Band offsets at the ZnSe/CuGaSe$_2$(001) heterointerface

Cite as: Appl. Phys. Lett. 74, 1099 (1999); https://doi.org/10.1063/1.123455
Submitted: 21 September 1998 • Accepted: 16 December 1998 • Published Online: 18 February 1999


ARTICLES YOU MAY BE INTERESTED IN

Microstructural study of the CdS/CuGaSe$_2$ interfacial region in CuGaSe$_2$ thin film solar cells
Journal of Applied Physics 85, 534 (1999); https://doi.org/10.1063/1.369486

Measurement of ZnSe–GaAs(110) and ZnSe–Ge(110) heterojunction band discontinuities by x-ray photoelectron spectroscopy (XPS)
Journal of Vacuum Science and Technology 21, 482 (1982); https://doi.org/10.1116/1.571684

Zn(O, S) buffer layers by atomic layer deposition in Cu(In, Ga)Se$_2$ based thin film solar cells: Band alignment and sulfur gradient
Journal of Applied Physics 100, 044506 (2006); https://doi.org/10.1063/1.2222067
**Band offsets at the ZnSe/CuGaSe₂(001) heterointerface**

A. Bauknecht, U. Blieske, T. Kampschulte, J. Albert, H. Sehnert, and M. Ch. Lux-Steiner  
Hahn-Meitner-Institut, Glienicker Straße 100, 14109 Berlin, Germany

A. Klein and W. Jaegermann  
Technische Universität Darmstadt, 64287 Darmstadt, Germany

(Received 21 September 1998; accepted for publication 16 December 1998)

The formation of the ZnSe/CuGaSe₂ heterointerface was studied by x-ray photoelectron spectroscopy (XPS). ZnSe was sequentially grown on CuGaSe₂(001) epilayers. *In situ* photoemission spectra of the Ga 3d and Zn 3d core levels as well as XPS valence bands were acquired after each deposition step. The valence-band offset is determined to be $\Delta E_V = 0.6 \pm 0.1$ eV. As a consequence, a nearly symmetric ‘‘type-I’’ band alignment for the ZnSe/CuGaSe₂ heterojunction with a conduction-band offset of $\Delta E_C = 0.4 \pm 0.1$ eV is found.

Concerning the band alignment ZnSe can, therefore, be expected to be a suitable buffer material for CuGaSe₂-based thin-film solar cells. © 1999 American Institute of Physics. [S0003-6951(99)01008-6]

---

Cu(In,Ga)(S,Se)₂-based thin-film solar cells reaching efficiencies of 17.7% on the laboratory scale are now ready to enter the stage of pilot production. The most efficient devices obtained so far use absorbers with low Ga and S contents, thus showing band gaps of $E_g \approx 1.2$ eV. Another challenge is to realize high-voltage devices on the basis of the ternary wide-energy-gap absorbers CuInS₂ ($E_g \approx 1.5$ eV) and CuGaSe₂ ($E_g \approx 1.7$ eV).

ZnO/CdS/CuGaSe₂ solar cells have reached efficiencies of up to 9.3% limited by open circuit voltages ($V_{OC}$) of 870 mV and fill factors of 63.7%. The loss in $V_{OC}$ observed for Cu(In,Ga)Se₂-based devices with Ga/(Ga+In) ratios larger than 50% has been attributed to changes in the transport mechanisms at the heterojunction to CdS. For the CdS/CuGaSe₂ interface a ‘‘type-II’’ band alignment, placing the CdS conduction-band minimum below that of CuGaSe₂ (cliff), has been measured. From numerical simulations it can be concluded that ‘‘type-II’’ heterojunctions show interface recombination dominated behavior, hence, suffering from a loss in $V_{OC}$. In addition to the optimization of CuGaSe₂ wide-energy-gap absorbers for photovoltaic applications it seems, therefore, favorable to investigate alternative materials to replace the standard CdS buffer layer of ZnO/buffer/Cu(In,Ga)Se₂ thin-film solar cells. As a possible candidate, ZnSe with its band gap of 2.7 eV has been studied. However, a lack of reference data and the possibility of photoelectron diffraction from single-crystalline surfaces could not reliably be deduced from the measured spectra.

ZnSe was deposited from a homemade Knudsen cell at a rate of less than 10 Å/min. During evaporation the sample was kept at room temperature. The preparation chamber was directly connected to the surface analysis chamber enabling an *in situ* characterization of the ZnSe/CuGaSe₂ interface formation without breaking the vacuum.

Photoelectron spectroscopy is a widely used tool to determine valence-band offsets ($\Delta E_V$) of semiconductor heterojunctions. One experimental approach is the measurement of (i) the core-level to valence-band maximum separation $BE_{CL}^{VBM}$ in both, substrate (CuGaSe₂) and film (ZnSe) as well as (ii) the difference between the core-level binding energies (BEs) ($\Delta E_{CL}$) at the heterointerface. The band offset is then given by

$$\Delta E_V = BE_{CL}^{VBM}(\text{CuGaSe}_2) - BE_{CL}^{VBM}(\text{ZnSe}) - \Delta E_{CL}. \quad (1)$$

X-ray photoelectron spectra, including Ga 3d and Zn 3d...
core levels as well as the valence-band region, recorded after each deposition step are shown in Fig. 1. The bottom-most spectrum is taken from the uncovered CuGaSe₂ surface. With increasing coverage the CuGaSe₂ emissions are gradually replaced by the ZnSe features. No evidence for additional chemical species is observed. All substrate emissions show a binding-energy shift of $eV_{bb} = -200$ meV to lower values with increasing film thickness. The Zn 3d level also follows this shift, indicating a shift of the surface Fermi level towards the valence-band maximum (bandbending). For all coverages, where both substrate and overlayer emissions are clearly identified, the binding-energy difference between the Ga 3d and the Zn 3d level is given by $\Delta E_{CL} = 9.55 \pm 0.05$ eV. The unusual direction of the binding-energy shift may be attributed to the formation of Cu₆Se₆-related defect states at the interface as also observed for CdS/CuInSe₂. However, in the previously published results, Cu₆S₆ as a bulk phase is only observed at elevated temperatures. Furthermore, upward bandbending is also observed when ZnSe is deposited on n-doped layered semiconductors at room temperature. In the latter case, a substrate decomposition is very unlikely, so that the upward bandbending is rather attributed to the defects of ZnSe films grown at low temperatures.

In Fig. 2 the determination of the position of the valence-band maximum from an XP spectrum of the clean CuGaSe₂ surface is shown. The experimental data are fitted to a linear density of states (DOS) broadened by the experimental resolution (800 meV). $BE_{VBM}(CuGaSe₂) = 0.57 \pm 0.05$ eV is found for the valence-band maximum of CuGaSe₂. With $BE_{Ga \, 3d} = 19.91 \pm 0.03$ eV (centroid position), this results in $BE_{VBM \, Ga \, 3d} = 19.34 \pm 0.05$ eV in close agreement with the value published by Turowski et al. Furthermore, values for $BE_{VBM \, Zn \, 3d}$ of 19.37 eV, and 19.33 eV for different samples measured with $h\nu = 80$ eV synchrotron radiation have been determined. With lower excitation energies at the synchrotron ($h\nu = 40$ eV) 200–300 meV smaller values are found, which, however, agree with determinations using He II radiation ($h\nu = 40.86$ eV). Since effects of band dispersion, which might account for the observed differences of $BE_{VBM}$ with $h\nu$, are only present at lower excitation energies, the value obtained with higher $h\nu$ is assumed to be more reliable. Consequently, we used $BE_{VBM \, Ga \, 3d} = 19.35 \pm 0.05$ eV for the determination of the band discontinuities. A value of $BE_{Zn \, 3d} = 9.20 \pm 0.05$ eV was determined for ZnSe films, thermally evaporated on different layered semiconductors at various substrate temperatures and measured by means of various excitation energies. In all cases the centroid position of the Zn 3d level has been used. The value is in good agreement with published data.

Figure 3 summarizes the experimental results. Using Eq. (1) the value for the valence band offset amounts to

$$\Delta E_V = 19.35 \, eV - 9.20 \, eV - 9.55 \, eV = 0.6 \pm 0.1 \, eV. \quad (2)$$

Together with the band gaps of CuGaSe₂ and ZnSe, the calculated conduction-band offset is

$$\Delta E_C = 2.7 \, eV - 1.7 \, eV - 0.6 \, eV = 0.4 \, eV. \quad (3)$$

Both the valence-band maximum and the conduction-band minimum are on the CuGaSe₂ side giving a nearly symmetric “type-I” band alignment as observed earlier for a number of interfaces between Cu–chalcopyrite semiconductors and vacuum-evaporated II–VI semiconductors.
The valence-band offset for ZnSe/CuGaSe$_2$ [Eq. (2)] is approximately 100 meV smaller than that observed for the ZnSe/CuInSe$_2$ interface. This agrees well with a theoretical calculation of the relative positions of the valence-band maxima between CuInSe$_2$ and CuGaSe$_2$ by Wei and Zunger, placing the valence-band maximum of CuGaSe$_2$ 40 meV below that of CuInSe$_2$. The calculated relative position of the band maxima for CuInSe$_2$ and CuInS$_2$ [$\Delta E_V = 0.28$ eV (Ref. 17)] also reproduces the different valence-band offsets determined for CdS/CuInSe$_2$ [$\Delta E_V = 0.9$ eV (Ref. 10)] and CdS/CuInS$_2$ [$\Delta E_V = 0.6$ eV (Ref. 16)].

Therefore, the transitivity rule for heterojunction band discontinuities seems to apply to the II–VI/I–III–VI$_2$ heterointerfaces, using the relative positions for the chalcopyrite band edges reported by Wei and Zunger. It is the possible to predict the valence-band offsets for CdS/CuGaSe$_2$ and ZnSe/CuInS$_2$ to be 0.8 and 0.4 eV, respectively. An experimental verification of these values should be a good test if the transitivity rule can be applied to these interfaces. The CdS/CuGaSe$_2$ value is smaller than that reported by Nadenau et al. However, as discussed above, a different value for $E_{\text{VBM}}^{\text{Ga}}$ has been used in Ref. 5 compared to this work and the CdS film has been prepared by chemical bath deposition. The different preparation technique of the film most likely leads to a different band alignment as observed for CdS/CuInS$_2$.

The increase in band gap with increasing Ga content in Cu(In,Ga)Se$_2$ mainly shifts the conduction-band maximum closer to the vacuum level leaving the ionization energy almost unchanged since the Ga and In orbitals mainly contribute to the conduction bands. For the same reason, the valence-band discontinuities of a II–VI compound with CuInSe$_2$ and CuGaSe$_2$ are similar. However, with increasing band gap this leads to a cliff in the conduction band as described for CdS/CuGaSe$_2$. In order to avoid this effect, which might limit the performance of a solar cell device, a material with a smaller valence-band offset and/or a larger band gap is required. At least for the case of interfaces prepared by thermally evaporated II–VI compounds, ZnSe will fulfill this requirement.

In summary, the determination of the band alignment between ZnSe and CuGaSe$_2$ using x-ray photoelectron spectroscopy has been presented. ZnSe films of increasing thickness were stepwise evaporated on an epitaxial CuGaSe$_2$(001) surface. The valence-band offset of $\Delta E_V = 0.6 \pm 0.1$ eV is in good agreement to an expectation from the transitivity rule using experimental values for ZnSe/CuInSe$_2$ and a theoretical calculation for CuInSe$_2$/CuGaSe$_2$ heterostructures.

This work was supported in part by the European Commission within the frame of the Joule III program under Contract No. JOR3-CT97-0135.

---