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Band offset at the $CuGaSe_2/In_2S_3$ heterointerface

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We have investigated the electronic properties of the $CuGaSe_2/In_2S_3$ heterointerface by photoelectron spectroscopy. In_2S_3 was evaporated by physical vapor deposition onto contamination free polycrystalline $CuGaSe_2$ surface prepared by the selenium decapping process. A valence band offset $\Delta E_{VB}=0.78\pm0.1$ has been determined. © *2004 American Institute of Physics*.
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Thin-film solar cells using polycrystalline Cu(In,Ga)Se_2 chalcopyrite semiconductors have reached conversion efficiencies of about 19%.[1,2] High conversion efficiency solar cells are prepared on soda lime glass substrates using a film sequence Mo (backcontact), Cu(In,Ga)$(S,Se)_2$ (absorber), CdS (buffer layer), ZnO (window). The *p*-Cu(In,Ga)$(S,Se)_2$/*n*-CdS heterointerface is thereby of crucial importance for obtaining best conversion efficiencies. These are achieved by depositing a CdS buffer layer in a wet chemical process. For environmental reasons it is suggested to eliminate or replace the CdS buffer layer. In addition, a buffer-free cell structure, or alternative dry buffer deposition techniques, promise reduced production costs. In this respect In_2S_3 is a promising candidate for Cd-free Cu(In,Ga)Se_2 thin-film solar cells. With this buffer layer material energy conversion efficiencies up to 16.4% on small area[3] and up to 12.9% on large area devices (30×30 cm^2)[4–6] have been reached by using an atomic layer chemical vapor deposition technique. Very recently also high energy conversion efficiencies of 15% have been obtained by physical vapor deposited In_2S_3 layers.[7]

Solar cells prepared with In_2S_3 buffer layers also exhibit good long-term stability, which is crucial for commercial application.[5] Alternative deposition methods of In_2S_3 films like chemical bath deposition or physical vapor deposition (PVD) are compared by Barreau *et al.*[8] These PVD layers were deposits of the constituents indium and sulfur onto a substrate followed by a postdeposition annealing step in flowing argon. The properties of both films can be adjusted similary, by using certain annealing conditions after the PVD deposition. This offers a new possibility to exchange the chemical bath deposition.

Polycrystalline $CuGaSe_2$, evaporated on molybdenum coated glass, has been used as substrate material. To protect the surface during storage at air, the surface was covered by a 1-μm thick selenium layer. This selenium layer was heated off in an ultrahigh-vacuum chamber and a clean $CuGaSe_2$ surface was restored. The de-capping procedure has been described in more detail elsewhere.[9] In_2S_3 with 99.999% purity was thermally evaporated out of a heated Al_2O_3 crucible and deposited onto the oxide free $CuGaSe_2$ surface for interface analysis and on SnO_2 coated glass substrates for bulk thin film analysis. Interface analysis was performed using the DAISY-MAT system (DArmstadt Integrated System for Materials Research) equipped with a Physical Electronics PHI 5700 photoelectron spectrometer with a monochromated AlKα x-ray source and a He discharge lamp and a directly connected preparation chamber. Chemical, electronic, and optical properties of the deposited layers were characterized by ultraviolet photoelectron spectroscopy (UPS), x-ray photoelectron spectroscopy (XPS), grazing incidence x-ray diffraction, and optical absorption.

X-ray diffraction at grazing incidence of films deposited at room temperature shows an increased background intensity at diffraction angles around 27° and 48° beneath the SnO_2 diffraction lines. This indicates growth of amorphous or very small grain material. The observed increase of the background fits to the two dominant characteristic diffraction lines of In_2S_3. The evaluation of the XPS core level intensities results in a sulfur excess of 20% with respect to the indium content, which we consider as being in good agreement with the stoichiometry of the In_2S_3 powder used as source material for evaporation.

By optical transmission we determine a band gap energy of 1.9 ± 0.1 eV. This value is in good agreement with Nomura *et al.*, who reported a value of 2.0 eV for the energy gap of β-In_2S_3 layers (deposited by single-source organometallic chemical vapor deposition at 300–400 °C substrate temperature).[10] In contrast, Spiering *et al.* assigned a bulk energy gap of 2.7–2.75 eV for In_2S_3 layers prepared by atomic layer chemical vapor deposition at substrate temperatures of 160 °C.[5]

Both values would concur with our UPS measurements of room temperature deposited films, which are shown in Fig. 1. By linear extrapolation of the onset of the photoemission at the valence band maximum and the secondary electron cut off, a work function of 5.3 eV and an ionization potential of 7.1 eV is determined. The distance between the Fermi level and the valence band maximum has been extracted to 1.8 eV, indicating *n*-type doping.

For the determination of the band alignment, it is necessary to characterize the core level lines of the substrate and the top layer during the interface formation. Because of the overlap between all important sulfur emission lines with the selenium emission lines, only the indium core level line can be used for this investigation. Although In containing Cu(In,Ga)Se_2 is technologically more important, we there-

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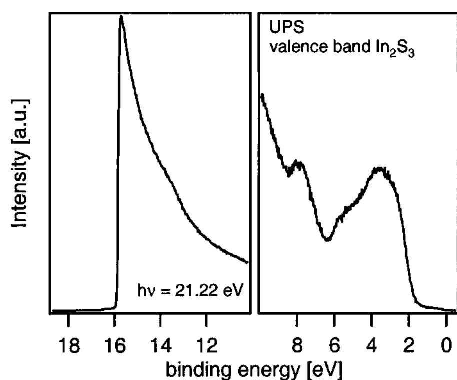

FIG. 1. Ultraviolet photoelectron spectra of an In_2S_3 layer with a work function of 5.3 eV and an ionization potential of 7.1 eV.

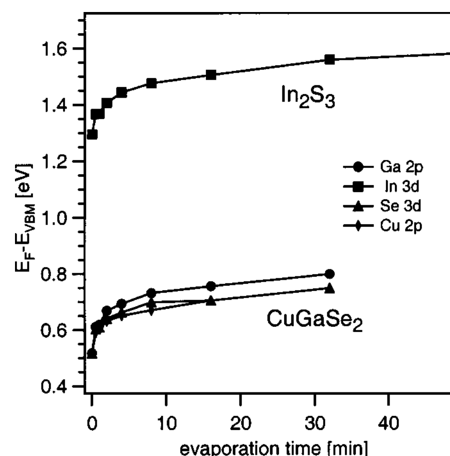

FIG. 3. Evolution of the valence band maximum of the $CuGaSe_2$ substrate and the In_2S_3 layer as a function of In_2S_3 film thickness. The energy difference between both valence band maxima indicates a valence band offset of $\Delta E_{VB}=0.78\pm0.1$ eV.

fore used In free $CuGaSe_2$ absorber layers. To investigate the band alignment at the $CuGaSe_2/In_2S_3$ interface, In_2S_3 was stepwise deposited onto the $CuGaSe_2$ surface. In Fig. 2 the core level emissions of Ga $2p_{3/2}$, Cu $2p_{3/2}$, In $3d_{5/2}$, Se $3d$ and the valence band are displayed. The first spectra series belongs to the clean $CuGaSe_2$ surface, which exhibits the characteristic Cu-poor $CuGa_3Se_5$ composition.[9,11] The following spectra show decreasing Cu, Ga, and Se signals of the substrate emission lines and the increasing In signal of the growing layer. After an In_2S_3 deposition time of 128 min, no emission of the substrate was detectable.

The core level lines do not change their shapes or widths during deposition, indicating a chemically nonreactive and abrupt interface between In_2S_3 and $CuGaSe_2$. To investigate the electronic properties of this interface, all core level lines have been fitted by using Voigt profiles. The XPS valence band maxima of clean $CuGaSe_2$ and the In_2S_3 film after 128 min deposition time were determined by fitting a straight line with a Gaussian broadening corresponding to the resolution of the spectrometer to the onset of the photoelectron emission. The binding energies with respect to the valence band maxima are determined as 1117.15 ± 0.05 eV (Ga $2p_{3/2}$), 931.59 ± 0.05 eV (Cu $2p_{3/2}$), and 53.65 ± 0.05 eV (Se $3d$)for $CuGaSe_2$ and as 443.64 ± 0.05 eV (In $3d_{5/2}$) for In_2S_3, respectively. By subtracting these energies from the corresponding core level binding energies at every deposition step, the evolution of the valence band maximum of the $CuGaSe_2$ substrate and of the In_2S_3 layer is followed during interface formation in dependence of film thickness. The result of this procedure is displayed in Fig. 3. Substrate and overlayer valence band maxima show a parallel shift, which indicates a bend bending in the $CuGaSe_2$ substrate induced by the In_2S_3 layer. The valence band offset corresponds to the difference between both valence band maxima, which is almost independent of film thickness and given as $\Delta E_{VB}=0.78\pm0.1$ eV.

Photoemission shows a direct way to determine the valence band alignment at a hetero-junction. For the absorber/buffer interface of thin film chalcopyrite solar cells, the conduction band offset is, however, of greater importance since electrons need to be transported across this interface. The conduction band offset cannot be directly determined using photoelectron spectroscopy. To draw the energy band diagram (see Fig. 4), the bulk band gap of $CuGaSe_2$ of 1.68 eV[12] and the optically measured band gap of 1.9 eV for In_2S_3 have been used. With these values a conduction band offset of $\Delta E_{CB}=-0.56$ eV (cliff) is calculated. A very small dipole potential of 0.09 ± 0.1 eV in the vacuum level is determined from the work function measurements using UPS.

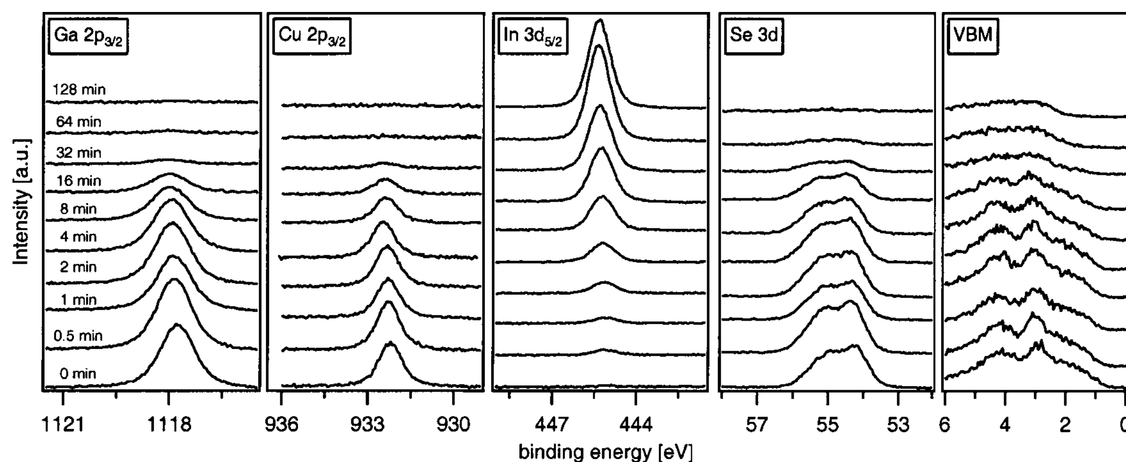

FIG. 2. Ga $2p_{3/2}$, Cu $2p_{3/2}$, In $3d_{5/2}$, and Se $3d$ core level lines of the $CuGaSe_2$ substrate and the In_2S_3 top layer. The clear line-shapes of all core level lines during In_2S_3 deposition indicate no hints of chemical interactions during interface formation. Additionally the change of the valence band shape can be followed.

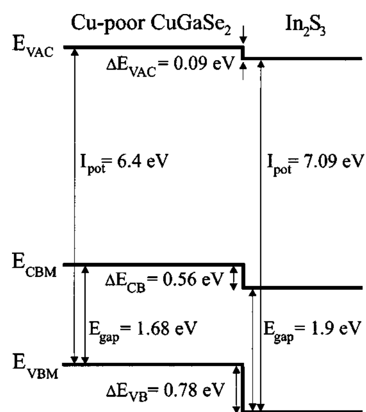

FIG. 4. Band alignment between PVD prepared In_2S_3 and the Cu-poor $CuGaSe_2$ surface.

There remains considerable uncertainty about the conduction band offset as the surface of $CuGaSe_2$ has a Cu poor surface composition. It has to be expected that the Cu-poor $CuGaSe_2$ surface exhibits a larger band gap than the stoichiometric bulk, as it does for $Cu(In,Ga)Se_2$.[13,14] Indeed surface band gaps of 2.0–2.2 eV have been reported.[15]

It is expected that the valence band offsets of a given material with $Cu(In,Ga)Se_2$ should be almost independent of the Ga content of the chalcopyrite material.[16,17] This has explicitly been tested for the $Cu(In,Ga)Se_2/CdS$ heterointerface for de-capped thin film chalcopyrite material with Cu-poor surface composition.[11] In good agreement with the expectation, the valence band offset only slightly increases by ~0.15 eV from $CuInSe_2/CdS$ to $CuGaSe_2/CdS$. It seems therefore reasonable to assume that the valence band offset at the $In_2S_3/Cu(In,Ga)Se_2$ interfaces are also very similar. Transferring the trend from the $Cu(In,Ga)Se_2/CdS$ interfaces, a valence band offset of $\Delta E_{VB}=0.68\pm0.1$ eV has to be expected for the technologically important $CuIn_{0.7}Ga_{0.3}Se_2/In_2S_3$ interface. With the smaller band gap of the low Ga content chalcopyrite a small conduction band offset would result for this interface.

In summary we have investigated the interface formation of the $CuGaSe_2/In_2S_3$ hetero-junction using photoelectron spectroscopy. Most important, a valence band offset of $\Delta E_{VB}=0.78\pm0.1$ eV was determined.

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