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Measurement of the valence band-offset in a PbSe/ZnO heterojunction by x-ray photoelectron spectroscopy

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A heterojunction of PbSe/ZnO has been grown by molecular beam epitaxy. X-ray photoelectron spectroscopy was used to directly measure the valence-band offset (VBO) of the heterojunction. The VBO, ΔE_V , was determined as 2.51 ± 0.05 eV using the Pb $4p^{3/2}$ and Zn $2p^{3/2}$ core levels as a reference. The conduction-band offset, ΔE_C , was, therefore, determined to be 0.59 ± 0.05 eV based on the above ΔE_V value. This analysis indicates that the PbSe/ZnO heterojunction forms a type I (Straddling Gap) heterostructure. © 2012 American Institute of Physics.

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The group IV-VI narrow gap semiconductor PbSe, with a direct band gap of 0.27 eV at room temperature, has been extensively used to fabricate mid-infrared detectors,¹ lasers,²⁻⁴ and thermoelectric devices.⁵ Polycrystalline PbSe has long been used for commercial uncooled mid-wave infrared (MWIR) detectors. Recently, great attention has also been paid to colloidal PbSe/ZnO nanostructure (CQDs) heterojunctions for applications in photovoltaics (PV).⁶⁻⁸ These structures have potential as a low cost solution for PV,⁹ with the additional possibility to manipulate multiple exciton generation (MEG).¹⁰⁻¹³ Indeed, PbSe/ZnO heterojunctions have also recently been shown to reduce excitonic losses and aid minority carrier extraction, in solar cell architectures^{9,14} increasing their power conversion efficiencies to >5%.

In order to further understand carrier transport at the PbSe/ZnO interface, detailed knowledge of the relative band positions must be gained. To date, however, there have been few reports regarding the band-offsets between PbSe CQDs and ZnO.^{8,15} Choi *et al.* used cyclic-voltammetry (C-V) to analyze band alignments in heterojunction solar cells.⁸ In this technique, the energy band offsets are determined via the investigation of the HOMO and LUMO energy levels of PbSe quantum dots in solution. As such, it is not clear how accurately the band offsets of heterojunction structures are reproduced using C-V, when a heterojunction is formed between PbSe QDs and other materials (such as ZnO, etc.). In addition, various other uncertainties are also introduced by C-V, which have been discussed recently in several publications in the literature.^{8,16-18} Alternatively, Timp and Zhu have reported measurements of the band-offsets in PbSe QDs/ZnO solar cells using ultraviolet photoelectron spectroscopy (UPS).¹⁵ In this measurement, the Fermi-levels

(E_F) are used as a reference to estimate the band-offsets of the heterojunction. However, this technique does not consider the overlap of the band edges in two-sided materials at the heterojunction interface, and/or effects due to Fermi-level pinning at the PbSe/ZnO interface, which may introduce errors.

X-ray photoelectron spectroscopy (XPS) has been proven to be a powerful tool for direct and precise measurement of the band offsets at heterojunction interfaces.¹⁹ Indeed, XPS was recently used to measure band offsets in an epitaxial PbTe/InSb heterostructure.²⁰ Since in this technique (XPS) band bending effects are negligible over the portion of the sample probed (using the core level (CL) as an energy reference²¹), improved accuracy is achieved using XPS as compared to other techniques. However, XPS measurements also require samples with good interfacial quality, which is difficult to achieve with interfaces formed via the solution-based techniques used to deposit PbSe QD layers on ZnO. It is, therefore, difficult to measure the band-offsets at the PbSe QDs/ZnO heterojunction by XPS, in such systems.

Here, we report XPS measurements of the band-offsets of high-quality PbSe and ZnO films. All samples, including one with a heterojunction interface, are prepared under ultra-high vacuum (UHV) conditions using molecular beam epitaxy (MBE). The band offsets of a PbSe (bulk)/ZnO heterojunction were yet to be reported. As such, this information may facilitate further important investigations of PbSe/ZnO heterojunctions, serving as a reference point for PbSe QDs/ZnO solar cells.

To measure the valence band-offset (VBO) by XPS, three samples were prepared. First, a 500 nm ZnO layer was deposited on a *c*-sapphire substrate by plasma-assisted MBE (P-MBE).²² The electron concentration and mobility deduced from Hall measurements were $8.2 \times 10^{16} \text{ cm}^{-3}$ and $9.6 \text{ cm}^2/\text{vs}$, respectively. Also investigated were a 600 nm PbSe film, and a heterojunction comprising a 5 nm PbSe film deposited on a 500 nm ZnO/*c*-sapphire composite substrate by MBE, using a compound source of PbSe and an elemental source of Se. A 10% Se to PbSe flux ratio was used for the

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growth of PbSe films. The substrate temperature was fixed at 300 °C during the growth. The growth rate was $\sim 1.5 \mu\text{m/h}$. As evidenced by RHEED, a polycrystalline PbSe film was formed on the ZnO/c-sapphire substrate. SEM measurements show that polycrystalline PbSe forms (100) orientated micro-crystal array with top area of each grain size about $0.5 \mu\text{m} \times 0.5 \mu\text{m}$ that is significantly larger than the area of boundary domain. Hall measurement on the 600 nm thick polycrystalline PbSe film grown on high resistance $1 \text{ cm} \times 1 \text{ cm}$ SiO_2/Si substrate in the same run shows p-type carrier concentration of $2 \times 10^{17} \text{ cm}^{-3}$ and mobility of $15 \text{ cm}^2/\text{vs}$. PbSe surface and grain boundary interfaces exposed in air is of p-type nature with concentration on the order of 10^{18} cm^{-3} due to oxygen. Thus, the actual concentration in the PbSe microcrystal should be much lower than the measured average Hall value. Therefore, scattering to XPS photoelectrons due to background concentration should not have significant impact on the XPS measurement results. The measurements of XPS were performed with a ESCA-LAB 250 XPS instrument using a $\text{Mg } K\alpha$ (1253.6 eV) X-ray radiation source, which can precisely calibrate the Fermi-level energy and work function of the materials assessed. All XPS spectra were calibrated by the C 1s peak (284.6 eV). To exclude the interference of surface contamination on the samples, the samples were bombarded using an Ar^+ ion beam with a voltage of 1 keV at a low sputtering rate of about 0.5 nm/min, before the measurements were performed.

The following expression to calculate the VBO of the PbSe/ZnO heterojunction interface:²³

$$\Delta E_V = \Delta E_{CL} + (E_{\text{Pb } 4p^{3/2}}^{\text{PbSe}} - E_{\text{VBM}}^{\text{PbSe}}) - (E_{\text{Zn } 2p^{3/2}}^{\text{ZnO}} - E_{\text{VBM}}^{\text{ZnO}}). \quad (1)$$

Here, $\Delta E_{CL} = E_{\text{Zn } 2p^{3/2}}^{\text{ZnO}} - E_{\text{Pb } 4p^{3/2}}^{\text{PbSe}}$ is the CL separation of the PbSe film and ZnO substrate at the interface of the PbSe/ZnO heterojunction system. $(E_{\text{Zn } 2p^{3/2}}^{\text{ZnO}} - E_{\text{VBM}}^{\text{ZnO}})$ is the energy difference between Zn $2p^{3/2}$ core level and the valence band maximum (VBM) in the ZnO epitaxial layer, and $(E_{\text{Pb } 4p^{3/2}}^{\text{PbSe}} - E_{\text{VBM}}^{\text{PbSe}})$ is the energy difference between Pb $4p^{3/2}$ core level and the valence band maximum in PbSe epitaxial layer.

Figure 1 shows the XPS spectra of core level and valence band edge (VBE) in the 500 nm ZnO film. Figure 1(a) displays a single peak located at $1021.82 \pm 0.05 \text{ eV}$ in the core level spectrum of Zn $2p^{3/2}$, which corresponds to the Zn-O bond state. The symmetrical XPS spectrum of the Zn $2p^{3/2}$ indicates the uniform bonding state in the ZnO film. The XPS spectrum of the VBE in the ZnO film is shown in

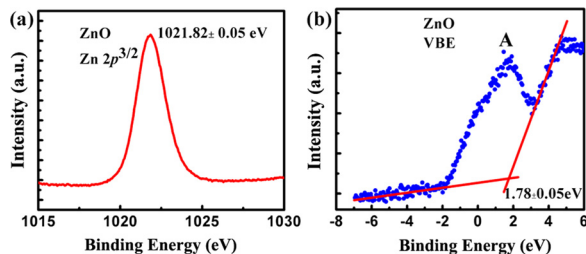


FIG. 1. XPS spectra of core Level (a) and VBE (b) recorded on 500 nm ZnO film.

Figure 1(b). One can see two features, one of which (labeled A) occurs around the E_F in Figure 1(b). This feature (A) is a characteristic of XPS spectra of ZnO films,²⁴ and has been attributed previously to surface states and/or an intrinsic defect within the band gap.²⁵ A similar peak also appears in the XPS spectra of InSb, Cu, and Si (amongst others), and is ascribed to surface states in those cases.²⁶ The VBM of the sample is obtained by the linear extrapolation of the leading edge and extended base line of the valence band (VB) spectrum, finding the intersection of the two lines. By the above linear approximation, the valence band maximum of ZnO deduced from Figure 1(b) is $1.78 \pm 0.05 \text{ eV}$, which is consistent with previously reported values.^{27–31} The XPS spectra of the core level and valence band edge in the 600 nm PbSe film are shown in the Figure 2. In Figure 2(a), a single peak is evident located at $644.53 \pm 0.05 \text{ eV}$, which is attributed to the core level spectrum of Pb $4p^{3/2}$. Figure 2(b) gives a VBM of $-0.88 \pm 0.05 \text{ eV}$ for the 600 nm PbSe sample, again, using the above linear method, comparable to previously measured values.¹⁵ The core level spectra of Zn $2p^{3/2}$ and Pb $4p^{3/2}$ in the PbSe/ZnO heterojunction are shown in Figure 3. As compared with the above core levels XPS spectra recorded on the PbSe and ZnO films, it is evident that the core level spectrum of the Pb $4p^{3/2}$ shifts to $644.76 \pm 0.05 \text{ eV}$, and the core level spectrum of the Zn $2p^{3/2}$ shifts to $1021.90 \pm 0.05 \text{ eV}$ (Figure 3) in the heterostructure. The parameters extracted via XPS, for the samples studied, are summarized in Table I for clarity.

The valence band offset (ΔE_V) was calculated to be $2.51 \pm 0.05 \text{ eV}$ using Eq. (1). The conduction band offset (CBO: ΔE_C) can be estimated by $\Delta E_C = E_g^{\text{ZnO}} - E_g^{\text{PbSe}} - \Delta E_V$, based on ΔE_V (determined above), at the interface of the heterojunction. The band gaps of ZnO and PbSe are 3.37 eV and 0.27 eV at room temperature,^{32,33} respectively. Considering this, the CBO is determined to be $0.59 \pm 0.05 \text{ eV}$. This leads to a ratio for the VBO and CBO of ~ 4.25 . A schematic representation of the band alignment diagram produced using XPS for the heterojunction system studied is shown in Figure 4. This confirms that a type I heterostructure is formed in the PbSe/ZnO heterojunction.

In order to obtain reliable measurement results from the heterojunction one must also consider *other* factors that may affect the experimental results. The main possibility for error occurs due to the effects of strain induced in the thin PbSe film, upon deposition on the ZnO layer. This strain has the potential to induce a large piezoelectric field.³⁴ Since the ZnO film is thick (500 nm), the strain induced at the ZnO-sapphire interface is completely relaxed. The critical thickness (t_c) of the PbSe film deposited on ZnO substrate by

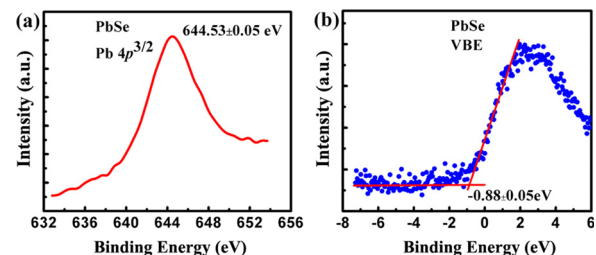


FIG. 2. XPS spectra of CL (a) and VBE (b) recorded on 600 nm PbSe.

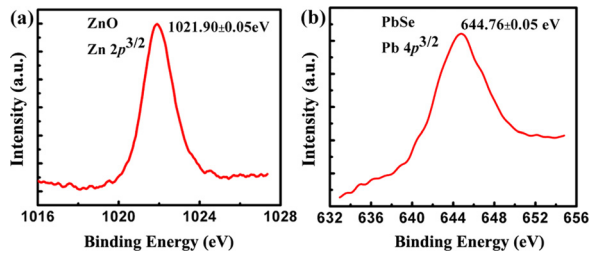


FIG. 3. The CLs spectra of $\text{Zn}2p^{3/2}$ (a) and $\text{Pb}4p^{3/2}$ (b) recorded on the PbSe/ZnO heterojunction.

MBE is estimated to be ~ 0.65 nm (about one monolayer) by the following empirical formula:³⁵

$$t_c = \frac{a_e^2}{2|a_e - a_s|}, \quad (2)$$

where a_e , a_s denote the crystal lattice constants of PbSe film and ZnO in the heterojunction. The lattice constant of ZnO along the a -axis direction is 0.325 nm, and that of the PbSe is 0.612 nm. Therefore, a 5 nm PbSe film is thick enough to be considered strain-relaxed. The effect of the piezoelectric field thus can be neglected in our experiment. This is similar to the case of an InN/ZnO heterojunction, in which one monolayer layer (0.28 nm) of InN is enough to relax the strain in the InN film.³¹ Since the lattice mismatch is larger in the PbSe/ZnO system relative to an InN/ZnO heterostructure, a single molecular layer should be enough to relax the strain in the PbSe thin-film.

Based on our previous MBE epitaxial PbSe growth on lattice mismatched substrates, initial 20 nm– 30 nm PbSe shows island growth with surface roughness of a few monolayers. The typical escape depth of photoelectrons for inorganic compound under current XPS condition is approximately 1 – 3 nm. To ensure that all ZnO surface is covered by PbSe and at the same time sufficient photoelectrons could be detected, a 5 nm (about 8 monolayers) PbSe film on ZnO was deposited. XPS signal was successfully detected with such thickness as confirmed by our measured core level shifts in previous discussions.

Consequently, the PbSe layer was narrower than the depletion width formed at the heterojunction. However, as discussed in Ref. 19, Poisson's equations predict a spatially varying electrostatic potential, which bends all of the bands and/or energy levels by the same amount, as a function of distance, away from the interface. As a result, any issues related to potential energy differences or non-idealities introduced at the interface should have a negligible effect on our

TABLE I. A summary of XPS CL peak positions and VBM position gained by linear fitting method in the PbSe/ZnO heterojunction system.

Samples	State	Binding energy (eV)
PbSe (600 nm)	$\text{Pb}4p^{3/2}$	644.53 ± 0.05
	VBM	-0.88 ± 0.05
ZnO (500 nm)	$\text{Zn}2p^{3/2}$	1021.82 ± 0.05
	VBM	1.78 ± 0.05
PbSe/ZnO	$\text{Zn}2p^{3/2}$	1021.90 ± 0.05
	$\text{Pb}4p^{3/2}$	644.76 ± 0.05

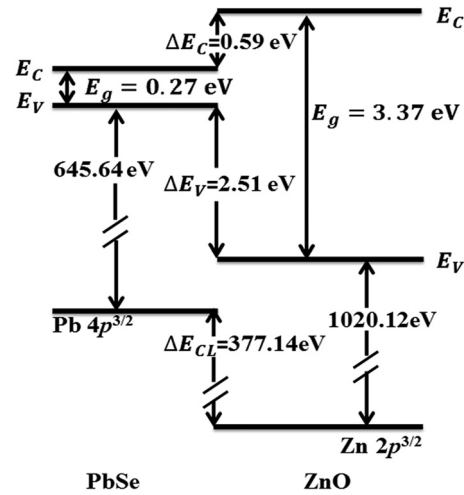


FIG. 4. The schematic diagram of the band alignment diagram in the PbSe/ZnO heterojunction system.

analysis and are therefore neglected. In addition, since the escape length of photoelectrons using XPS is small, any complications caused by these potential variations spread over a few atomic layers at the abrupt interface will also be small, again, making the system relatively insensitive to band bending at the PbSe/ZnO interface, which occurs over a typical width of a few thousand Å.

In summary, the valence band offset of a PbSe/ZnO heterojunction has been measured by X-ray photoelectron spectroscopy. A VBO of 2.51 ± 0.05 eV was obtained for this system, leading to a CBO determined to be 0.59 ± 0.05 eV, based on this analysis. This result indicates a type-I band alignment, which is suitable for many optoelectronic device applications, and provides an accurate reference point for PbSe QDs/ ZnO band offset.

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