

Solar cell device architectures for candidate photoferroic absorbers enargite and bournonite from band offsets and lattice matching

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Received Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

First published on the web Xth XXXXXXXXXX 200X

DOI: 10.1039/b000000x

A vital part of the development of efficient solar cell devices to take candidate photovoltaic (PV) absorber materials from the lab benchtop through to commercial solar cell devices is the optimisation of the full device architecture, layer-by-layer. We recently proposed the naturally occurring minerals enargite (Cu_3AsS_4) and bournonite (CuPbSbS_3) as materials that are likely to be stable and with many desirable optoelectronic properties for use as the absorber layer in a thin-film PV device. Additionally, the internal electric fields and possible ferroelectricity of these materials may allow for enhanced carrier separation and novel PV effects. In this work, we aim to accelerate the optimisation of solar cell devices made from these materials to aid in experimental investigations of photoferroic solar cells. We calculate the band alignment of the materials and propose suitable contact materials for the back contacts and for forming p-n heterojunctions by matching the electronic band edges to a set of candidate contact materials. We then screen these candidates further by matching the lattices of the two materials to limit ourselves to only those that are likely to minimise strain and achieve good epitaxy.

Note:

- Enargite as non-optimal CIGS architecture to explain low Voc of SCs made so far¹
- Bournonite candidate contacts for a spike for n- or p-type absorber? (c.f. Elisabetta's work on ZnSnN_2)
- Consider just doing for p-n junctions??

Add to SI:

- Convergence data: for unit cell relaxations fro slabs?
- Extra slab potential plots from MacroDensity
- Visuals of slab structures?

1 Introduction

Solar power is a very attractive contender as a source of sustainable electrical power. Technological breakthroughs to enable high-efficiency photovoltaic (PV) devices without the need to use scarce material components and with lower manufacturing costs would secure solar power as a viable future power source. Exploiting ferroelectricity in photoactive materials to allow for novel PV phenomena, such as the

anomalous² and bulk³ PV effects, could provide new pathways to high-efficiency PV devices. Photoactive ferroelectric or 'photoferroic' materials could allow for solar cell devices with larger photovoltages and the internal electric fields in polar crystals could enhance carrier separation and suppress electron-hole recombination^{4,5}. On-going research efforts are exploring the theory behind the observed phenomena in photoferroic materials^{6–8}.

We recently identified three naturally-occurring minerals as candidate photoferroic materials, with many desirable optoelectronic properties for an absorber layer in a PV device⁹, including enargite (Cu_3AsS_4) and bournonite (CuPbSbS_3). To our knowledge, to date only one study has fabricated solar cells out of any of these materials. In Ref. 1 solar cells were fabricated from solution processed enargite using a device architecture developed for $\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGS) solar cell technology. In this study the authors list non-optimal band alignment of the absorber layer with the device architecture as a likely limitation of the current solar cell performance. This has been shown to be the case for CuSbS_2 solar cells also using device architecture optimised for CIGS absorber layers¹⁰. More mature technologies, such as CIGS-based devices, are still being continually optimised through improved band alignment with the n-type buffer layer. A recent study set a record open circuit voltage for a wide gap chalcopyrite solar cell through further optimisation of the buffer layer¹¹. Non-optimal band alignments are also being considered as a possible limiting factor on the performance of $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ -based solar cells¹².

For many of the materials being studied for use as absorber layers in thin-film solar cells, such as chalcogenide-based materials, it is not possible, or is very difficult, to achieve ambipolar doping. Therefore to achieve a p-n junction for many thin-film PV devices it is necessary to form an interface between two different materials with different energy gaps, lattice constants and even slightly different crystal structures¹³. Differences in lattice constant and crystal structure at a heterojunction interface can introduce strain, resulting in poor epitaxy at the interface if the two materials are poorly matched¹⁴. Furthermore, differences between the crystal structure or lattice constants at the interface generally introduce intra band gap defect states, which enhance Shockley-Read-Hall recombination, increasing dark currents and reducing the open circuit voltage of the device¹⁵.

In this work, we aim to accelerate the optimisation of solar cell device architectures for enargite (Cu_3AsS_4) and bournonite (CuPbSbS_3) by screening for candidate contact layers that could have optimal electronic band offsets and crystal lattices well-matched to minimise strain at the interfaces. We screen for candidate contact layers to form a p-n junction and a back contact with each absorber layer using the principles for optimal band offsets outlined in the next section.

1.1 Band offsets for p-n junctions

****Emphasise in discussion:** If minority carriers have heavy calculated m^* - must look for a small cliff offset. If minority carrier have light m^* , necessary but not sufficient condition

for high carrier mobility - look for both small cliff and spike offsets.

The band alignment when forming a p-n junction is crucial to facilitate the separation of photo-excited electrons and holes to allow for extraction of the charge carriers before recombination can occur¹⁸. Although the internal electric fields in the materials in this study may allow for the bulk photovoltaic effect (where a p-n junction is not required for a photocurrent to be generated), a p-n junction would provide a global driving force for carrier separation towards collection electrodes, while internal electric fields from the polar crystal structure could enhance carrier separation locally.

Heterojunctions are classified as type I, II or III based on their band alignments, however only type I and type II are of interest for PV applications. A type II heterojunction can also be referred to as a 'cliff-like' offset and a type I can also be referred to as a 'spike-like' offset, as illustrated schematically in Fig 1. For a p-type absorber layer, the minority carriers are electrons promoted into the conduction band (CB) of the absorber, therefore it is transport of electrons from the CB of the p-type absorber to the n-type contact layer that is important for determining device performance. The parameter of interest here is therefore the conduction band offset (CBO) between the p-type and n-type layers. However, for n-type absorbers it is holes that are the minority carriers and so it is the magnitude of the valance band offset (VBO) between the n-type absorber and p-type contact material that is important for charge extraction.

It has been observed that for the p-type absorbers CIGS and CdTe, solar cell p-n junctions with a type I 'spike' offset (with a CBO producing a small barrier within the range of 0.1 and 0.3 eV), as shown in Fig. 1a, is a more defect-tolerant interface and gives better device performance^{16,19}. The central idea to this 'defect-tolerant interface' is that a small positive spike CBO creates an absorber inversion, resulting in a large hole barrier at the interface¹⁶, whilst only creating a modest barrier to electron transport across the interface so that electrons may still tunnel across the interface¹⁵. Electron-hole recombination at an interface with high defect densities will then be suppressed due to an insufficient hole supply at the interface. In contrast, for a type II or 'cliff' offset where the CBO is negative, as shown in Fig 1b, there may be high concentrations of holes in the vicinity of the interface to assist interface recombination, thereby reducing the open circuit voltage¹⁶.

For the n-type absorber ZnSnN_2 the opposite trend has been observed, where a spike VBO is expected to give a poorer performance¹⁷. In the case of ZnSnN_2 , it is believed that a

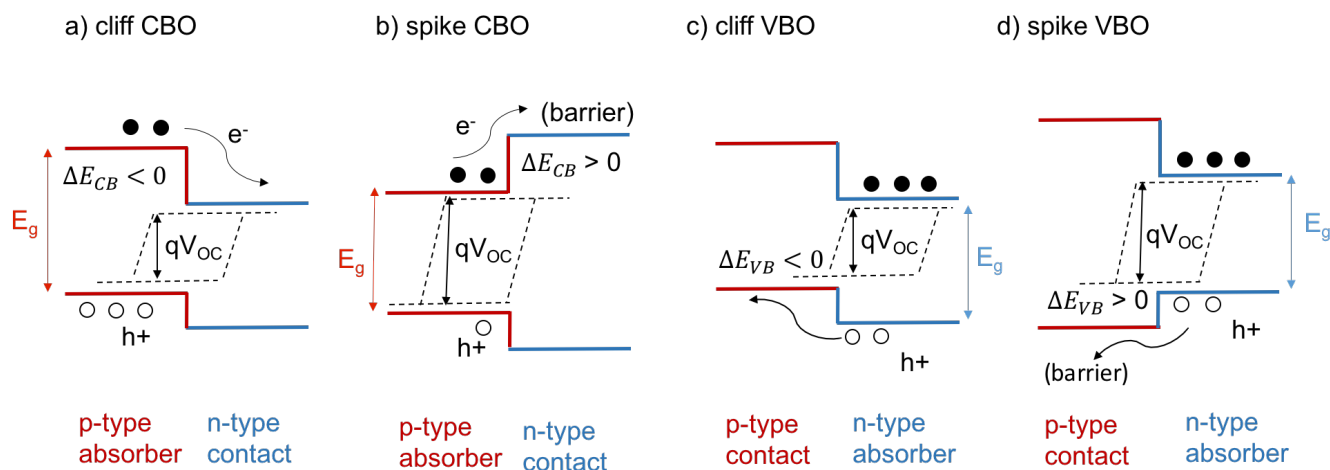


Fig. 1 a) A type II heterojunction between a p-type absorber and an n-type contact material where photoelectrons flow across the interface with no barrier at the negative ‘cliff’ conduction band offset (CBO), but the open circuit voltage is reduced relative to the absorber band gap if the cliff is large. b) A type I heterojunction between a p-type absorber layer and an n-type contact material with a small positive (‘spike’) CBO. If the spike is small enough electrons can tunnel through the barrier and across the interface. Holes are repelled from the interface region. c) A type II heterojunction between an n-type absorber and a p-type contact material where photoelectrons flow across the interface with no barrier at the negative ‘cliff’ valence band offset (VBO), but the open circuit voltage is reduced relative to the absorber band gap if the cliff is large. d) A type I heterojunction between an n-type absorber layer and a p-type contact material with a small positive (‘spike’) VBO. If the spike is too large this barrier is thought to impede transport across the interface if hole mobility is low. Figures adapted from Ref. 16 and 17.

spike offset may provide too large of a barrier to charge transport across the interface due to the larger effective mass of holes (compared to typical effective masses for minority carrier electrons in CIGS and CdTe²⁰) and associated lower hole mobility¹⁷. For ZnSnN₂, a ‘small cliff’ is thought to be the optimal band alignment to avoid the barrier to charge transport from a spike offset but without the open circuit voltage (V_{OC}) being limited too greatly as would be the case for a ‘large cliff’. This can be seen from the decrease in qV_{OC} relative to the absorber band gap (E_g) in the cliff offsets in Fig. 1. Therefore in this study, we use calculated effective masses to inform our choice of optimal band offsets for forming p-n heterojunctions.

1.2 Band offsets for back contacts

****Double check screening criteria for this section****

Basically want to form an Ohmic contact/ low energy barrier at the back contact to extract photoexcited majority carriers? So low barrier at VBO for p-type absorbers and low barrier for CBO for n-type absorbers?

At the back contact of our absorber layer, we want to extract the majority carriers from the absorber layer. It is therefore alignment of the contact material to the VBM of a p-type absorber (and extraction of holes from the absorber

layer) and alignment of the contact material to the CBM of an n-type absorber (and extraction of electrons from the absorber layer) that is important for devices with a p-type and n-type absorber layer respectively. For an effective back contact, the Fermi level of the contact metal should be slightly lower in magnitude than the valence band maximum (VBM) of a p-type layer and the ****check****(CBM of an n-type absorber layer). This slight off-set provides the localised field effect that is the driving force for the migration of photoexcited majority carriers towards the interface for extraction²¹.

Notes from discussion with Lee: back contact for p-type absorber - Fermi level of metal slightly above absorber VBM for small driving force for hole (without sacrificing Voc). back contact for n-type absorber - Fermi level slightly of metal below absorber CBM (but... this may mean a reactive metal! high workfunction implies ‘unhappy electrons’)

2 Methodology

2.1 Band alignment

**** See end of comp methods section in Lee’s paper: ²¹**

The alignment of the VBM to the vacuum level, i.e. the ionisation potentials (IPs), are physically well-defined quantities. IPs can be measured using x-ray photoelectron spectroscopy

or Kelvin probe microscopy and can be computed using first-principles calculations of surface slab models²², as is done in this study. The electron affinity (EA) is defined as the CBM with respect to the vacuum level. This value can be obtained by adding the value of the electronic band gap onto the IP of the material. The difference between the IPs and EAs of two materials forming a heterojunction can be used to obtain the VBO and CBO of the two materials respectively.

Experimental results from two decades of photoelectron spectroscopy experiments on CdTe and CIGS thin-film solar cells have been compared to density functional theory (DFT) calculations¹³, where it was found that the energy band alignments for many interfaces were in good agreement. However, for cases where there was poor agreement and in particular where deviations in measured and calculated band alignments were sensitive to interface preparation methods, this is thought to be related to the presence of high defect-concentrations in the materials forming the contact. For this reason, theoretically predicted band alignments are usually considered as the ‘intrinsic’ or ‘natural’ alignment for a particular combination of materials forming an interface¹³, i.e. that which could be expected to form naturally for a perfect interface, in the absence of defects. A predicted ideal band alignment therefore is not guaranteed to be ideal in reality, but acts as a good starting point to limit the search space for combinations of materials that are more likely to have an ideal band alignment.

2.2 Computational details

IPs are dependent upon the surface orientations, therefore we construct slab models for all possible non-polar surface terminations of the materials. We consider only non-polar surface models as these are the most energetically likely to form.

Yoyo’s paper for methodology for cutting non-polar, symmetric slabs²³.

Paper for method of calculating IP from macroscopic average of potential²² + justification for not relaxing surfaces because difference in IP and EA between relaxed and unrelaxed surfaces shown to be very small in Fig. 7.

Overview of slab calculations: non-polar terminations, LOCPOT files from FHI-aims?, MacroDensity: Local potential w.r.t vacuum, using slabs with vacuum gap and bulk VBM eigenvalues.²²

Refer to MacroDensity repo?

Schematic showing IP and EA + state that we use the band gap calculated using HSE in⁹ to obtain the EA from the IP.

Show sample slabs and refer to rest in SI?

2.3 Electronic and lattice matching

Overview of ELS method + paper using Keith’s ELS setup¹⁴.

Modify ‘scan-for-spike’ edits made to ELS to allow to scan for CBO or VBO offsets (based on EA and IP respectively) to look for either small spike or small cliff, depending on effective mass. (since holes are heavier than electrons in sulfosalts, look for spike CBO for p-type and small cliff for n-type). May also be nice to have feature to check how good/bad particular contact material is with ELS and maybe even on-the-fly Walsh diagram? ** discuss with Keith **

Using ELS to scan for an ideal type II if heavy minority carrier: 0 to - 0.3 eV?? and a type I spike-like if light minority carrier: +0.1 to 0.4 eV?? (barrier of spike to minority carriers crossing junction is negligible, carriers can tunnel, if less than 0.4 eV, Nelson pg 244 (iii)¹⁵. But +0.2 eV optimal for CIGS?¹⁹

Outline how lattice matching to minimise strain is done in ELS and ref paper used by ELS

Refer to ELS repo?

What is and isn’t accounted for in our model c.f experimental measurements of band alignments, defects, etc.¹³ We consider no defect states at the interface and allow no intermixing at the interface, which is known to be present to a large extent at the CdTe:CdS interface²⁴. However, for final candidate contacts we speculate the likely extent of interface intermixing based on the chemical similarities of the components of the two materials forming the heterojunction. ** Also expect less intermixing if less electrostatic potential at interface (less driving force)?? ...something to tune with a FE material?... **

3 Results and discussion

- Separate section for each material, giving candidate contact materials for each non-polar termination - type II and type I n- or p-type candidates?
- Show samples of surface slabs? (or just give termination for non-polar and refer to visuals in SI)
- IPs and EAs and sample potential plots when extracting values? or in SI? Present numbers in a table?

- Band diagrams with candidate contacts: spike CBO for p-type, spike VBO for possible n-type?, also type II within reasonable offset range
- Known data on p- or n-type of candidate contact
- Speculate likely extent of interface intermixing based on chemical similarity?
- Check enargite:CdS alignment to see if this was the explanation for¹?
- Also think about possibility that solution processing could have given random orientation of polar domains in enargite example? CVD may be necessary for better performance? (c.f. discussion with Katie at NREL)
- Comment on termination dependence of sulfosalt IPs and also for candidate contact materials (expect cheaper, most robust synthesis if less dependent of surface termination!?)

3.1 Candidate p-n junction layers

If any sulfosalts are n-type, possible that devices (and transport across p-n junction) will be hindered due to typically heavier holes? (from paper1)

Limited experimental data available for enargite suggests that the materials will exhibit p-type intrinsic conductivity^{25,26}. For bournonite, there is contradiction in the literature between experimental measurements on natural samples measuring n-type conductivity²⁶ and theoretical prediction of the defect physics suggesting the material will be intrinsically p-type and difficult to dope n-type²⁷. We will therefore screen for optimal contact materials for whether the absorber materials exhibit either p- or n-type conductivity. We will decide if a spike or small cliff VBO or CBO will be the optimal offset in each case based on the calculated effective mass for the minority carriers. If the conductivity effective mass is less than $0.5m_0$ we will look for a small spike offset in addition to a small cliff offset. We will then further screen the candidate contact materials by looking for those which minimize strain at the interface.

** Add table show conductivity effective masses? Cite paper 1 but value are in table from EMRS talk **

3.1.1 Scanning for spikes Add Walsh diagram for each material (see tutorial on ELS or MacroDensity repo?)

3.1.2 Scanning for small cliffs Add Walsh diagram for each material (see tutorial on ELS or MacroDensity repo?)

3.2 Candidate back contacts

Add Walsh diagram for each material (see tutorial on ELS or MacroDensity repo?)

4 Conclusions

- Highlight key contact materials (do not know if currently n- or p-type, so suggest both electron and hole transport layers for each sulfosalt)
- Limitations of methodology: we consider all non-polar surfaces, but for our candidates we assume no defects at the interface and no interface mixing
- Possibly infer likely extent of interface mixing of candidates based on size and chemical similarity with sulfosalt layer?
- Further work: Notes from Jisangs group research day talk on a priori knowledge of interface intermixing (way of quantifying one limitation in ELS) + ideas for more thorough modelling of interfaces with contact candidates
- Possibly touch upon alignment of electric field of polar material with the contact material at the interfaces? Preferential growth to suppress intermixing etc.?
- Also think about possibility that solution processing could have given random orientation of polar domains in enargite example? CVD may be necessary for better performance? (c.f. discussion with Katie at NREL) - explain low Voc in enargite SC paper?
- Look into Xudong Wang's work (from MRS) on ferroelectric semiconductor p-n junctions - tuning ease of transport across interface by direction of polarisation.

5 Data access

Link to MacroDensity and ELS repos?

6 Acknowledgements

Yoyo for non-polar surface slab structures. Jake Bowers and Elisabetta and Katie (NREL) and Oliver Hoffmann for discussions. Tong for FHI-aims LOCPOT routine? Lee Burton for discussions.

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