The band alignment of nonpolar $m$-plane $\text{ZnO}_{1-x}\text{S}_x/\text{Mg}_0.4\text{Zn}_0.6\text{O}$ heterojunctions

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ABSTRACT
Heterostructures such as heterojunctions, quantum wells, and superlattices are core components of advanced optoelectronic devices. Herein, we attempted the first investigations on the band alignment of nonpolar m-plane oriented \( \text{ZnO}_{1-x}\text{S}_x/\text{Mg}_0.4\text{Zn}_{0.6}\text{O} \) heterojunctions by X-ray photoelectron spectroscopy. All the heterojunctions were revealed to show a type-I band alignment, and the valence band offset (VBO; \( \Delta E_V \)) decreased insignificantly with increasing S content in the \( \text{ZnO}_{1-x}\text{S}_x \) layer. Specifically, for the \( \text{ZnO}_{1-x}\text{S}_x/\text{Mg}_0.4\text{Zn}_{0.6}\text{O} \) heterojunctions with \( x = 0, 0.13, \) and 0.22, \( \Delta E_V \) was determined to be 0.24 (0.22), 0.61 (0.17), and 0.79 (0.11) eV, respectively. The VBOs of \( \text{ZnOS}/\text{MgZnO} \) heterojunctions are significantly larger than those of heterojunctions involving only cation-substituted alloys (\( \text{ZnO}/\text{MgZnO} \) or \( \text{ZnO}/\text{CdZnO} \)) due to the opposite shift in the VB maximum of \( \text{ZnOS} \) and \( \text{MgZnO} \) with respect to \( \text{ZnO} \). Knowing band alignment parameters of the \( \text{ZnOS}/\text{MgZnO} \) interface can provide a better understanding of the carrier transport mechanism and rational design of \( \text{ZnO} \)-based optoelectronic devices.

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I. INTRODUCTION

\( \text{ZnO} \) is a typical wide bandgap semiconductor suitable for a large variety of device applications.\(^{1,2} \) The advantageous characters of \( \text{ZnO} \) that distinguish it from other semiconductors include direct and wide bandgap (\( E_g \sim 3.3 \) eV at room temperature), large exciton binding energy (60 meV), large piezoelectric constants, strong luminescence, large nonlinear optical coefficients, high melting temperature (2248 K), good biocompatibility, low toxicity, and low cost.\(^{3,4} \) In order to optimize the performance of \( \text{ZnO} \)-based optoelectronic devices, most designs rely on different kinds of heterojunctions for providing carrier and/or optical confinement. A heterojunction is composed of layers of different compositions, whose key parameters are the bandgap of each layer and the valence/conduction band offset between the individual layers. The dynamics of charge carriers in the heterojunction depends on the potential barrier heights, which are quantified by the values of the valence/conduction band offset at the interface between two contacting layers. Following extensive investigations on the bandgap engineering of \( \text{ZnO} \) by isovalent cation substitution (e.g., \( \text{MgZnO} \), \( \text{CdZnO} \), and \( \text{BeZnO} \) alloys),\(^{5-8} \) construction and fabrication of \( \text{ZnO} \)-based heterojunctions such as \( \text{ZnO}/\text{MeZnO} \) (\( \text{Me} = \text{Mg}, \text{Cd}, \text{Be}, \) and \( \text{Ni} \)\(^{9-12} \)) on various substrates have been demonstrated with different growth techniques. In particular, several experimental studies on the determination of band offsets of the \( \text{ZnO}/\text{MgZnO} \) and \( \text{ZnO}/\text{CdZnO} \) heterojunctions have been reported.\(^{13,14} \) On the other hand, replacing \( \text{O}^{2-} \) ions with isovalent anions is another important way for bandgap engineering of \( \text{ZnO} \).\(^{15} \) For example, introducing S into \( \text{ZnO} \) can form \( \text{ZnS} \) alloys that show a nonlinear variation in bandgaps with the S concentration and show different electrical and optical properties with respect to \( \text{ZnO} \) due to large electronegativity and size differences between \( \text{S} \) and \( \text{O} \).\(^{16-18} \) At present, high-quality \( \text{ZnOS} \) thin films with different compositions can be epitaxially grown on sapphire substrates by pulsed laser deposition (PLD). In our previous work, the \( \text{S} \) solubility limit in single-phase \( \text{ZnOS} \) epitaxial films was determined, and variations of both the bandgap and lattice...
constants were quantitatively correlated with the S content in the ZnOS alloys. Because MgZnO and ZnOS alloys show opposite variations in the bandgap energy with the substituent (Mg or S) concentration, we proposed the design of ZnOS/MgZnO heterostructures, such as superlattices (SLs) and quantum wells (QWs), that have a larger barrier height than ZnO/ZnMgO with appropriate S and Mg concentrations. Although such cation- and anion-substituted ZnO alloy composed heterostructures hold great potential, in reality, ZnO-based heterojunctions involving anion-substituted alloys such as ZnOS remain unexplored to date.

Returning to the ZnO/MeZnO heterojunctions documented so far in the literature, the most heterojunctions were grown on a polar surface, such as c-plane oriented sapphire substrates. When a single QW is grown along the c-axis of a hexagonal crystal structure, a built-in electric field arising from the spontaneous polarization occurs, leading to band bending in the QW along the growth direction, which confines the electrons and holes in the conduction band minimum (CBM) and valence band maximum (VBM) of the QW, respectively. The overlap of the electron and hole wave-function is reduced by increasing the well width, leading to an increment in the radiative recombination lifetime (i.e., quantum confined Stark effect, QCSE). These effects encumber the performance and efficiency of light emitting devices. In order to avoid the QCSE, ZnO-based alloy thin films and heterojunctions with nonpolar surface orientation should be developed.

In the present study, based on our previous work on the PLD growth of high-quality ZnOS epitaxial films with a nonpolar surface, we attempted and achieved the growth of nonpolar m-plane oriented ZnOS/MgZnO heterostructures on an m-plane sapphire. Then, we used X-ray photoelectron spectroscopy (XPS) to investigate the band alignment of the grown heterojunctions. XPS has been employed to determine the offsets of both valence and conduction bands between the two layers in the ZnOS/MgZnO heterojunctions.

II. EXPERIMENTAL

In this work, seven samples including three single-layer ZnO$_{1-x}$S$_x$ (ZnOS) including ZnO ($x = 0$) films, one single-layer Mg$_{0.4}$Zn$_{0.6}$O (MgZnO) film, and three bilayer ZnO$_{1-x}$S$_x$/Mg$_{0.4}$Zn$_{0.6}$O (ZnOS/MgZnO) heterojunctions were grown on single-crystal m-plane sapphire substrates by PLD. While the Mg$_{0.4}$Zn$_{0.6}$O thick film and thin layers in the ZnOS/MgZnO heterostructures were grown using a MgZnO ceramic target at a fixed O$_2$ pressure of 0.5 Pa, ZnOS thick films and thin layers in the heterojunctions with different S contents were prepared applying a Zn ceramic target under varying O$_2$ pressures of 5 Pa and 3.5 Pa; the ZnO thick film and thin layer in ZnO/MgZnO were deposited with a ZnO ceramic target under 3 Pa of oxygen pressure. Details regarding the PLD process were published elsewhere. Eventually, three 300 nm-thick ZnO$_{1-x}$S$_x$ ($x = 0, 0.13,$ and 0.22) films, a 300 nm-thick Mg$_{0.4}$Zn$_{0.6}$O film, and three 20 nm-ZnO$_{1-x}$S$_x$/300 nm-Mg$_{0.4}$Zn$_{0.6}$O heterojunctions were fabricated and used for further studies in this work.

Composition analysis of the single-layer films and band alignment determination of the bilayer heterojunctions were accomplished by XPS core-level (CL) and valence band (VB) spectra measurements using an Escalab 250Xi system (Thermo Fisher Scientific, USA) with a photon energy of 1486.6 eV (Al Kα radiation from a monochromatic x-ray source) under ultrahigh vacuum conditions. Ar-ion sputtering was used to clean surfaces of the films and perform step-wise etching of the bilayer heterojunctions. The sputtering parameters for etching were fixed at an Ar pressure of 5 × 10$^{-4}$ mbar, Ar$^+$ ion energy of 1 keV, and sputtering period of 2 min. Multiple cycles of the sputtering-XPS test were performed until the CL signal of Mg 2p from MgZnO was detected by XPS. This eventually allowed simultaneous detection of CL signals from both layers of the ZnOS/MgZnO heterojunctions. The final thickness of the ZnOS layer was estimated to be ~5 nm. All spectra presented in this paper were calibrated by two steps: first, the charging effect induced by Ar$^+$ bombardments was removed by considering the binding energy shifts of Zn 2p$_{3/2}$ before and after sputtering. Then, recalibration referring to the C 1s hydro-carbon peak at 284.5 eV was performed to remove the charging effect induced by x-ray irradiation. The S contents in the ZnOS films deposited under oxygen pressures of 5 Pa and 3.5 Pa were determined to be approx. 13% and 22%, respectively, while the Mg content in the MgZnO films was measured to be and maintained at 40%. X-ray diffraction (XRD) was performed using a four-circle single-crystal diffractometer (D8 Discover, Bruker GmbH) with a Cu Kα monochromatic radiation source ($λ = 0.1546 	ext{ nm}$) for the structural characterization of the films and heterojunctions. Optical transmittance of the films was measured by using a UV–Vis–NIR spectrophotometer (Shimadzu UV 3600) to evaluate optical bandgaps of the films.

III. RESULTS AND DISCUSSION

Figure 1(a) shows θ–2θ XRD patterns of the single-layer ZnO$_{1-x}$S$_x$ ($x = 0, 0.13,$ and 0.22) and Mg$_{0.4}$Zn$_{0.6}$O films deposited on the m-plane sapphire substrates. For all the films, along with the (10-10) diffraction peak of the m-sapphire, one can observe diffraction peaks around 31° and 66°, originating, respectively, from (10-10) and (20-20) planes of the hexagonal ZnO or MgZnO. The patterns show no additional peaks and signs of polycrystalline or amorphous phases, confirming the achievement of single-phase ZnOS and MgZnO films with a preferential (10-10), i.e., m-plane orientation.
Bandgaps of the ZnOS and MgZnO films were estimated based on UV-Vis spectroscopy. The absorption coefficients $\alpha$ of the films were calculated from the transmittance measurements and plots of $(ahv)^2$ as a function of photon energy $h\nu$, which are shown in Fig. 1(b). Due to an allowed direct transition of ZnOS and MgZnO, the relationship $(ahv)^2 \propto (h\nu - E_g)$ holds good, from which the optical bandgap can be estimated by extrapolating the linear portion of the $(ahv)^2$ curve to the axis of $h\nu$.

The bandgaps are found to be 3.32, 3.00, and 2.88 eV for ZnO$_{1-x}$S$_x$ ($x = 0$, 0.13, and 0.22), and 3.78 eV for Mg$_{0.4}$Zn$_{0.6}$O, respectively. The decrease in the bandgap of ZnOS with increasing S concentration is consistent with our previous report.\cite{previous_report}

Band offset measurements for the ZnOS/MgZnO heterojunctions were performed following the widely spread method suggested by Kraut et al.\cite{kraut1980estimation} The method makes use of XPS for high-accuracy measurements of heterojunction band discontinuities by determining binding energy differences between the CL and VBM. In the specific case of ZnOS/MgZnO, the value of the valence band offset (VBO) $(\Delta E_{VBO})$ is a specific case of ZnOS/MgZnO, the value of the valence band offset $\Delta E_{VBO}$ is determined by extrapolating the linear portion of the $(ahv)^2$ curve to the axis of $h\nu$.\cite{kraut1980estimation}

The calculated band offsets between ZnOS and MgZnO, the $\Delta E_{VBO}$ values of ZnOS/MgZnO heterojunctions, as well as the VBM of both single-layer films, respectively. Then, the conduction band offset $(\Delta E_C)$ can be calculated using the following equation:

$$\Delta E_C = \Delta E_g - \Delta E_{VBO}. \tag{2}$$

Here, $\Delta E_{VBO}$ is the energy difference between ZnOS and MgZnO, $\Delta E_g$ is the energy difference between the MgZnO and ZnOS single-layer films.

According to this method, for deducing $\Delta E_V$ between ZnOS and MgZnO, we need to determine the binding energies of Zn 2p$\frac{3}{2}$ in the ZnOS, MgZnO single-layer films, and the bilayer ZnOS/MgZnO heterojunction, as well as the VBM of both single-layer films. Figure 2(a) presents detailed XPS narrow-scan spectra of Zn 2p$\frac{3}{2}$ for the ZnO$_{1-x}$S$_x$ ($x = 0$, 0.13, and 0.22) and Mg$_{0.4}$Zn$_{0.6}$O single-layer films, which show a single and symmetric peak at 1021.82 $\pm$ 0.02, 1022.15 $\pm$ 0.02, 1022.23 $\pm$ 0.02, and 1021.90 $\pm$ 0.02 eV, respectively. This implies a predominant Zn-O bonding state in all films. Figure 2(b) displays the narrow-scan spectra of Zn 2p$\frac{3}{2}$ for the three ZnO$_{1-x}$S$_x$/Mg$_{0.4}$Zn$_{0.6}$O ($x = 0$, 0.13, and 0.22) heterojunctions. Similarly, each spectrum shows a single and symmetric peak, located at 1021.66 $\pm$ 0.02, 1022.07 $\pm$ 0.02, and 1022.07 $\pm$ 0.02 eV for $x = 0$, 0.13, and 0.22, respectively. The full width at half maximum (FWHM) of a peak is obtained by a smoothing spline calculation, after performing a background subtraction. The values of the FWHM of these peaks (around 1.85 eV) are almost identical to those of Zn 2p$\frac{3}{2}$ peaks of the single-layer films. This implies that the Zn 2p$\frac{3}{2}$ signals of ZnOS and MgZnO in the ZnOS/MgZnO bilayer heterojunctions coincide in the spectra, and, therefore, $\Delta E_{VBO}$ is 0. VB spectra of the ZnOS and MgZnO single-layer films are shown in Fig. 3. The VBM positions of the films can be estimated by extrapolating the linear portion to the extended baseline of the VB spectra, following the widely used procedure.\cite{widely_used_procedure} The VBM values of the ZnO$_{1-x}$S$_x$ films with $x = 0$, 0.13, and 0.22 are deduced to be 2.94 $\pm$ 0.02, 2.90 $\pm$ 0.04, and 2.80 $\pm$ 0.03 eV, respectively.
and 2.80 \pm 0.05 \text{ eV}, respectively, while that of Mg_{0.6}Zn_{0.4}O is 3.26 \pm 0.04 \text{ eV}. It is noteworthy that there exists another portion with a smaller slope at the end of the VB edge for all the samples, which is known as the band tail originating from defects. A similar phenomenon has been frequently found in the VB region of a variety of semiconductor materials.

Table 1 summarizes the experimental results of $E_g$, $E_{Zn2p3/2}$, $E_{VBM}$, and $E_{Zn2p3/2} - E_{VBM}$ for the single-layer ZnOS and MgZnO films. According to these data, a diagram of band alignments among the ZnOS/MgZnO heterojunctions can be schemed, as shown in Fig. 4. Clearly, all the ZnO$_{1-x}$S$_x$/ZnO heterojunctions exhibit a type-I (straddling) band alignment, where both the VBM and CBM of the layer with a narrower bandgap (ZnO) lie energetically within the wider band gap of the barrier layer (Mg$_{0.4}$Zn$_{0.6}$O). With increasing S content, both the VBM and CBM rise while the bandgap shrinks in ZnO$_{1-x}$S$_x$, leading to a strongly increasing valence band offset and weakly decreasing conduction band offset at the ZnO$_{1-x}$S$_x$/Mg$_{0.4}$Zn$_{0.6}$O heterojunctions (cf. Fig. 5). Based on the experimental data in Table 1 and Eqs. (1) and (2), $\Delta E_V$ and $\Delta E_C$ of ZnO$_{1-x}$S$_x$/ZnO$_{1-x}$S$_x$/Mg$_{0.4}$Zn$_{0.6}$O heterojunctions are specifically quantified to be 0.24 and 0.22 eV, 0.61 and 0.17 eV, and 0.79 and 0.11 eV for $x = 0, 0.13,$ and 0.22, respectively. The accumulated errors for the band offset values are in the range of 0.10–0.13 eV.

Compared with similar heterojunctions with a type-I band alignment in the literature, the valence band offsets of ZnOS/MgZnO heterojunctions (up to 0.79 eV) are significantly larger than those of the heterojunctions such as ZnO/MgZnO and ZnO/CdZnO (less than 0.17 eV). Generally, for ZnO and related alloys, the top of the valence band is a bonding state with a significant contribution from the coupling between the anion-$p$ and cation-$d$ orbitals, while the bottom of the conduction band, being an antibonding state, stems primarily from both the anion-$s$ and cation-$s$ orbitals. Since Zn, but not Mg, contains 3$d$ electrons, the anion-$p$ and cation-$d$ coupling in MgZnO would be weakened as a result of the absence of Mg 3$d$ electrons, resulting in the lowered VBM of MgZnO with respect to ZnO, which becomes more pronounced in MgZnO with a higher Mg content. This effect, however, leads only to small valence band offsets between ZnO and MgZnO alloys according to the general “common anion rule”. For the anion-substituted ZnOS alloys, due to the much enhanced $p$-$d$ coupling between S and Zn as evidenced by a higher VBM of ZnS than ZnO, their VBMs lie significantly higher than those of ZnO or MgZnO, as illustrated in Fig. 4. The VBM of ZnOS shifts upwards with an increasing S content, which is in good agreement with theoretical calculations of Persson et al. It is the opposite shifts of VBM in ZnOS and MgZnO relative to ZnO that lead to larger valence band offsets in the ZnOS/MgZnO heterojunctions than in ZnO/MgZnO. This is an advantageous character for device applications where holes play a major role. It is noteworthy that our present work further indicates a type-II (staggered) band alignment for the ZnO/ZnOS heterojunctions, as seen from the
left side of Fig. 4. As this is an indirect deduction from the different band alignments of various ZnOS including ZnO with respect to Mg$_{0.4}$Zn$_{0.6}$O rather than direct measurements of the ZnO/ZnOS heterojunctions, the real interface of ZnO/ZnOS is not assured to show exactly the same behavior. Based on these pieces of information, various ZnO alloy-based heterostructures can be deliberately designed for making optoelectronic devices with desired performance. For instance, QWs based on ZnOS/MgZnO including ZnO/MgZnO with the type-I band alignment, in which holes are confined in separate quantum wells, are desirable for solar cells and photodetectors.

IV. CONCLUSIONS

In summary, the band alignment of ZnO$_{1-x}$S$_x$/Mg$_{0.4}$Zn$_{0.6}$O heterojunctions was determined by XPS. It was found that type-I heterojunctions were formed between ZnOS and MgZnO. Valence band offsets $\Delta E_v$ were determined to be 0.24, 0.61, and 0.79 eV, while conduction band offsets $\Delta E_c$ were calculated to be 0.22, 0.17, and 0.11 eV for $x = 0, 0.13$, and 0.22, respectively. Extending the most studied ZnO/MgZnO heterojunctions to both anion- and cation-substituted ZnO-based heterojunctions enabled us to first find the type-II band alignment in the ZnO/ZnOS heterojunctions. More importantly, it implies a great freedom for the rational design of various ZnOS/MgZnO heterostructures with a desired band alignment for high-performance optoelectronic devices as both the cation- and anion-substitutes can tune the ZnO band structure in different ways, leading to various VBMs and CBMs of corresponding ZnO alloys.

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