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Band alignment at the CdTe/InSb (001) heterointerface

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CdTe/InSb heterojunctions have attracted considerable attention because of its almost perfect lattice match and the presence of nonoctal interface bonding. This heterojunction is a model heterovalent system to describe band offsets. In this research, molecular beam epitaxy was used to deposit a \sim 5 nm epitaxial CdTe (001) layer on an InSb (001) surface. Monochromatic x-ray photoemission spectroscopy and ultraviolet photoemission spectroscopy were used to characterize the electronic states of clean InSb and CdTe surfaces and CdTe/InSb (001) heterostructures. A room temperature remote hydrogen-plasma process was used to clean the surfaces prior to characterization. The results indicate a valence band offset of 0.89 eV and a type-I (straddling gap) alignment for the CdTe/InSb (001) heterostructure interface. In addition, In-Te bonding was observed at the interface. Downward band bending of the InSb is attributed to excess electrons introduced by nonoctal In-Te interface bonding. Published by the AVS. https://doi.org/10.1116/1.5022799

I. INTRODUCTION

Heterojunctions of II-VI and III-V semiconductors have been studied for several decades. The CdTe/InSb heterojunction is a model heterovalent system because of its almost perfect lattice match and the potential for nonoctal interface bonding. Electron-counting methods have been used for qualitative analysis of the interface bonding. For zincblende structure II-VI and III-V semiconductors, the group II, III, V, and VI elements, respectively, contribute 2/4, 3/4, 5/4, and 6/4 of an electron to the tetrahedral bonds. In the bulk, bonding stability relies on the tetrahedral bonding arrangement, and a full complement of two electrons in each bond. While at heterointerfaces, bonds between III and VI atoms give $9/4 e^-$ and bonds between II and V atoms give $7/4 e^-$, which yields an excess or deficit of $1/4 e^{-}$, respectively. These nonoctal bonding configurations across heterovalent interfaces act as donors or acceptors in adjacent layers and affect the carrier distribution and band bending at interfaces. For the zincblende structure, an ideally terminated (001) surface would display a single kind of atom. Thus, if an abrupt interface forms between II-VI and III-V semiconductors, the bonding at the interface is anticipated to be between II-V atoms or III-VI atoms. In this case, nonoctal bonding, which provides an unbalance of electrons, can occur at each type of interface. This makes understanding the interface electronic state properties considerably more complicated than isovalent interfaces.^{1,2} As an example, the CdTe/GaAs heterojunction has shown an excess interface electron density of $\sim 1 \times 10^{14} \text{ cm}^{-2}$.³ Based on the electron counting method, atomic interface models were proposed to explain the heterointerface charge.^{2,4,5}

CdTe and InSb are both zincblende structure and have a small room temperature lattice mismatch $(|\Delta a|/a \le 5)$ $\times 10^{-4}$).⁶ Early reports of II–VI/III–V heterojunctions focused on the interface band alignment. For the CdTe/InSb heterojunction, an experimental valence band offset (VBO) of $0.87 \pm 0.1 \text{ eV}$ was reported. However, the interface bonding and the charge distribution were left unclear.⁷ Recently reported cross-sectional transmission electron microscopy results on CdTe/InSb (001) heterojunctions similar to those studied here show exceptional structural quality and an interface without visible extended defects. In addition, the absence of extensive interfacial compounds other than an atomically thin layer was suggested.⁸ These heterojunctions also show optimum optical and electronic properties because of their low interface defect density.^{9,10} In this report, we present photoemission spectroscopy (PES) results on CdTe/ InSb (100) heterojunctions. The PES results indicate that an interface layer of ~1.5 nm mainly with In-Te bonding occurs between InSb and CdTe. The heterojunction shows type-I band alignment and band bending consistent with the presence of an electron accumulation layer on the InSb side of the interface.

II. EXPERIMENT

The samples were grown on commercially obtained n-type single crystal (001) InSb substrates (doped with Te at $\sim 5 \times 10^{17}$ atoms/cm³). The InSb and CdTe epitaxial growth processes were performed in a dual-chamber molecular beam epitaxy system, which consists of separate II-VI and III-V growth chambers connected by an ultrahigh vacuum (UHV) preparation chamber. The InSb surfaces were prepared by thermal oxide desorption at 476-480 °C under an Sb flux (all substrate temperatures measured by an optical

pyrometer). Following the oxide removal step, a 600 nm InSb buffer layer was grown at 390 °C. The sample was then transferred under UHV to the II–VI growth chamber. The sample temperature was ramped gradually $(10 \degree C/min)$ to 250 °C, wherein the surface was flooded with Cd to prevent undesired reactions between group III (In) and group VI (Te) elements as the substrate temperature was ramped further to 280 °C. At 280 °C, a Te flux was then supplied at a Cd to Te flux ratio of 3:1 and a Te-limited growth rate of 1.6 Å/s as measured by reflection high energy electron diffraction. The CdTe film thickness was determined to be 4.5 nm from x-ray photoemission spectroscopy (XPS) analysis.

For band alignment measurements, the samples were transferred to the NanoScience Lab UHV system, which consists of six sample preparation and deposition chambers, five surface characterization chambers and an $\sim 22 \,\mathrm{m}$ long UHV transfer line that connects all the processing and characterization chambers. Prior to loading, the samples were cleaned with a jet of ultrahigh purity nitrogen gas. To minimize the effects from contaminants, an *in situ* room temperature remote hydrogen-plasma process was used prior to the photoemission experiments. The research-grade hydrogen flow rate was set to 90 standard cubic centimeters per minute (sccm). The plasma was excited using RF power (13.56 MHz, 100 W) applied to a helical copper coil wrapped around a \sim 32 mm diameter quartz tube. The base of the quartz tube was \sim 200 mm away from the sample. The remote plasma generated predominantly atomic H with low densities of ions and excited neutrals. The surface contamination was monitored using XPS scans of the carbon and oxygen 1s spectra.

The band offsets and band bending were deduced from in situ XPS and ultraviolet photoemission spectroscopy (UPS) measurements. The XPS system consists of a high intensity monochromatized Al Ka x-ray source (1486.7 eV) with a bandwidth of 0.2 eV and a Scienta R3000 high-resolution electron energy analyzer with a resolution of 0.1 eV. The core level peaks were analyzed using CASAXPS, and peak positions could be determined with a relative uncertainty of 0.05 eV. Two UPS systems both optimized for He I radiation at 21.2 eV were used for the measurements. One system, which used the R3000 analyzer operating with 2 eV pass energy yielding an analyzer resolution of 3 meV, was employed for InSb valence band scans. A VSW HAC 50 mm mean radius hemispherical analyzer operating in FAT mode with 15 eV pass energy, which has a resolution of 0.15 eV, was utilized for CdTe on InSb valence band scans. During the UPS scans, a bias of -4.0 or -8.0 V was applied to the substrate to overcome the work function of the analyzer. The photoemission systems were calibrated using a plasma cleaned gold foil.

III. RESULTS

The hydrogen plasma cleaning process provides a lower cleaning temperature compared with thermal desorption cleaning, which limits antimony desorption, retains the sample stoichiometry, and mitigates surface roughening.^{11,12} The XPS results of the carbon and oxygen 1s core levels of InSb and CdTe/InSb before and after H-plasma cleaning are

shown in Fig. 1. In Fig. 1(b-i), the Sb $3d_{5/2}$ peak from antimony oxide and the O 1s peak merged together. After the H-plasma clean, the carbon, antimony oxide, and oxygen peaks were below the XPS detection limit, indicating the species were effectively removed. The stoichiometry analysis based on the XPS peak intensities indicates that the composition of the CdTe film was retained.

The XPS scans of the H-plasma cleaned InSb and CdTe/ InSb heterojunction are presented in Fig. 2. The In and Sb 3d intensities are noticeably lower after the CdTe thin film deposition indicating the coverage of the CdTe film. After CdTe deposition, the Sb peak does not show a noticeable shoulder. Thus, the Sb 3d core-level shift was used to determine the InSb band bending. After CdTe deposition, the Sb $3d_{3/2}$ and $3d_{5/2}$ core-level energies increased 0.2 eV, which indicates a 0.2 eV downward band bending.

XPS was also employed to investigate the low binding energy regime which ranged from the Sb 4d peaks to the valence band maximum (VBM). The results are shown in Fig. 3. A 0.2 eV shift to higher binding energy was observed for the Sb 4d peaks, which is consistent with the 3d peak shifts. To determine the VBO of the CdTe/InSb heterojunction, the Sb 4d peaks were aligned to the same position as



FIG. 1. (Color online) X-ray photoemission spectroscopy scans of (a) the C 1s peak and (b) the O 1s and Sb 3d peak. The scans were as follows: (i) InSb before the H-plasma clean, (ii) InSb after 5 min. H-plasma clean, (iii) CdTe on InSb before H-plasma clean, and (iv) CdTe on InSb after 30 s H-plasma clean.



Fig. 2. (Color online) From left to right: XPS spectra for Te 3d, Sb 3d, In 3d, and Cd 3d peaks: (i) H-plasma cleaned InSb and (ii) H-plasma cleaned CdTe/InSb.

shown in Fig. 3. Scan (i) determines the InSb VBM relative to the Sb 4d level, and scan (ii) determines the VBM of the CdTe layer relative to the Sb 4d level in the heterostructure. The difference of the Sb 4d to VBM of the two scans was 0.9 eV, which is used to determine the VBO. Consequently, a VBO of 0.9 eV was determined between InSb and CdTe in the CdTe/InSb heterojunction.

Ultraviolet (21.2 eV) photoemission spectra after Hplasma cleaning are presented in Fig. 4. For the InSb surface, the VBM was measured at 0.11 eV below the Fermi level, and for the CdTe surface (on the InSb substrate), the VBM was located 1.2 eV below the Fermi level.

The PES results are summarized in Table I. Electron affinity (χ) values were calculated using the following equation:

$$\chi = \phi + E_{\rm VBM} - E_g,\tag{1}$$

where ϕ is the work function of the surface, $E_{\rm VBM}$ is the relative difference between the valence band maximum and Fermi level, and E_g is the band gap of the material. For the calculation, 1.51 eV was used for the CdTe band gap and 0.17 eV was used for the InSb band gap.^{13,14}

IV. DISCUSSION

A. Interface layer

As shown in Fig. 5, shoulder peaks that appeared in the In 3d and Te 3d spectra suggest the existence of indium-tellurium



FIG. 3. (Color online) XPS scans for close to VBM regime (i) InSb substrate (ii) after CdTe deposition.

bonding. Meanwhile, no obvious shoulder peak is observed in the Cd 3d and Sb 3d spectra, which indicates the absence of Cd–Sb bonding. The shoulder peaks are located at 452.7, 445.1 eV for the In 3d peaks and 582.8, 572.4 eV for the Te 3d peaks. As reported in previous studies, multiple phases of indium telluride could be components at the interface. InTe and In₂Te₃ are two possible phases.⁷ It has been reported that surface Sb atoms are volatile at ~300 °C.^{15,16} Thus, during the CdTe deposition, the excess Sb atoms could evaporate from the surface.

XPS peak intensities were used for the interface layer thickness calculation. Abrupt CdTe/In-Te layer/InSb interfaces are assumed for the calculation. Wolfram Mathematica was employed to solve the integral equations. The photoelectron signal intensity is attenuated in the film at a distance z from the surface, and the total peak intensity is provided by¹⁷

$$I = \int I_0 e^{-z/\lambda} dz, \tag{2}$$

where I_0 is the photoemission intensity from the atoms at the surface, and λ is the photoelectron inelastic mean free path. The inelastic mean free path of In 3d, Sb 3d, and Te 3d core level photoemission electrons were 2.6, 2.1, and 2.0 nm, respectively, obtained using the TPP-2M equation.^{18,19}

Before the interface layer thickness calculation, the total thickness of the CdTe layer and interface layer was calculated using the Sb 3d peak intensities. The post- and pre-CdTe



Fig. 4. (Color online) Ultraviolet photoemission spectra of (i) InSb surface and (ii) CdTe on InSb.

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TABLE I. XPS fitting results for Cd 3d, Te 3d, In 3d, and Sb 3d core levels and VBO; UPS results for valence band maximum value (E_{VBM}) and work function (ϕ); and deduced results for electron affinity (χ). All the values are presented in electron-volt.

Surface	Cd 3d	Te 3d	In 3d	Sb 3d	$E_{\rm VBM}$	ϕ	χ	VBO
InSb			444.1/451.6	527.9/537.2	0.11	4.0	3.9	
CdTe on InSb	405.6/412.4	473.0/483.4	444.5/452.0	528.1/537.4	1.2	3.9	3.6	0.9

deposition peak intensity ratio is measured to be 0.12. Thus, we have

$$0.12 = \frac{\int_{t_{\text{Total}}}^{\infty} I_0 e^{-z/\lambda} dz}{\int_0^{\infty} I_0 e^{-z/\lambda} dz},$$
(3)

where t_{Total} is the total thickness of the CdTe layer and interface layer, and it was determined to be 4.5 nm based on the above equation. Then, the interface layer thickness was calculated based on the In 3d and Te 3d peaks, respectively. The shoulder peak of the In 3d was considered to be from In-Te bonding in the interface layer, and the main peak was from In-Sb bonding. The ratio of the shoulder peak to full peak area can be calculated as

$$\operatorname{ratio}_{\text{In3d}} = \frac{\int_{I_{\text{Total}}-I_{\text{Interface}}}^{I_{\text{Total}}} I_0 e^{-z/\lambda} dz}{\int_{I_{\text{Total}}-I_{\text{Interface}}}^{\infty} I_0 e^{-z/\lambda} dz}.$$
(4)

From XPS analysis, the area ratio between shoulder peak and full peak is measured to be 0.37, which indicated an interface layer thickness of 1.2 nm.

When calculating the interface layer thickness from the Te 3d peak, the Te 3d main peak was considered to contribute to the Cd-Te bonding, and the shoulder peak was attributed to In–Te bonding. Similarly, the area ratio of the shoulder peak and full peak can be calculated using

$$\operatorname{ratio}_{\mathrm{Te3d}} = \frac{\int_{t_{\mathrm{Total}}-t_{\mathrm{Interface}}}^{t_{\mathrm{Total}}} I_0 e^{-z/\lambda} dz}{\int_0^{t_{\mathrm{Total}}} I_0 e^{-z/\lambda} dz},$$
(5)

with the measured area ratio of 0.18, an interface layer thickness of 1.8 nm was determined. Since the CdTe film is close to the surface, the In-Te layer contribute relatively weaker signal to the Te 3d peak compared with the CdTe layer, which may lead to uncertainty when calculating the peak area ratio. Besides, in the calculation based on the In 3d peak area, the total thickness of the CdTe layer and interface layer is not involved. However, it is employed in the interface layer thickness calculation based on the Te 3d peak intensity, which may be responsible for the discrepancy of interface layer thicknesses deduced from the In 3d and Te 3d peaks. Taking the average, we consider the interface layer thickness to be ~ 1.5 nm.

B. Band alignment schematic

The valence band offset could also be calculated using the method proposed by Waldrop and Grant, and Kraut *et al.*, $^{20-22}$

$$VBO = (E_{CL}^{InSb} - E_{VBM}^{InSb}) - (E_{CL}^{CdTe} - E_{VBM}^{CdTe}) - \Delta E_{CL}, \quad (6)$$

where E_{CL}^{InSb} and E_{CL}^{CdTe} represent the respective binding energies of the Sb and Cd 3d core levels, E_{VBM}^{InSb} , E_{VBM}^{CdTe} represent the InSb and CdTe valence band maxima measured by UPS, and ΔE_{CL} is the Sb and Cd 3d core level difference at the interface. The calculation indicates a VBO value of 0.89 eV, which is consistent with the value of 0.9 eV from the XPS valence band edge measurement described in Sec. III.

The schematic band alignment for the CdTe and InSb heterojunction is presented in Fig. 6. It is notable that a type I semiconductor heterojunction is observed with this structure. In addition, a 0.2 eV downward band bending appears at the InSb side of the interface.



Fig. 5. (Color online) Peak fitting analysis for XPS spectra of hydrogenplasma cleaned CdTe on InSb: (i) Te 3d and (ii) In 3d peaks.



Fig. 6. (Color online) Schematic of band alignment of CdTe/InSb heterojunction.

C. Interface charge model

According to the XPS analysis, the bonds at the heterointerface are between In and Te atoms. The downward band bending at the boundary of InSb and CdTe could be caused by charge transfer from donor-type bonds at the heterointerface. Since each In–Te bond contributes 9/4 electrons (instead of two electrons for octal bonding), each In–Te bond provides 1/4 excess electron and acts as a donor. The free movement of these excess electrons allows accumulation at the InSb side of the heterointerface since the InSb conduction band minimum (CBM) is lower than the CdTe CBM. The excess electrons could separate into a depletion region of several nanometers in the InSb.

However, it needs to be noted that the CBM of InSb extends below the Fermi level at the interface, and electrons could accumulate in the conduction band. The high density of accumulated electrons could cause sharp downward band bending in a small region close to the interface layer. This sharp band bending would be difficult to detect using XPS; thus, the actual band bending at the interface could be larger than 0.2 eV.

V. SUMMARY AND CONCLUSIONS

In this research, MBE was used for the growth of a CdTe/ InSb (100) heterostructure. A room temperature H-plasma was found to be an efficient way to clean air-exposed InSb and CdTe surfaces. The XPS results indicated the existence of In–Te bonding at the interface, and the peak analysis indicated the formation of a ~1.5 nm interface layer. The band alignment of the CdTe/InSb heterostructure was deduced from XPS and UPS measurements. A type-I heterojunction was observed with a valence band offset of 0.89 eV. The CdTe on InSb can confine both electrons and holes in the InSb. The donor-type bonds between In and Te would provide 1/4 e^- on average leading to an electron accumulation layer at the InSb side of the interface.

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