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Band alignment of type I at (100)ZnTe/PbSe interface

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A junction of lattice-matched cubic semiconductors ZnTe and PbSe results in a band alignment of type I so that the narrow band gap of PbSe is completely within the wider band gap of ZnTe. The valence band offset of 0.27 eV was found, representing a minor barrier during injection of holes from PbSe into ZnTe. Simple linear extrapolation of the valence band edge results in a smaller calculated band offset, but a more elaborate square root approximation was used instead, which accounts for parabolic bands. PbSe was electrodeposited at room temperature with and without Cd²⁺ ions in the electrolyte. Although Cd adsorbs at the surface, the presence of Cd in the electrolyte does not influence the band offset. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). [<http://dx.doi.org/10.1063/1.4955092>]

Zinc telluride (ZnTe) semiconductor, having band gap of 2.26 eV at room temperature,³ is a promising material for various optoelectronic devices including light emission devices in the green spectral region^{1,2} and next generation solar cells.¹⁰ Lead selenide (PbSe) is a well known narrow band semiconductor with a band gap of 0.28 eV at room temperature.⁴ Knowledge of the band alignment at the ZnTe/PbSe interface is a key requirement for the design of various heterojunction devices, like cascade lasers, high electron mobility transistors, etc. An injection device requires either a p-n junction, or a heterojunction with a suitable band offset for the selective injection of the minority carriers. Good lattice match is an additional requirement for optimal epitaxial growth and low interface defect concentration in heterojunctions. The lattice constant of cubic lead selenide matches that of ZnTe within 0.54 % at room temperature.^{3,5} According to Anderson's rule,⁶ taking into account the difference of electron affinities, a conduction band offset of 0.7 eV (type I) may be expected.^{7,8} The correspondent valence band offset then amounts to 1.3 eV, both offsets being large for possible injection of charge carriers. Although a larger band gap would be beneficial for strongly asymmetric injection into ZnTe, suitable injection may be also expected from a narrow-band emitter, given an appropriate band offset. A further possible application is the surface passivation of PbSe nanoparticles by lattice-matched core-shell structures. The aim of this paper is the measurement of the valence band offset directly by X-ray photoelectron spectroscopy (XPS). Contrary to the above estimations, as shown below, the band alignment is particularly suitable for the injection of holes into ZnTe. Similar strong deviations of band offsets from predictions by Anderson's rule (non-transitivity) are known in the literature^{9,10} for other material combinations.

The formation of heterojunctions is possible with various deposition techniques, most common being vacuum evaporation/sublimation, sputtering, chemical vapor deposition and chemical bath deposition. Relatively new is the electrochemical underpotential deposition of compound semiconductors, including electrochemical epitaxy.^{11,12} Electrochemical deposition offers the following advantages: 1) room temperature deposition avoids thermal mechanical stress induced by otherwise necessary cooling down of the structure; 2) it is simpler to recycle liquid waste products, than to deal with fine dispersed powder after vapor deposition of toxic materials like Pb, Cd, Se and Te compounds; 3) the working electrolyte can be used in more than one deposition cycle; 4) the

average thickness can be easily controlled by the amount of charge flow and 5) the cost of mass production can potentially be reduced by using this non-vacuum technique. The band alignment in heterostructures grown by electrochemical epitaxy, measured and presented here, may eventually differ slightly from that in heterostructures grown by different deposition techniques.

Ultrathin films of PbSe were electrochemically deposited on polished and chemically cleaned (100)ZnTe of p-type doped by phosphorus to a concentration of $1 - 1.2 \times 10^{17} \text{ cm}^{-3}$. The substrates were previously contacted by vacuum evaporation of silver onto the cleaned back surface of the wafer, resulting in contact resistance below 1 k Ω . The deposition of PbSe was carried out in electrolyte containing 50 mM Pb(NO₃)₂, 1 mM Se from standard solution (1 g/l Se in 2% HNO₃) and in some experiments additionally 0.5 M Cd(NO₃)₂.^{12,13} All films were deposited potentiostatically at alternating -400 mV /+200mV potential vs. the saturated KCl Ag/AgCl reference electrode under illumination by a 460 nm super bright light emission diode. After the deposition, the samples were rinsed, dried, transferred and measured ex-situ by XPS equipment with a monochromatic Al K α (1486.6 eV) X-ray source. Reference measurements were performed on cleaved surfaces of ZnTe and PbSe crystals.

Froment et al. described the benefit of additional Cd²⁺ ions in the working electrolyte for facilitating epitaxial growth of PbSe on indium phosphide (InP) substrates.¹³ Here, it was possible to electrodeposit 20nm thick PbSe epitaxial film also on ZnTe in the presence of cadmium. Figure 1 shows the scanning electron micrograph of PbSe film after deposition. X-ray dispersive microanalysis confirms the presence of Pb and Se in similar quantities, both in smooth and in rough regions of the micrograph. The inset in figure 1 shows the pole diagram of the PbSe film structure on (100) ZnTe, measured by electron back scattering diffraction (EBSD). Epitaxy is attained at most locations at the surface. Thinner films cannot be adequately assessed by EBSD, which information depth amounts to about 20 nm, but it can be anticipated, that also 3 - 7 nm PbSe films grown in presence of Cd²⁺ for XPS measurements are single crystalline. However, the presence of Cd²⁺ in the process may influence the band offset. We studied the influence of Cd²⁺ in the electrolyte on the band offset in detail.

Figure 2 shows a survey spectra of a thin PbSe film on (100)ZnTe in the absence and in the presence of Cd²⁺ in the electrolyte. The thickness of the PbSe films, estimated from Faraday law, amounts to 2.2 nm without Cd²⁺ and 7.2 nm with Cd²⁺ in the electrolyte. The survey spectra show all lines of the elements of ZnTe and PbSe and of contamination by oxygen and carbon due to ex-situ measurement. The spectrum of the film deposited in the presence of Cd²⁺ shows additionally the cadmium lines. The band offset at the heterointerface was calculated using the well-known approach of Kraut described in detail elsewhere¹⁴ and modified here for the use with

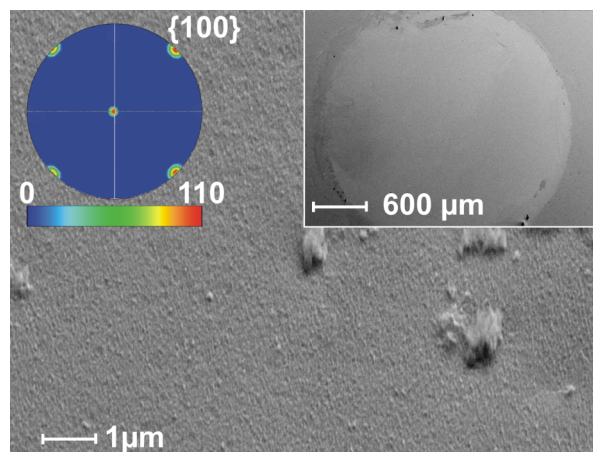


FIG. 1. Micrograph of 20nm PbSe film on (100)ZnTe substrate after underpotential electrodeposition. The sample tilt is 70 degrees relative to the image plane. Left inset: EBSD pole figure as result of orientation analysis at 8153 pixels of this region (with 114 zero solutions, 1.7%). Right inset: round-shaped PbSe-plated region, surrounded by uncovered ZnTe substrate.

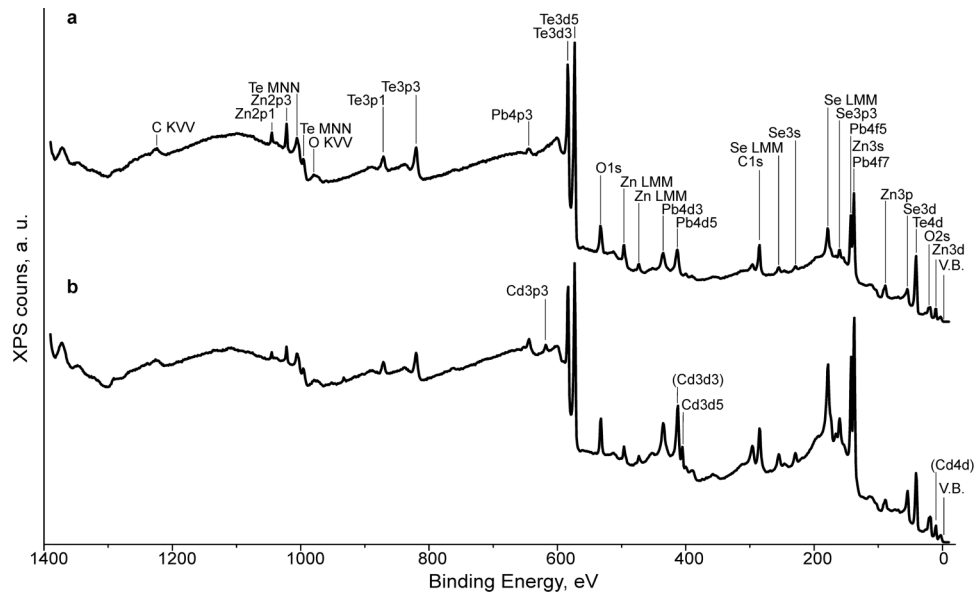


FIG. 2. Survey XPS spectra of PbSe/ZnTe heterojunction deposited in the absence (a) and in the presence of Cd^{2+} ion in the electrolyte (b). The lines in brackets are strongly overlapped.

ex situ measurement. The energy difference between various core levels and the valence band edge are measured separately in both pure binary semiconductors. These differences are considered as material constants. They are applied to calculate the binding energy of both valence band edges in the heterojunction from the measured energy of the respective core levels. The line shape of the core levels was analyzed using UNIFIT software¹⁵ in order to precisely determine the peak positions in each material. Additional spectral components often appear in the line shape due to surface oxidation/reaction during ex-situ transport and measurement. The correct identification of the spectral components of PbSe and ZnTe in the line shape of each element is not a trivial but a vital task. The binding energy of the valence band edges in the semiconductors at both sides of the heterointerface was determined independently through Zn3d, Zn3p, Zn2p, Te4d and Te3d core level doublets for ZnTe and Pb4f, Pb5d, Pb4d and Se3d core level doublets for PbSe. For each heterojunction, the valence band offset is calculated as the difference between the binding energies of the valence band edges in both materials. We excluded Se2p and Te2p core levels from consideration because of the wide line shape and poor reproducibility of XPS peak fitting, even measured on pure binary crystals (see Table I).

TABLE I. Measured energy difference ΔE between the core levels and the valence band edge in PbSe and ZnTe single crystals according to square root band edge fit. The data is averaged over several independent samples resulting in the given 95 % statistical confidence interval.

Peak	ΔE , eV	Peak	ΔE , eV
Pb4d _{3/2}	434.13 ± 0.17	Te4d _{5/2}	39.28 ± 0.09
Pb4d _{5/2}	412.02 ± 0.45	Te4d _{3/2}	40.74 ± 0.09
Pb5d _{5/2}	18.03 ± 0.24	Te3d _{5/2}	571.74 ± 0.07
Pb5d _{3/2}	20.59 ± 0.11	Te3d _{3/2}	582.12 ± 0.06
Pb4f _{5/2}	141.73 ± 0.18	Te3p _{3/2}	818.45 ± 0.13
Pb4f _{7/2}	136.88 ± 0.13	Te3p _{1/2}	869.48 ± 0.18
Se3p _{3/2}	159.13 ± 0.80	Zn3d	9.27 ± 0.08
Se3p _{1/2}	164.97 ± 0.84	Zn3p _{3/2}	87.81 ± 0.11
Se3d _{5/2}	52.69 ± 0.04	Zn3p _{1/2}	90.79 ± 0.09
Se3d _{3/2}	53.54 ± 0.06	Zn2p _{1/2}	1044.16 ± 0.07
		Zn2p _{3/2}	1021.09 ± 0.06

The correct calculation of band offset relies on the correct determination of the energy of valence band edge in the individual binary semiconductors. Traditionally, a simple linear extrapolation of the band edge was used.^{16–18} Alternatively, the hypothesis about parabolic band structure close to the band edge results in density of states being square root of the energy difference from the edge.¹⁹ This density of states is further blurred by calculation of the product with a normal distribution to account for limited measurement resolution and random influence. We applied both these approaches and compared the results. Figure 3 shows an example, how the same experimental spectrum may be interpreted using the two approaches with significantly different results. The difference of the band edge energies by the two methods does not completely cancel out during band offset calculation, so a decision should be made to choose the most reliable method. For PbSe, the binding energy of the valence band edge can be independently estimated from the known band gap of 0.28 eV at room temperature.⁴ The material content of 99.99% in PbSe single crystals means that the maximal impurity concentration amounts to 1.7×10^{18} , which is smaller²⁰ than the intrinsic carrier concentration of $3.5 \times 10^{18} \text{ cm}^{-3}$ at room temperature. The effective masses for electrons and holes in PbSe are very similar,²¹ so that the Fermi level in intrinsic PbSe is at the midgap position. Therefore, neglecting also the surface charge density with respect to the large bulk carrier density, the expected binding energy of the valence band edge is $E_g/2 = 0.14 \text{ eV}$. This value is closer to the binding energy obtained by the parabolic fit of the band edge spectrum. Also in the case of ZnTe the simple parabolic fit is expected to be correct, because of relatively large spin-orbit splitting in the valence band of 0.9 eV.²²

Table I shows the energy difference between the specified core levels and the band edge in the binary semiconductors, averaged across several reference samples. The binding energy of the band edges was taken from square root approximation.

The statistical distribution of the band offset, calculated via various pairs of core levels in each single heterojunction (of a set of 4) is close to the normal one (Fig. 4), as though all individual deviations were random. Any deviation from the normal distribution would imply some systematic error, which may originate from a false identification of spectral components.

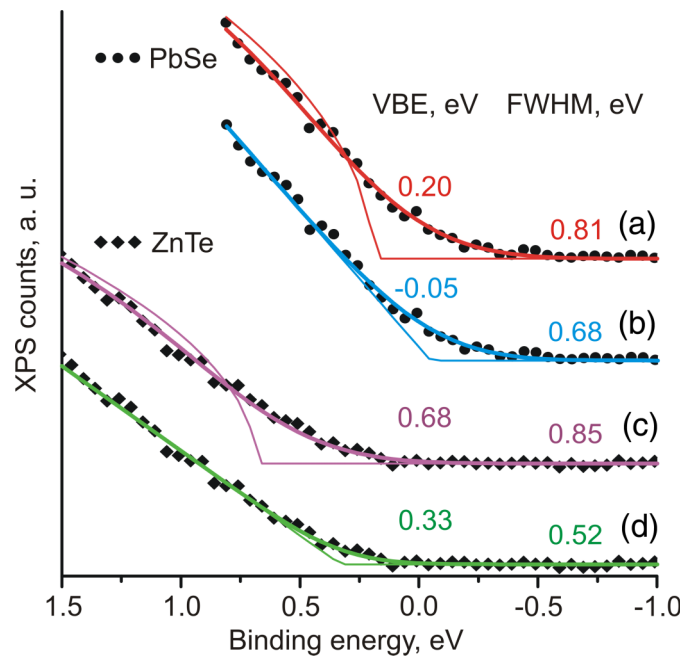


FIG. 3. Results of the linear and the square root approximation of the valence band edge (VBE) in PbSe and ZnTe. Scatter – experimental photoelectron spectra of ZnTe (diamonds) and PbSe (circles), thick solid lines – resulting fits of valence band spectra: (a) and (c) – square root approximation and (b) and (d) – linear approximation of density of states, thin solid lines – assumed density of states. Values for full width at half maximum (FWHM) and binding energy at valence band edge are given for each plot.

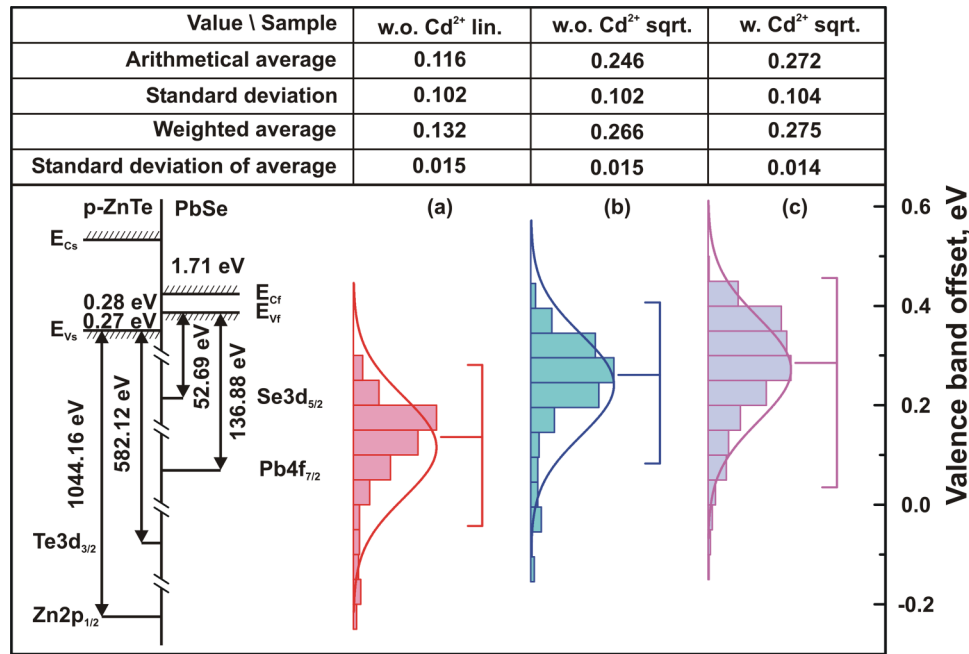


FIG. 4. Resulting band alignment in the heterostructure p-ZnTe/PbSe. Band diagram of the structure (left inset): E_{Cs} , E_{Cf} – conduction band edges and E_{Vs} , E_{Vf} – valence band edges in ZnTe substrate and in PbSe film respectively. Distribution of valence band offset in ZnTe/PbSe heterostructure across various samples and measurements (inserted plots). Plots and values: (a) and (b) represent band offset in samples deposited in the absence of Cd²⁺ ions estimated using (a) – linear and (b) – square root approximation of reference band edges. Plot and values (c) represent band offset in samples deposited in the presence of Cd²⁺ ions in the electrolyte (square root approximation).

The band offset in heterojunctions grown with and without Cd²⁺ is the same within the experimental uncertainty. This observation indirectly confirms the model of electrolytic PbSe growth by Froment et al., where Cd²⁺ ions stay at the surface and locally inhibit the growth.^{12,13} Therefore, both ZnTe/PbSe interface and the PbSe film are Cd-free so that there is no influence of Cd on band offset. The Cd signal in the overview XPS spectrum (Fig. 2(b)) originates from the adsorbed atoms at the PbSe surface.

According to the presented results, type I band alignment was observed at the interface. The large conduction band offset of 1.71 eV can be deduced from the bulk band gaps of both materials.

In conclusion, the valence band offset at the PbSe/ZnTe interface amounts to 0.27 ± 0.05 eV in the presence of Cd ions in the electrolyte and remains constant independently of cadmium content. The valence band offset deviates strongly from that predicted by Anderson's rule (0.7 eV). The band offset may depend slightly on the deposition technique. Hot deposition may induce strain at the interface upon cooling down. Since the strain is known to influence the band gaps, it should also influence the band offsets. Hot deposition is capable to induce interdiffusion between the materials and relaxation of defects upon cooling. From this point of view, the measurement at the same temperature as that of deposition is the most general one.

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