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Band alignment at the BaCuSeF/ZnTe interface

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In situ photoemission spectroscopy experiments are used to characterize the interface between ZnTe and the wide band gap *p*-type semiconductor BaCuSeF. The contact is characterized by a null valence-band offset, a large conduction-band offset, and a chemically graded interface. By applying the transitivity rule for band offset and on the basis of similarities in chemical composition, BaCuSeF contact to chalcogenide photovoltaic absorber materials would be expected to have similar properties. By extension, BaCuChF (Ch=S, Se, Te) materials are suitable as *p*-layers in *p-i-n* double-heterojunction solar cells fabricated with CdTe, Cu(InGa)Se₂, and Cu₂ZnSnS₄ absorbers. © 2010 American Institute of Physics. [doi:10.1063/1.3405757]

One of the contemporary challenges of applied physics is the advancement of photovoltaic (PV) technologies. For example, development of *p*-type windows for *p-i-n* chalcogenide solar cells is currently needed to improve efficiencies. An ideal *p*-window layer would have (i) a high concentration of free holes for higher conductivity, (ii) a band gap wider than the absorber, *i*-layer, (iii) a small valence-band (VB) offset relative to the absorber for facile hole extraction, (iv) a large conduction band (CB) offset relative to the absorber to reflect electrons, and (v) a chemically graded interface to limit the formation of interfacial states.¹ ZnTe is one studied *p*-window material in CdTe solar cells.^{2,3} Cu and Cu_xTe_y also form Ohmic contacts to CdTe but their band alignments are not ideal.^{4,5}

Here we propose using chalcogen-based transparent conductors,⁶ such as BaCuChF (Ch=S, Se, Te) (Refs. 7 and 8) for anode applications in chalcogenide *p-i-n* PV devices. These materials have high concentrations of free holes (10¹⁸–10²⁰ cm⁻³) (Refs. 9 and 10) and tunable^{10,11} wide¹² optical band gaps (2.9–3.5 eV). BaCuChF are likely to form graded interfaces with the chalcogenide absorbers since these materials contain chalcogen atoms. However, to date, the band alignment of BaCuChF with inorganic compounds has not been studied. In this paper, we report x-ray- and ultraviolet-photoemission spectroscopy results (XPS/UPS) for BaCuSeF/ZnTe interfaces, and discuss possible applications of BaCuChF in chalcogenide solar cells based on CdTe, Cu(InGa)Se₂ (CIGS), and Cu₂ZnSnS₄ (CZTS) absorbers.

BaCuSeF thin films (200 nm) were prepared by pulsed laser deposition from stoichiometric BaCuSeF targets on Si (001) and amorphous SiO₂ substrates. BaCuSeF films were polycrystalline, single phase, *p*-type, and on average 75% transparent over the wavelength range 400–2500 nm. The transparency is partly limited by the reflective losses (~15%) at the front surface. Bulk and surface compositions of the thin films were determined by electron probe microanalysis and XPS, respectively. BaCuSeF thin films were capped with 1000 nm of amorphous Se for protection¹³

during transportation from Corvallis, OR to Darmstadt, Germany. This protection was necessary, since uncapped BaCuChF surfaces were oxidized and contaminated,¹⁴ which could have been a contributing reason for the poor performance of BaCuTeF in PV devices reported before.¹⁵ For the *in situ* interfacing experiments, 280 nm thick ZnTe layers were sequentially deposited on the BaCuSeF film at room temperature in a stepwise manner, and XPS/UPS were recorded after each step using the DAISY-SOL.¹⁶ Details of these and similar experiments appear elsewhere.¹⁴

The XPS and UPS spectra of the BaCuSeF/ZnTe interface are shown in Fig. 1. For a thick ZnTe layer (>25 Å), BaCuSeF and ZnTe XPS peaks shift to higher binding energies (BE) with increasing ZnTe thickness, indicating downward VB bending of BaCuSeF caused by electron transfer to this material. The BE of the secondary electron edge changes for low ZnTe thickness (<25 Å), indicating the change of

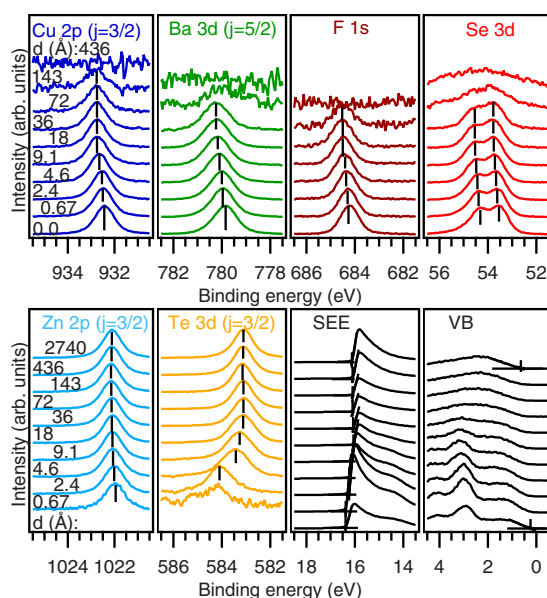


FIG. 1. (Color online) Normalized photoemission spectra of the BaCuSeF/ZnTe interface. ZnTe thicknesses d are the same for all panels in a row. The vertical lines indicate binding energies used to plot Fig. 2.

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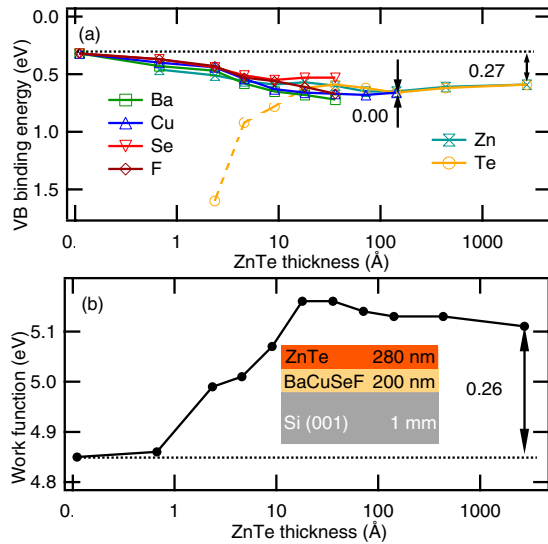


FIG. 2. (Color online) (a) Binding energy of the BaCuSeF and ZnTe valence bands calculated from XPS core-level spectra. The dashed line represents the shift in Te $3d_{3/2}$ states due to charge transfer from Te atoms. (b) Work function of the BaCuSeF/ZnTe interface. The final configuration of the sample is schematically depicted in the inset.

the work function (WF) due to change in an interface dipole. In this thickness range, the Te $3d_{3/2}$ and the Zn $2p_{3/2}$ XPS peaks do not shift in parallel. We attribute a strong shift in the Te $3d_{3/2}$ line at low coverage to the transfer of electrons from Te atoms. The Zn $2p_{3/2}$ peak does not show this charge-transfer shift, because Zn atoms do not contribute to the VB of ZnTe. Similar effect has been observed at the BaCuSeF/ZnTe interface.¹⁴

There is interdiffusion at the BaCuSeF/ZnTe interface. In Fig. 1, the Cu $2p_{3/2}$ XPS peak is present at 143 Å ZnTe coverage, whereas the Ba $3d_{5/2}$ and F $1s$ peaks that have lower BE are absent. The bulk of ZnTe films is Te-poor by 4 at. % but the surfaces are Te-rich by 20 at. %, so it is likely that Cu atoms diffuse into ZnTe and form Cu–Zn–Te or Cu–Te phases. The interdiffusion layer has been confirmed using high-resolution STEM/EDX measurements that will be published elsewhere. Similar effect was also observed at the CdTe interfaces with other Cu-containing back contacts.^{4,5}

BaCuSeF and ZnTe VB BE and the WF as a function of ZnTe thickness are shown in Fig. 2. Decapped BaCuSeF surface has a VB BE of 0.32 ± 0.10 eV, larger than for the thin film bulk deduced from measured carrier concentration and calculated density of states (-0.04 eV). The WF is 4.85 ± 0.05 eV, larger than for the pressed pellets measured by UPS (3.6 eV).¹⁷ A thick ZnTe layer (280 nm) has a VB BE of 0.59 ± 0.10 eV and a WF of 5.11 ± 0.05 eV.

Measured VB BEs and the WFs (Fig. 2) were used to establish band alignment of BaCuSeF and ZnTe before contact [Fig. 3(a)]. After contact, BaCuSeF and ZnTe have the same VB BE [Fig. 2(a)], so the VB offset is 0.00 ± 0.10 eV [Fig. 3(b)]. The CB offset is 0.94 ± 0.10 eV, as calculated from the BaCuSeF (Ref. 12) and ZnTe (Ref. 18) band gaps [Fig. 3(c)]. The band bending of 0.27 eV [Fig. 2(a)] and the change of the WF of 0.26 eV [Fig. 2(b)] sum to a vacuum level shift in 0.53 ± 0.10 eV [Fig. 3(b)]. The higher vacuum level in ZnTe would correspond to an interface dipole with the negative end toward ZnTe. This direction is contraindicated by the direction of the BaCuSeF band bending and by the high binding energy of the Te $3d_{3/2}$ line at low coverage

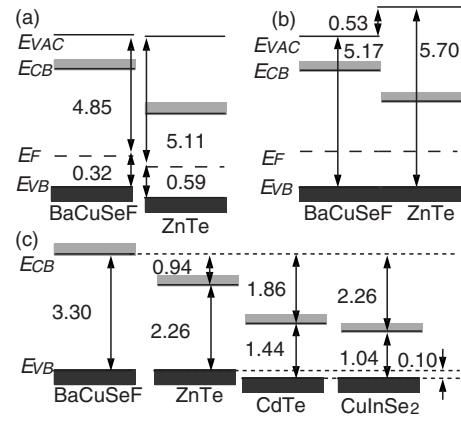


FIG. 3. Alignment of the energy levels of BaCuSeF and ZnTe (a) before and (b) after contact as measured by PES. (c) Band offsets of BaCuSeF with CdTe and CuInSe₂ calculated from the literature values of the band offsets of these materials with ZnTe. All energies are in electron volt.

[Fig. 2(a)], which both point to an opposite direction of the charge transfer. Possible reasons for the opposite direction of the charge transfer are the graded character of the interface or a large surface dipole contribution to the work function of decapped BaCuSeF, which is modified during interface formation. The latter is likely, as the measured ionization potential ($E_{VAC} - E_{VB}$) of BaCuSeF (5.17 ± 0.15 eV) is much smaller, e.g., than that of CuInSe₂ (6.1 eV),¹⁹ which has a similar VB structure.

The band alignment of BaCuSeF with the chalcogenide PV materials is shown in Fig. 3(c). It was calculated from the ZnTe/CdTe and CdTe/CuInSe₂ band offsets using the transitivity rule.^{20,21} BaCuSeF/CdTe and BaCuSeF/CuInSe₂ interfaces have VB offsets of 0.10 ± 0.10 eV, and CB offsets of 1.86 ± 0.10 eV and 2.26 ± 0.10 eV, respectively. The small VB offsets are expected, because the Se $4p$ -Cu $3d$ repulsion in BaCuSeF is stronger than the Te $5p$ -Cd $4d$ repulsion in CdTe, and the VB character of BaCuSeF is similar to that of CuInSe₂.¹⁷ The VB character of Cu₂ZnSnS₄ is more similar to BaCuSeF than BaCuSeF, so the two sulfides constitute a good match for CZTS solar cells.²² BaCuChF interfaces with ZnTe, CdTe, CuInSe₂, and Cu₂ZnSnS₄ are likely to have similar interdiffusion because of the similar chemical compositions of II-VI, (I-III)-VI₂, and (I₂-[II-IV])-VI₄ semiconductors.

Overall, BaCuChF materials with appropriate surface protection or fully *in situ* processing should make good *p*-type contacts in chalcogenide *p-i-n* solar cells. In addition, BaCuSeF has the potential to replace the Cu or Cu_{2-x}Te back contact in CdTe PV devices, due to its better band alignment with CdTe. Finally, BaCuChF are transparent enough to be used in tandem chalcogenide solar cells. Related LaCuOCh materials^{23,24} are also promising for these applications, since the VB characters of BaCuChF and LaCuOCh are similar.¹⁷

In summary, we have measured the VB offset between BaCuSeF and ZnTe by XPS/UPS. There is no measurable VB discontinuity and the interface is graded, which makes BaCuSeF an ideal *p*-type contact to ZnTe. A small VB offset and a similar chemistry of ZnTe, CdTe, and CuInSe₂ suggest that BaCuSeF is likely to make a good *p*-layer for the chalcogenide *p-i-n* solar cells.

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