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Band offsets at the $ZnSe/CuGaSe_2(001)$ heterointerface

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The formation of the $ZnSe/CuGaSe_2$ heterointerface was studied by x-ray photoelectron spectroscopy (XPS). ZnSe was sequentially grown on $CuGaSe_2(001)$ 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 $ZnSe/CuGaSe_2$ 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 $CuGaSe_2$-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[1] 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 $E_g \leq 1.2$ eV.[2] Another challenge is to realize high-voltage devices on the basis of the ternary wide-energy-gap absorbers $CuInS_2$ ($E_g = 1.5$ eV) and $CuGaSe_2$ ($E_g = 1.7$ eV).

$ZnO/CdS/CuGaSe_2$ 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%.[3] The loss in V_{OC} observed for $Cu(In,Ga)Se_2$-based devices with Ga/(Ga+In) ratios larger than 50%[4] has been attributed to changes in the transport mechanisms at the heterojunction to CdS. For the $CdS/CuGaSe_2$ interface a ''type-II'' band alignment, placing the CdS conduction-band minimum below that of $CuGaSe_2$ (cliff), has been measured.[5] From numerical simulations it can be concluded that ''type-II'' heterojunction devices show interface recombination dominated behavior, hence, suffering from a loss in V_{OC}.[6] In addition to the optimization of $CuGaSe_2$ wide-energy-gap absorbers for photovoltaic applications it seems, therefore, favorable to investigate alternative materials to replace the standard CdS buffer layer of $ZnO/buffer/Cu(In,Ga)Se_2$ thin-film solar cells. As a possible candidate, ZnSe with its band gap of 2.7 eV has been studied in this work. The lattice constants of ZnSe and $CuGaSe_2$ are closely matched, which should result in almost strain-free interface formation.

$CuGaSe_2$ was grown by metal organic vapor phase epitaxy (MOVPE) on GaAs(001) substrates using CpCuTEP, TEGa, and DTBSe (Ref. 7) as precursors. Growth temperature was 570 °C. A reduced reactor pressure of 50 mbar as well as substrate rotation was used to ensure homogeneous epitaxial growth with respect to layer thickness and elemental composition. The surface morphology of $CuGaSe_2/GaAs(001)$ epilayers shows a characteristical dependence on its elemental composition. For Cu-rich layers segregation of Cu_xSe_y has been observed, whereas slightly Ga-rich layers reveal smooth surfaces. Therefore, molar flows of the different precursors were adjusted so as to achieve a near-stoichiometric but slightly Ga-rich composition of the epilayers resulting in a smooth surface morphology as determined by electron microscopy and atomic force microscopy. X-ray diffraction and electron channeling measurements prove the *c*-axis-oriented epitaxial growth of $CuGaSe_2$ on GaAs(001) resulting in a (001)-oriented $CuGaSe_2$ surface. For x-ray photoelectron spectroscopy (XPS) measurements the $CuGaSe_2$ epilayers were transferred to the ultra-high-vacuum (UHV) surface analysis system (VG-ESCAlab MKII) in an atmosphere of dried nitrogen without any exposure to air. Mg $K\alpha$ radiation (1253.6 eV) was used as the excitation source. The electron analyzer was operated at 20 eV pass energy. No contamination of the surface with oxygen and carbon was detected by XPS after heating the sample to 200 °C for 1 h. Unfortunately, due to the lack of reference data and the possibility of photoelectron diffraction from single-crystalline surfaces[8] stoichiometry could not reliably be deduced from the measured spectra.

ZnSe was deposited from a homemade Knudsen cell at a deposition 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 $ZnSe/CuGaSe_2$ interface formation without breaking the vacuum.

Photoelectron spectroscopy is a widely used tool to determine valence-band offsets (ΔE_V) of semiconductor heterojunctions.[9] One experimental approach is the measurement of (i) the core-level to valence-band maximum separation BE_{CL}^{VBM} in both, substrate ($CuGaSe_2$) and film (ZnSe) as well as (ii) the difference between the core-level binding energies (BEs) (ΔE_{CL}) at the heterointerface. The band offset is then given by

$$\Delta E_V = BE_{CL}^{VBM}(CuGaSe_2) - BE_{CL}^{VBM}(ZnSe) - \Delta E_{CL}. \quad (1)$$

X-ray photoelectron spectra, including Ga $3d$ and Zn $3d$

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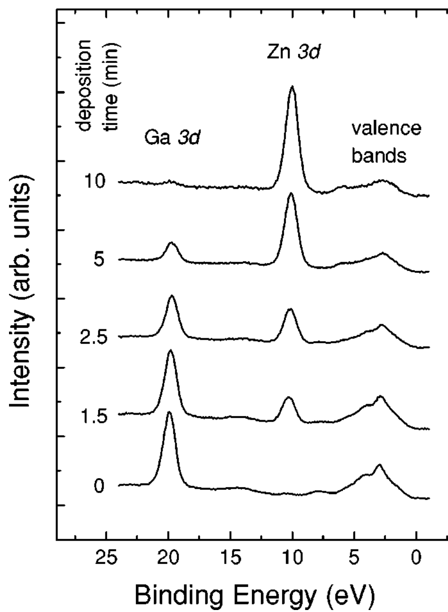

FIG. 1. XP spectra of Ga 3*d*, Zn 3*d* core levels and valence bands of $CuGaSe_2$ in the course of ZnSe deposition. Excitation energy was 1253.6 eV (Mg $K\alpha$). Spectra are shown after numerical subtraction of Mg $K\alpha$ satellites. Zero of energy is at the Fermi energy of the metallic sample holder.

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 $CuGaSe_2$ surface. With increasing coverage the $CuGaSe_2$ 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 $eV_{bb}=-200\,\mathrm{meV}$ to lower values with increasing film thickness. The Zn 3*d* 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 3*d* and the Zn 3*d* level is given by $\Delta E_{\mathrm{CL}}=9.55 \pm 0.05\,\mathrm{eV}$. The unusual direction of the binding-energy shift may be attributed to the formation of Cu_xSe_y-related defect states at the interface as also observed for $CdS/CuInSe_2$.[10] However, in the previously published results, Cu_xS_y 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.[11] 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 $CuGaSe_2$ surface is shown. The experimental data are fitted to a linear density of states (DOS) broadened by the experimental resolution (800 meV). $\mathrm{BE_{VBM}}(CuGaSe_2) =0.57\pm0.05\,\mathrm{eV}$ is found for the valence-band maximum of $CuGaSe_2$. With $\mathrm{BE_{Ga\,3\mathit{d}}}=19.91\pm0.03\,\mathrm{eV}$ (centroid position), this results in $\mathrm{BE^{VBM}_{Ga\,3\mathit{d}}}=19.34\pm0.05\,\mathrm{eV}$ in close agreement with the value published by Turowski *et al.*[12] Furthermore, values for $\mathrm{BE^{VBM}_{Ga\,3\mathit{d}}}$ of 19.37 eV, and 19.33 eV for different samples measured with $h\nu=80\,\mathrm{eV}$ synchrotron radiation have been determined. With lower excitation energies at the synchrotron ($h\nu=40\,\mathrm{eV}$) 200–300 meV smaller values are found, which, however, agree with determinations using He II radiation ($h\nu=40.86\,\mathrm{eV}$).[5,13] Since effects of band dispersion, which might account for the observed differences of $\mathrm{BE^{VBM}_{Ga\,3\mathit{d}}}$ 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 $\mathrm{BE^{VBM}_{Ga\,3\mathit{d}}}=19.35 \pm0.05\,\mathrm{eV}$ for the determination of the band discontinuities.

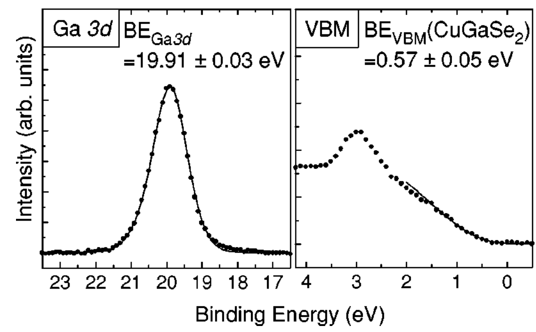

FIG. 2. Ga 3*d* core level and valence-band maximum region of a $CuGaSe_2(001)$ surface measured with Mg $K\alpha$ radiation. Core-level fitting is done using a Gauss–Lorentzian function. The energetic position of the valence-band maximum is determined from fitting an experimentally broadened linear DOS. The results of the fits are shown as solid lines.

A value of $\mathrm{BE^{VBM}_{Zn\,3\mathit{d}}}=9.20\pm0.05\,\mathrm{eV}$ 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 3*d* level has been used. The value is in good agreement with published data.[14,15]

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

$$\Delta E_V=19.35\,\mathrm{eV}-9.20\,\mathrm{eV}-9.55\,\mathrm{eV}=0.6\pm0.1\,\mathrm{eV}. \quad (2)$$

Together with the band gaps of $CuGaSe_2$ and ZnSe, the calculated conduction-band offset is

$$\Delta E_C=2.7\,\mathrm{eV}-1.7\,\mathrm{eV}-0.6\,\mathrm{eV}\cong0.4\,\mathrm{eV}. \quad (3)$$

Both the valence-band maximum and the conduction-band minimum are on the $CuGaSe_2$ 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.[10,14,16]

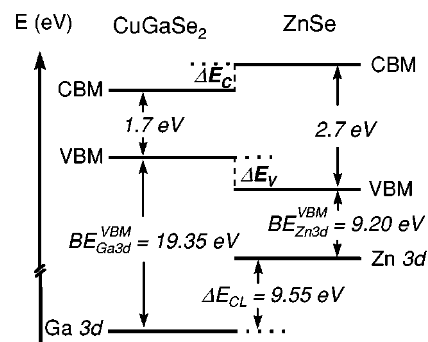

FIG. 3. Schematic energy-level diagram of the $ZnSe/CuGaSe_2$ heterojunction. The experimentally determined core-level energies with respect to valence-band maxima ($\mathrm{BE^{VBM}_{CL}}$) as well as the difference between core-level binding energies (ΔE_{CL}) are given. The resulting valence-band offset amounts to $\Delta E_V=0.6\pm0.1$ eV. Using the band-gap energies of $CuGaSe_2$ and ZnSe, a conduction-band offset of $\Delta E_C=0.4\pm0.1$ eV is deduced.

The valence-band offset for $ZnSe/CuGaSe_2$ [Eq. (2)] is approximately 100 meV smaller than that observed for the $ZnSe/CuInSe_2$ interface.[14] 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,[17] 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[9] 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.[17] 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.*[5] However, as discussed above, a different value for $BE^{VBM}_{Ga\,3d}$ 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 $CdS/CuInS_2$.[16]

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.[17] 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 $CdS/CuGaSe_2$.[4] 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.

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[1] J. R. Tuttle, J. S. Ward, A. Duda, T. A. Berens, M. A. Contreras, K. R. Ramanathan, A. L. Tennant, J. Keane, K. Emery, and R. Noufi, Mater. Res. Soc. Symp. Proc. **426**, 143 (1996).
[2] V. Nadenau, D. Braunger, D. Hariskos, M. Kaiser, Ch. Köble, A. Oberacker, M. Ruckh, U. Rühle, R. Schäffler, D. Schmid, T. Walter, S. Zweigart, and H. W. Schock, Prog. Photovoltaics **3**, 363 (1995).
[3] V. Nadenau, D. Hariskos, and H. W. Schock, *Proceedings of the 14th European Photovoltaic Solar Energy Conference*, Barcelona (H. S. Stephens and Associates, Felmersham, Bedford, U.K., 1997), p. 1250.
[4] R. Herberholz, V. Nadenau, U. Rühle, Ch. Köble, H. W. Schock, and B. Dimmler, Sol. Energy Mater. **49**, 227 (1997).
[5] V. Nadenau, D. Braunger, D. Hariskos, and H. W. Schock, Inst. Phys. Conf. Ser. **152**, 955 (1997).
[6] G. B. Turner, R. J. Schwartz, and J. L. Gray, *Proceedings of the 20th IEEE Photovoltaic Specialists Conference*, Las Vegas (IEEE, New York, 1988), p. 1457.
[7] Cyclopentadienyl–copper–triethylphosphine, triethylgallium, ditertiary-buthylselenide.
[8] See, e.g., S. Hüfner, *Photoelectron Spectroscopy* (Springer, Berlin, 1995).
[9] *Heterojunction Band Discontinuities*, edited by F. Capasso and G. Margaritondo (North-Holland, Amsterdam, 1987).
[10] T. Löher, W. Jaegermann, and C. Pettenkofer, J. Appl. Phys. **77**, 731 (1995).
[11] A. Klein, W. Jaegermann, R. Rudolph, E. Schaar-Gabriel, and C. Pettenkofer (unpublished).
[12] M. Turowski, G. Margaritondo, M. K. Kelly, and R. D. Tomlinson, Phys. Rev. B **31**, 1022 (1985).
[13] D. Schmid, M. Ruckh, and H. W. Schock, Appl. Surf. Sci. **103**, 409 (1996).
[14] A. J. Nelson, C. R. Schwerdtfeger, S.-H. Wei, A. Zunger, D. Rioux, R. Patel, and H. Höchst, Appl. Phys. Lett. **62**, 2557 (1993).
[15] G. Bratina T. Ozello, and A. Franciosi, J. Vac. Sci. Technol. B **14**, 2967 (1996).
[16] A. Klein, T. Löher, C. Pettenkofer, and W. Jaegermann, Appl. Phys. Lett. **70**, 1299 (1997).
[17] S.-H. Wei and A. Zunger, J. Appl. Phys. **78**, 3846 (1995).

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