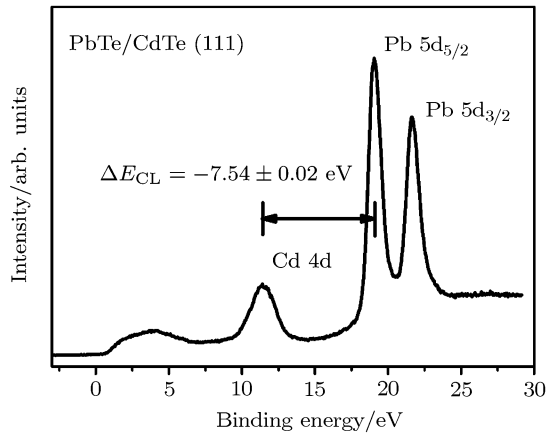


Fig. 4. A UPS spectrum of the PbTe/CdTe(111) heterojunction sample in the vicinity of Cd 4d and Pb 5d5/2 CLs.

Substituting the above measured ($E^{\rm PbTe}_{\rm Pb5d_{5/2}} - E^{\rm PbTe}_{\rm VBM}$) $= 18.47 \pm 0.05$ eV, ($E^{\rm CdTe}_{\rm Cd4d} - E^{\rm CdTe}_{\rm VBM}$) $= 10.84 \pm 0.05$ eV, and $\Delta E_{\rm CL} = E^{\rm CdTe}_{\rm Cd4d} - E^{\rm PbTe}_{\rm Pb5d_{5/2}} = -7.54 \pm 0.02$ eV, into Eq. (1), we obtain the VBO of PbTe/CdTe (111) interface is $\Delta E_{\rm V} = 0.09 \pm 0.05$ eV. The band-bending effect is a factor that may affect the UPS results and is difficult to be quantitatively evaluated in the measurement of $\Delta E_{\rm CL}$. In our case, the band-bending effect can be neglected due to following reason. For a heterojunction at thermal equilibrium, the ratio of the potential drops at the two sides of the interface can be expressed as: $V_{\rm D1}/V_{\rm D2} = \varepsilon_2 N_2/\varepsilon_1 N_1$, where N is the doping levels. It is known that the carrier concentration N of the PbTe epitaxial layer is around 10^{17} cm^{-3}, much larger than that of undoped CdTe (semi-insulating). Besides, the static dielectric constant ε for PbTe is very high (400), much larger than the value of 10.2 for CdTe.[16] It is evident that the band-bending is much more pronounced in CdTe than in PbTe for the PbTe/CdTe heterojunction. Considering the small escape depth of photoelectron($\sim$ 1 nm), the band bending effect can be neglected.

The conduction band discontinuity, $\Delta E_{\rm C}$, can be evaluated from the following equation: $\Delta E_{\rm C} = E^{\rm CdTe}_{\rm g2} - E^{\rm PbTe}_{\rm g1} - \Delta E_{\rm V}$. At 300 K, the bandgap of PbTe, $E_{\rm g1}$, is 0.32 eV,[17] and the bandgap of CdTe, $E_{\rm g2}$, is 1.60 eV,[18] and as a result the conduction band offset $\Delta E_{\rm C}$ is obtained to be 1.19±0.12 eV.

4. Conclusions

We have carried out the experimental measurement of the valence band offset of PbTe/CdTe (111) heterojunction by UPS using synchrotron radiation. Because the synchrotron radiation source provides a high-brightness incident photon flux and changeable photon energy, the UPS spectra shows good signal-to-noise characteristics. The VBO of $\Delta E_V = 0.09 \pm 0.12$ eV and the CBO of $\Delta E_{\rm C} = 1.19 \pm 0.12$ eV are obtained. These offsets indicate a type-I energy-band alignment for the PbTe/CdTe (111) heterojunction interface, which is consistent with the intense photoluminescence observation from the PbTe/CdTe heterostructures, such as PbTe/CdTe quantum wells and PbTe/CdTe quantum dots. The accurate determination of the valence band and conduction band offsets is useful for the fundamental understanding of the mid-infrared light emission from the PbTe/CdTe heterostructures and its application in devices.

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