The Steady Rise of Kesterite Thin-Film Solar Cells

Viewpoint for ACS Energy Letters

Suzanne K. Wallace[a,b], David B. Mitzi[c,d], and Aron Walsh[b,e]

[a] Centre for Sustainable Chemical Technologies, Department of Chemistry, University of Bath, Claverton Down, Bath, BA2 7AY, United Kingdom
[b] Department of Materials, Imperial College London, Exhibition Road, London SW7 2AZ, United Kingdom
[c] Department of Mechanical Engineering and Materials Science, Duke University, Durham, NC 27708, USA
[d] Department of Chemistry, Duke University, Durham, NC 27708, USA
[e] Department of Materials Science and Engineering, Yonsei University, Seoul 03722, South Korea

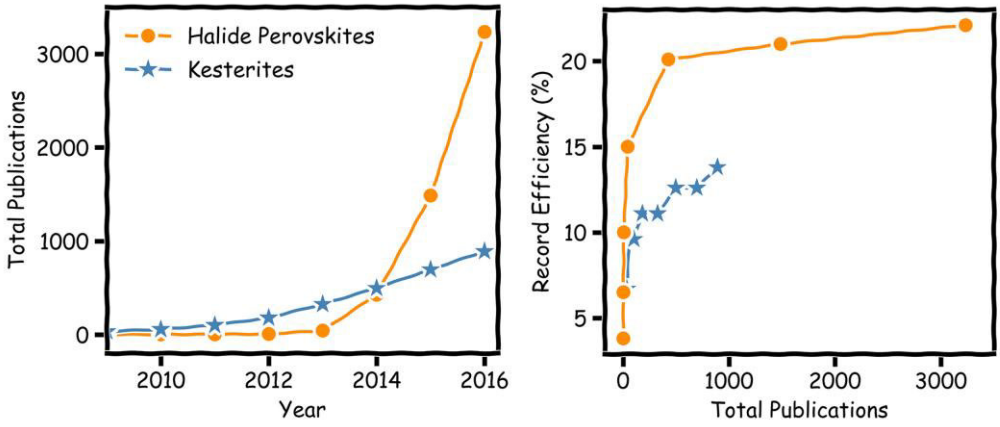

Figure 1. Comparison of the cumulative research output for $Cu_2ZnSn(S,Se)_4$ (kesterite) and $CH_3NH_3PbI_3$ (halide perovskite) related photovoltaic technologies against year and the record light-to-electricity conversion efficiency. The publication data has been generated from Web of Science (15th February 2017) for kesterite (search terms: `kesterite OR stannite` AND `solar cell`) and halide perovskite (search terms: `halide perovskite OR iodide perovskite OR hybrid perovskite` AND `solar cell`) solar cells.

Could slow and steady win the race to sustainable energy generation? While perovskite solar cells are currently at the forefront of photovoltaic research activity, we argue in this viewpoint that devices based on the mineral kesterite could be the dark horse of next-generation solar energy conversion. The most urgent research challenges for this technology are outlined.

Thin-film photovoltaic (PV) technologies offer an economically promising and flexible means to harness solar energy[1]. Compared to silicon, the use of materials that absorb sunlight strongly allow for less material to be used, lowering cost and opening up more possibilities for integrating the solar cell modules with buildings. Only a small number of commercial thin-film technologies have achieved power conversion efficiencies (PCEs) greater than 20%: CdTe and $Cu(In,Ga)(S,Se)_2$ (CIGS) have champion device PCEs of 21%[2]. The toxicity of cadmium and competition in the demand for indium are limiting factors for the large-scale utilisation of these technologies.

In the emerging thin-film PV market, hybrid halide perovskites such as methylammonium lead iodide ($CH_3NH_3PbI_3$) have received an immense amount of research interest, with over 3,000 publications in relation to solar cells since 2009. The efficiency of laboratory-scale halide perovskites devices has risen sharply, especially over the course of the first 500 publications focused on the material (see Figure 1). The current record for a perovskite solar cell is 22.1%[2]. Progress in PCE with respect to the number of publications on this material is beginning to plateau. Furthermore, stability issues and concerns over the lead content of halide perovskites remain a challenge for the commercialization of this technology[3].

Solar cells based on the kesterite mineral structure, including Cu_2ZnSnS_4 (CZTS), $Cu_2ZnSnSe_4$ (CZTSe) and their alloys $Cu_2ZnSn(S_xSe_{1-x})_4$ (CZTSSe), stand out from other thin-film PV candidates for being composed of earth-abundant and non-toxic elements. These materials have been the subject of several excellent technical reviews. Since the first kesterite solar cell was fabricated in 1997, the PCE of the champion device has risen from 0.66%[4] to the current certified record of 12.6% set in 2013[5], with a 13.8% small-area device reported in late 2016[6]. These efficiencies fall far below the 28% predicted for this technology from the Shockley–Queisser limit. However, kesterites have achieved relatively little attention, with fewer than 1,000 publications to date related to photovoltaic applications. A directed focus in research effort may see this sustainable PV technology achieving PCEs approaching those of hybrid perovskites or commercial thin-film PV technologies, perhaps as well with much improved operational stability.

There are numerous synthetic routes to kesterite thin-films, including both vacuum-based deposition and non-vacuum-based solution processing. Non-vacuum approaches are desirable for scalability and feasible industrial production, including: electrodeposition[7,8,9,10], nanocrystal dispersion[11,12,13], hydrazine-based deposition[14] and other pure-solution approaches[15,16,17]. The current champion CZTSSe solar cell was fabricated using the hydrazine-based solution method developed at the IBM T. J. Watson Research Center[5]. Most record devices since 1997 have been produced by solution-based film deposition approaches[18], alluding to the potential for large-scale fabrication, which is required to support a terawatt PV industry.

The low efficiency of kesterite-based solar cells is attributed to a large deficit in the open circuit voltage (V_{OC}) relative to the band gap of the absorber layer. This is universal for high-performance kesterite devices, with the deficit being even larger for the pure sulphide material. While there is a consensus that the V_{OC} deficit is the key limiting factor for devices, the origin remains very much an open question[19]. There are a number of hypotheses to account for the V_{OC} deficit, which can be separated into three categories:

(i) a non-Ohmic back electrical contact, usually Mo/CZTS, which results in high recombination velocity;
(ii) a poorly optimised interface between CZTS and the CdS buffer layer, which could also result in rapid electron-hole recombination;
(iii) large amounts of defects and disorder in the bulk of the absorber layer, limiting minority charge-carrier lifetimes and enhancing recombination processes.

In the best devices, it has been shown that the back contact with Mo is Ohmic in nature[20]. The borrowed device architecture from CIGS solar cells involves the use of a CdS buffer layer and analysis of the conduction band offset between CdS and CZTSSe also does not imply any

major limitation on device performance[21]. This then leaves us with consideration of defects and disorder in the bulk of the absorber layer.

Advances in defect engineering – through modification of synthesis, deposition and/or annealing procedures – enable a reduction in the impact of extended defects such as grain boundaries, passivation of surfaces, and production of pinhole free thin-films. However, point defects such as site vacancies and antisites will remain present even for carefully processed samples[22]. Devices fabricated from high-quality single-crystals have demonstrated PCEs of 10%, with a V_{OC} similar deficit to thin-film solar cells[23].

Kesterites are an example of a multinary semiconductor, with a zinc-blende-related structure (space group type $I\bar{4}$) and the general chemical formula of Cu_2-M^{II}-M^{IV}-X_4 (X = O, S, Se, Te). A consequence of the many components of the material is an increase in the number of possible lattice defects, with particular concern for cation disorder[24]. In CZTS, disorder amongst Cu and Zn metals would seem particularly likely due to the chemical similarity of the two species, which are neighbours in the periodic table. Indeed, first-principles calculations predicted that the neutral defect pair [Cu_{Zn}^{-} + Zn_{Cu}^{+}] has a low formation energy[25], implying a high equilibrium concentration and there is a large body of experimental evidence for Cu/Zn disorder from neutron diffraction, synchrotron X-ray diffraction, and near-resonant Raman studies[22]. It is now universally accepted that Cu/Zn disorder will be present to a high degree even in high-quality thin films. However, the impact of this type of disorder on device performance is the subject of on-going debate in the community[19,26].

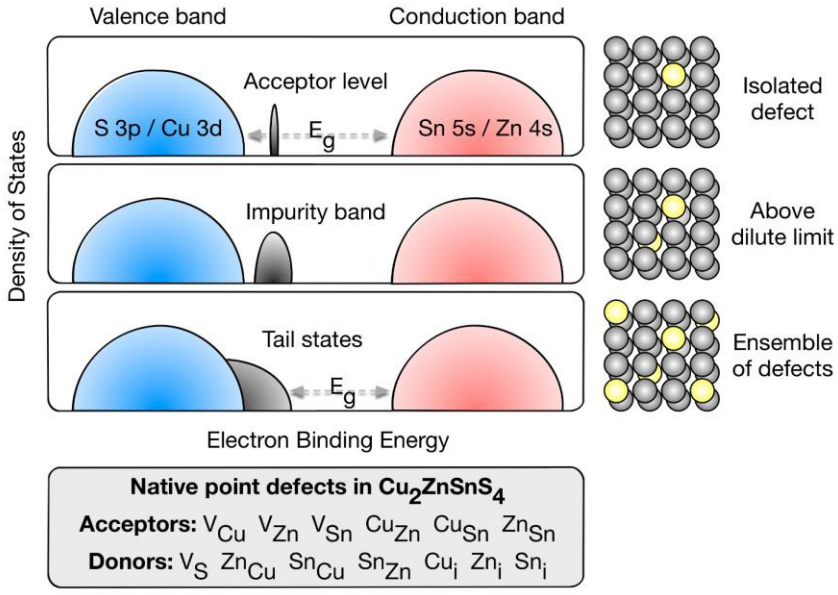

Figure 2. An acceptor defect-induced energy level within the band gap of a semiconductor, broadening to an impurity band with increased defect density until at sufficiently high defect concentrations the band merges with the valence band maximum, resulting in a reduced band gap. Such tail states would limit the open-circuit voltage accessible in a photovoltaic device, and could explain the voltage deficit observed in kesterite based solar cells. Also listed are the range of possible acceptor defects in Cu_2ZnSnS_4 – a large number of possible charge-neutral defect clusters can also be formed.

The open-circuit voltage of a PV device is limited by the band gap of the absorber material, but defects can modify the underlying electronic band structure. Lattice disorder can result in localized states near the top of the valence band or at the bottom of the conduction band.

At sufficiently high concentrations, these interact to form a defect band. As the density of defects increases, the tail states become more prevalent and penetrate further into the band gap. Localized states and associated band tailing in the electronic structure lead to band gap narrowing[22,27]. As such, peaks in the photoluminescence spectra are red-shifted to energies below those of the optical band gap obtained from internal quantum efficiency measurements (which only reflects extended electronic states)[28]. Band tailing in CZTSSe devices is roughly twice as severe as that in CIGS devices and it has been suggested that Cu/Zn disorder in CZTSSe is one contributing factor. In comparison, cation disorder in CIGS could be expected to be less prevalent as Cu is less chemically similar to Ga/In than Cu is to Zn, increasing the energy cost associated with making substitutions amongst any of these two species with Cu compared to that of Zn with Cu. Furthermore, it has been observed that band tailing is less severe in devices made from $Ag_2ZnSnSe_4$[29], where cation disorder could be expected to be suppressed due to the greater ionic radii mismatch between Ag^+ and Zn^{2+} than Cu^+ and Zn^{2+}.

To our knowledge no direct connection between bulk disorder in the kesterite absorber layer and photovoltaic performance has yet been made. Post-annealing treatments can be used to reduce the prevalence of Cu/Zn antisites[30]. Devices of varying degrees of Cu/Zn disorder in the absorber layer produced in this way demonstrated that the V_{OC} changed by the same amount as the optical band gap. The post-annealing treatment therefore had no impact on V_{OC} deficit[19]. The lack of direct connection between Cu/Zn antisite concentration and photovoltaic performance could either be because, despite reduction in Cu/Zn disorder, the antisite concentration is still high from the perspective of device performance. Alternatively, it could be because there are other defects that are more important for controlling device properties at the current performance level. It is worth noting that the primary factors limiting performance could differ considerably for devices produced using different absorber fabrication procedures or for different performance levels for samples produced using the same approach.

Beyond Cu/Zn antisite defects, another explanation for the V_{OC} deficit is the presence of defects with levels deep in the band gap that could be acting as centres for non-radiative recombination. In particular, defects involving Sn result in deeper charge transition states owing the high charge and larger radius of Sn relative to Cu and Zn[31]. Deep-level defects in CZTS have been predicted to have a higher formation energy than the shallow defects[16] and so it could be expected that they will be less prevalent. However, the presence of 'killer centres'[32] even in low concentrations could be limiting device performance. It is possible that the formation energy of such centres may be reduced by the specific environmental conditions during synthesis and chemical potentials of the constituent elements.

To summarise, some key challenges and opportunities for kesterite solar cells include:

1. **Missing activation step** – for CdTe a post-deposition chemical treatment of $CdCl_2$ or similar is required to "activate" the absorber layer[33] (e.g., passivate grain boundaries, enlarge grain size), while for CIGS a Cu-rich processing stage is needed during the 3-stage evaporation process[34]. Perhaps a similar process could be developed for kesterites that results in a step-change in PV action.
2. **Accurate material and device measurements** – the wide variety of demonstrated growth processes and conditions makes comparison of reported physical properties

challenging. Accurate and consistent measurements concerning carrier generation, transport, recombination and collection for different absorbers would provide valuable insights to overcome device bottlenecks.

3. **Quantifying defects and disorder** – a number of different descriptors are being used in the field to quantify disorder, including Raman spectra, optical spectra, and neutron diffraction. However, the site disorder averaged over a macroscopic sample does not provide insights into the microscopic cation distribution that will interact with photogenerated electrons and holes. More accurate local structure techniques and materials simulations could provide valuable insights.
4. **Alternative device architectures** – relatively little effort has been spent on looking at alternatives to the standard Mo/CZTS/CdS device configuration. Beyond simple component replacement (e.g. Mo for W or ZnS for CdS), other device configurations such as *p-i-n* could result in enhanced photovoltaic performance.

Two large research consortia have recently been funded to address some of these questions. One is *PVTEAM*, led by L. M. Peter at the University of Bath (UK) that links with the SPECIFIC Innovation and Knowledge Centre for scale-up, and *STARCELL* led by E. Saucedo at IREC (Spain) that combines 13 partners across Europe, Japan and the USA. At a time when further breakthroughs in perovskite solar cells will become increasingly difficult to achieve, a focused effort on kesterites and related materials could have major impacts. While this technology has been relatively slow to emerge, the combination of earth-abundant and non-toxic elements in a chemically stable compound is the solution that sustainable thin-film photovoltaics requires.

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