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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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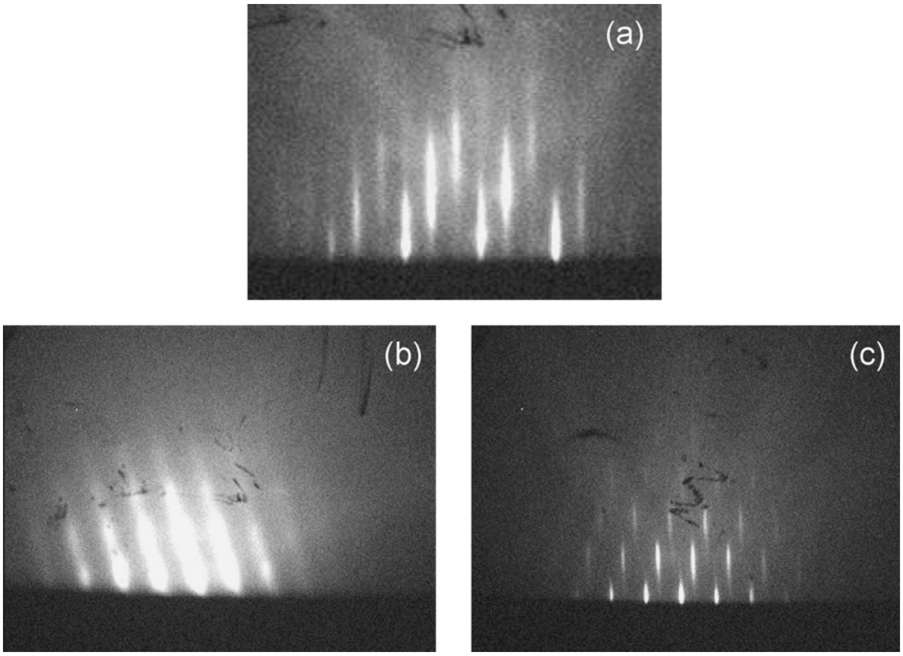

Fig. 1. RHEED patterns of (a) deoxidized GaAs(2 1 1)B surface under Te flux, (b) 2 nm ZnTe growth, (c) 40 nm ZnTe growth on GaAs(2 1 1)B surface. The electron beam is directed along [0 $\bar{1}$ 1].

[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

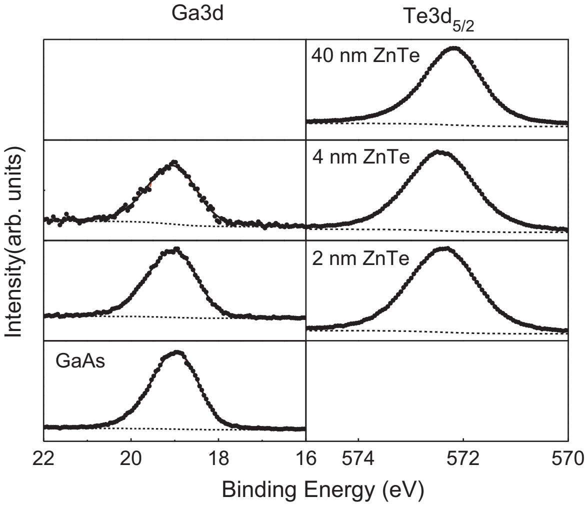

Fig. 2. XPS core level spectra for various thickness of ZnTe on GaAs. Ga3d was fit with mixed Gaussian–Lorentzian doublets and Te$3d_{5/2}$ was fit with an mixed Gaussian–Lorentzian singlets. A nonlinear (Shirley-type) background was used to fit all spectra.