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ZnTe/GaAs(2 1 1)B heterojunction valence band discontinuity measured by X-ray photoelectron spectroscopy

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ABSTRACT

Thin ZnTe layers were grown by molecular beam epitaxy on single crystal GaAs(2 1 1)B substrates. Reflection high energy electron diffraction monitored the deoxidation of substrate and entire growth process. Valence band offset was calculated with X-ray photoelectron spectroscopy. Also interface formation of the ZnTe/GaAs was studied. Analysis shows that interface is abrupt and calculated valance band offset is 0.25 ± 0.1 eV and indicates type I alignment. The experimental result agrees well with the theoretical predictions involving interface dipole effect as well as electron affinity rule.

1. Introduction

ZnTe is a II–VI semiconductor with a zinc-blende crystal structure and a lattice constant of 6.104 Å. ZnTe is an attractive material for its optoelectronic applications such as light emitting diodes (LED) which has been explored for the last few decades [1–3]. Moreover since ZnTe is intrinsically p-type due to native defects [4], it can be combined with an n-type ZnO, another II–VI semiconductor which shows tremendous potential for optoelectronic devices operating in the visible or ultraviolet range, to make heterojunction diodes [5]. The benefit of exploring such a diode is to avoid using p-type ZnO which has not been realized with good reliability and reproducibility [5]. Recently, ZnTe has attracted growing attention for solar cell applications because its direct bandgap energy (2.25 eV at room temperature) is convenient for the short-wavelength range of the solar spectrum which accounts for over 25% of the entire solar radiation energy at AM1.5 G [6]. It has been proposed [7] that combination of ZnTe with other II–VI semiconductor alloys (ZnCdMg, SeTe) with various compositions could produce multi-junction solar cells covering a wide range of the solar spectrum which is desirable to have high efficiency [8,9]. Additionally, ZnTe diluted with oxygen has been reported to introduce states in the band gap of ZnTe which provides a broader response to the solar spectrum and thus potentially enhanced conversion efficiency [10–12].

Among many substrates available for II–VI semiconductor growth by molecular beam epitaxy, GaAs is one of the best choices because of its availability in large wafer size, closer bonding character and the well established surface preparation procedure. Therefore GaAs has been a very popular substrate for ZnTe growth by MBE [11,13–16]. (2 1 1) is the major orientation for epitaxy of II–VI semiconductors such as CdTe or ZnTe on GaAs or Si [17–19] since these high index substrates provide a periodic array of energetically favourable sites at the surface as step edges formed by (1 0 0) crystal planes for initial nucleation in a uniform and regular fashion [20,21]. Additionally the twin defects could be suppressed effectively due to symmetry of the (2 1 1) surface [18] leading to a considerable improvement of crystalline quality [22]. Therefore, GaAs(2 1 1)B substrates were chosen in the present work.

Band alignment is an important property of semiconductor heterojunctions which is required by the analysis of interface electronic properties such as modelling of device behaviour and interpretation of experimental spectra. Specifically it determines the energy barriers for electron and hole transport, which are key to the operation of heterojunction optoelectronic devices such as LEDs and solar cells [23,24]. However, unlike the structure of ZnTe/GaAs heterointerfaces which have been studied intensively [25–29], the band alignment of ZnTe/GaAs has received less attention especially in experimental approach. Theoretical predictions of valence band offset have been reported in the literature by different groups

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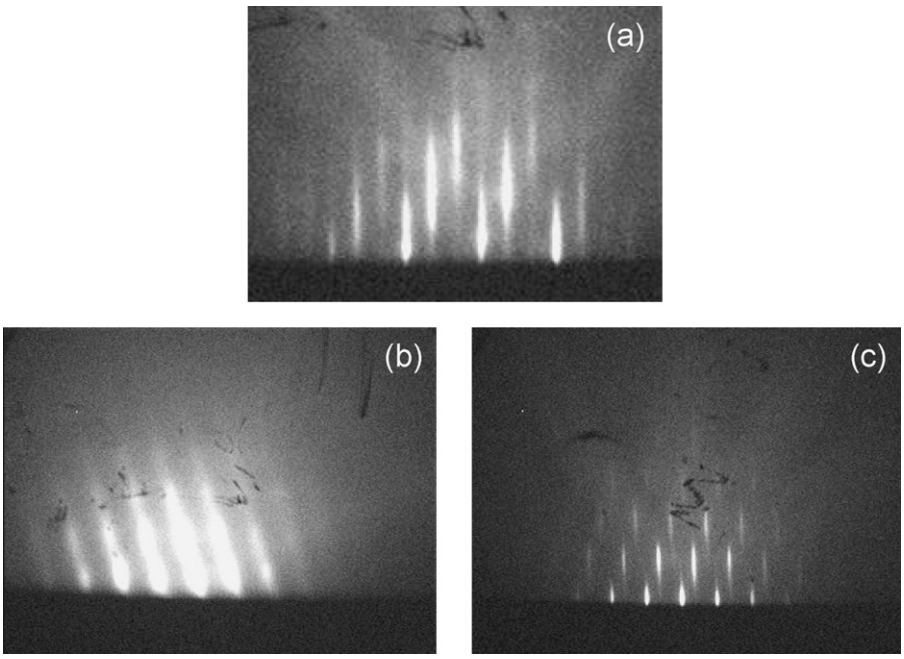

Fig. 1. RHEED patterns of (a) deoxidized GaAs(2 1 1)B surface under Te flux, (b) 2 nm ZnTe growth, (c) 40 nm ZnTe growth on GaAs(2 1 1)B surface. The electron beam is directed along [0$\bar{1}$1].

[30–34]. Those theoretical works are summarized and discussed in Section 3. Therefore in this work, we measured the valence band offset of ZnTe/GaAs(2 1 1) heterojunction by X-ray photoelectron spectroscopy and compared the result with theoretical prediction.

2. Experiment

ZnTe layers were grown in a RIBER 2300 MBE system. Single crystalline undoped GaAs(2 1 1) substrates, cut into 2 cm × 2 cm pieces, were used. The detail of substrate preparation is described elsewhere [35]. GaAs substrate was deoxidized at 580 °C for 5 min under Te flux in order to prevent the deterioration of the substrate surface. Then, the substrate was cooled down to the growth temperature of 300 °C and growth was initiated after ZnTe flux was stabilized. Stoichiometric ZnTe of 99.9999% purity was used for the growth, and Te of 99.9999% purity was used to create a Te flux during oxide desorption from GaAs.

Reflection high energy electron diffraction (RHEED) was employed to monitor the deoxidation process and the entire growth. A SSX-100 spectrometer with a monochromatic and focused Al Kα source ($h\nu$ = 1486.6 eV) was employed to measure the X-ray photoelectron spectra. Core level spectra were recorded with a 600 μm spot diameter and 50 eV pass energy. The XPS spectrometer is connected to the RIBER 2300 MBE chamber through a system of UHV transfer modules.

3. Results

Fig. 1(a) shows the RHEED patterns of the deoxidized GaAs surface under Te flux. The long and bright streaks in the patterns are typical of a smooth GaAs (2 1 1) surface. In Fig. 1(b) and (c) the patterns of 2 and 40 nm of ZnTe growth are shown respectively. The initial growth of ZnTe results in a very bright and somewhat diffuse pattern. As the thickness of the ZnTe increases a sharp and streaky pattern is seen indicating that ZnTe grows as a single crystal.

The interface between GaAs and ZnTe was studied by XPS. We have grown 2, 4 and 40 nm of ZnTe and recorded the core levels of Zn 3p and 3d, Te 3d and 4d, Ga 3d and As 3d peaks as well as the valence band. First we studied the interface formation of ZnTe grown on GaAs. In order to determine the exact position of the core level peaks all the peaks were fit using Winspec program [36]. Ga 3d peaks were fit with mixed Gaussian–Lorentzian doublets and Te $3d_{5/2}$ peaks were fit with mixed Gaussian–Lorentzian singlets. In both cases, a nonlinear (Shirley-type) background was included. Spin–orbit splitting of 0.45 eV was used to fit all Ga 3d peaks [37,38]. Also intensity ratio was fixed at 0.66 which is the expected value for d level. Fig. 2 shows the core level spectra of Ga 3d and Te $3d_{5/2}$ for various thicknesses. The BE for Ga 3d of GaAs and Te $3d_{5/2}$ of thick ZnTe surface were found to be 18.90 and 572.10 eV respectively. Ga3d peaks could fit with only one mixed doublets and Te$3d_{5/2}$ peaks could fit with only one mixed singlet peak very well. This indicates that the interface of GaAs and ZnTe is abrupt and no indication of intermixing was found. This result was confirmed with

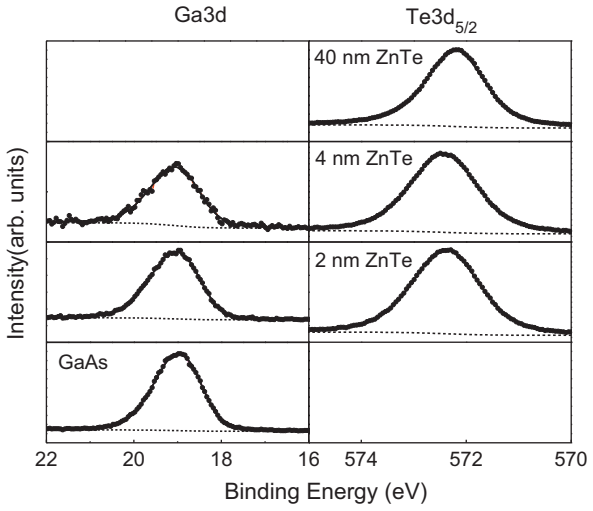

Fig. 2. XPS core level spectra for various thickness of ZnTe on GaAs. Ga3d was fit with mixed Gaussian–Lorentzian doublets and Te$3d_{5/2}$ was fit with an mixed Gaussian–Lorentzian singlets. A nonlinear (Shirley-type) background was used to fit all spectra.

Table 1
Binding energies from core levels of clean GaAs, ZnTe and from interface regions after fitting.

Sample	Ga3d (eV)	$Te3d_{5/2}$ (eV)
GaAs (clean)	18.84	–
ZnTe (clean)	–	572.10
ZnTe(2 nm)/GaAs	18.90	572.39
ZnTe(4 nm)/GaAs	18.90	572.43

cross sectional high resolution transmission electron microscopic (HRTEM) image of ZnTe/GaAs as shown in the previous work from our group [22]. HRTEM also confirms that the ZnTe film is single crystalline with epitaxial relationship of ZnTe [2 1 1]||GaAs [2 1 1]. This can also be seen from the RHEED pattern of clean GaAs (2 1 1) and ZnTe in Fig. 1. The BE of $Te3d_{5/2}$ for 2 nm of ZnTe is found to be 572.39 eV. It is found that the BE of $Te3d_{5/2}$ decreases as the thickness of the ZnTe increases. The core level positions are summarized in Table 1. On the other hand there is not a significant change in the BE of Ga3d core level.

In order to calculate the valance band offset (VBO) one needs three samples: spectra from the clean substrate, spectra from the interface region and from a thick overlayer film. The schematic of the principle of calculation of valence band offset is shown in Fig. 3

The valance band offset can be calculated using the following formula [39]:

$$\Delta E_V = (E_V^{GaAs} - E_{Ga3d}^{GaAs}) - (E_V^{ZnTe} - E_{Te3d}^{ZnTe}) + (E_{Ga3d}^{interface} - E_{Te3d}^{interface}) \quad (1)$$

where $E_V^{GaAs} - E_{Ga3d}^{GaAs}$ is the distance between the Ga3d core level and the valence band maximum for clean GaAs, $E_V^{ZnTe} - E_{Te3d_{5/2}}^{ZnTe}$ is the distance between the $Te3d_{5/2}$ core level and the valence band maximum for a thick ZnTe overlayer and $E_{Ga3d}^{interface} - E_{Te3d_{5/2}}^{interface}$ is the separation between Ga3d and $Te3d_{5/2}$ core levels measured at the interface region. We can rearrange Eq. (1) as follows:

$$\Delta E_V = (E_{Ga3d}^{interface} - E_{Te3d}^{interface}) - (E_{Ga3d}^{GaAs} - E_{Te3d}^{ZnTe}) + (E_V^{GaAs} - E_V^{ZnTe}) \quad (2)$$

Binding energies found from fitting the core level peaks are given in Table 1. The first and the second terms in Eq. (2) are found to be

$$E_{Ga3d}^{GaAs} - E_{Te3d}^{ZnTe} = -18.84 + 572.10 = 553.26 \text{ eV}$$

$$E_{Ga3d}^{interface} - E_{Te3d}^{interface} = -18.90 + 572.41 = 553.51 \text{ eV}$$

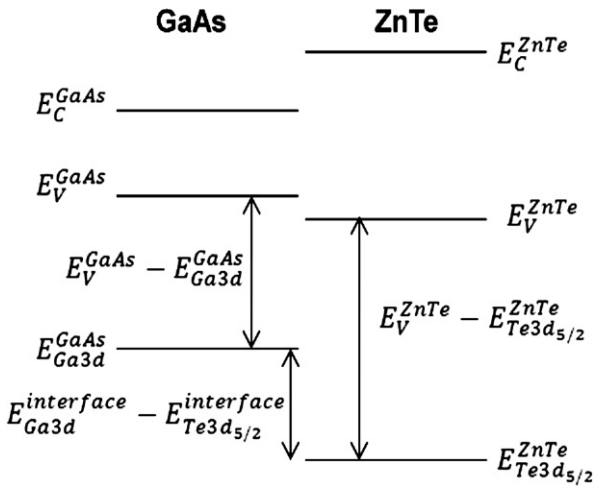

Fig. 3. The schematic of the principle of measurement of valence band offset using XPS.

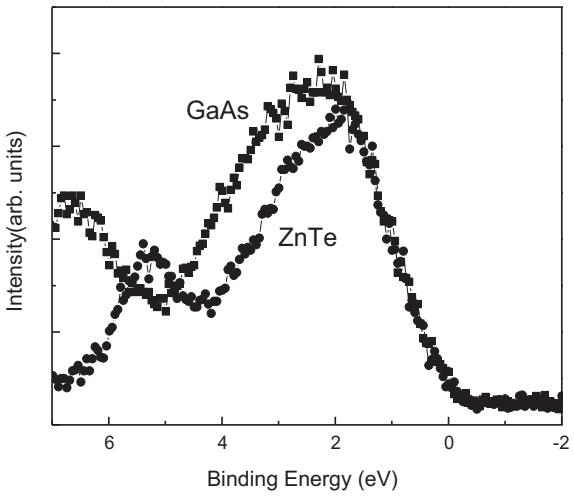

Fig. 4. Valance band spectra of clean GaAs and clean ZnTe samples. These are the raw data, that is the spectra have not been shifted to align the valence band maxima.

It is very important to determine accurately the third term in Eq. (2) which requires to locate the valance band maximum (VBM) to a high precision. VBM can be found by fitting the measured valance band spectra with Gaussian broadened valance band density of states (VBDOS) [39]. The VBM can also be located by taking the intercept between a linear fit of the leading edge in the spectrum and a horizontal background if the shape of the density of states near the VBM of both spectra has similar structures [40]. Another way is to shift the valance band spectra to align the VBM if the VB spectra are similar. In this work, the separation between the VBM (third term in Eq. (2)) was found using the latter method. Fig. 4 shows the raw data of valence band spectra of GaAs and ZnTe. As is seen both spectra have similar density of states near the valance band maximum. Therefore we do not need to know exactly where the VBM is located. As the alignment of the two spectra near the VBM is very good, the difference between the VBM of both clean GaAs and ZnTe spectra ($E_V^{GaAs} - E_V^{ZnTe}$) can be taken as zero.

Using Eq. (2) we found $\Delta E_V = 0.25 \pm 0.1$ eV. This indicates that the band alignment is type I.

The conduction band offset (CBO) can also be determined using

$$\Delta E_C = (E_{bg}^{ZnTe} - E_{bg}^{GaAs}) - (\Delta E_V) \quad (3)$$

where E_{bg}^{ZnTe} and E_{bg}^{GaAs} are the band gap energies of ZnTe and GaAs respectively. The band gap energy for ZnTe 2.25 eV and for GaAs is 1.49 eV at room temperature. Using measured ΔE_V and evaluating Eq. (3) we found a CBO of 0.54 eV.

It is worthwhile to compare our result with previous theoretical work. In general, the experimental valence band offset is in a good agreement with most theoretical predictions if the dipole effect is taken into account. Tersoff's theory for band alignment which takes zero interface dipole as a criterion to determine the band discontinuity gives a valence band offset value of 0.34 eV that is obtained by subtracting midgap energy of GaAs from that of ZnTe [32,41]. Harrison's theory based on a LCAO (linear combination of atomic orbitals) band structure calculation formalism added with interface dipole effect as a correction gives the value of 0.23 eV [33]. In contrast, the original LCAO calculation by Harrison [34] that does not contain any dipole contribution predicted the value of 0.03 eV. By comparing the theoretical predictions and experimental result, it is obvious that the theoretical calculations including interface dipole are in much better agreement with our measurement. Therefore it is suggested that the interface dipole plays a non-negligible role for the band alignment at the interface of ZnTe/GaAs(2 1 1)B. Harrison and Tersoff however pointed out [42] that theories which neglect

the interface dipole often give reasonably good prediction for nearly lattice-matched heterojunctions, since the dipoles are too small to considerably alter the characteristic energy level. However the lattice mismatch between ZnTe and GaAs is as large as 8% consequently the interface dipole cannot be ignored in the theoretical calculations.

It is interesting and necessary to compare the experimental VBO with theoretical prediction by electron affinity rule (EAR) which is the oldest rule for prediction of band alignment. Using electron affinity of ZnTe as 3.52 eV and electron affinity of GaAs as 4.07 eV [31] together with well known energy gaps of two semiconductors, we obtain a valence band offset of 0.22 eV that is very close to our measured value. As Kroemer argued that [43] the EAR would only be valid when the interface dipoles were somehow the same as a simple linear superposition (difference) of the two free-surface dipoles. The ZnTe/GaAs(2 1 1)B system may pose an interesting case where this condition holds for some reason which deserve further investigation in the future.

The value of the VBO might be affected by the strain introduced in thin films by lattice mismatch. For most heterojunctions that have low lattice mismatch, less than 1.5%, the growth is likely in 2-dimensional mode and the strain is relaxed by misfit dislocations beyond the critical thickness. However if the lattice mismatch is greater than 3% the growth is in Stansky–Krastanow mode. In this case the initial strain relaxation occurs by the formation of islands [44] rather than by the misfit dislocations.

We propose that strain has no significant effect on the calculated value of the VBO for our work. The lattice mismatch between the GaAs surface and ZnTe is 7.5% at 340 °C. This is a large mismatch which will result in compressive strain in the ZnTe thin layers. As the thickness of the epilayer increases beyond critical thickness (h_c), misfit dislocations are created in the film and strain relaxes by plastic deformation. The experimental critical thickness for ZnTe/GaAs(1 0 0) is found to be 1.2 nm for ZnTe grown at 250 °C [45]. Therefore we can state that the strain is relaxed to a large extend for the interface region where we measured the VBO, which is 2 and 4 nm.

4. Conclusions

Single crystal epitaxial ZnTe thin films were grown on GaAs(2 1 1)B substrates. Exposing the substrate to Te flux during deoxidation results in smooth surface. RHEED pattern indicated that the growth of ZnTe is two dimensional. XPS analysis of core level peaks does not show any sign of intermixing at the interface region and the interface is fairly sharp as confirmed by HRTEM. The valence band offset was found to be 0.25 ± 0.1 eV corresponding to type I alignment with conduction band offset of 0.54 ± 0.1 eV. Our VBM value agrees well with theoretical predictions. Strain, due to large lattice mismatch, does not seem to affect the value found for VBO.

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