

# The path towards a high-performance solution-processed kesterite solar cell<sup>☆</sup>

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## ABSTRACT

Despite the promise of thin-film  $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$  (CIGSSe) chalcopyrite and CdTe photovoltaic technologies with respect to reducing cost per watt of solar energy conversion, these approaches rely on elements that are either costly and/or rare in the earth's crust (e.g., In, Ga, Te) or that present toxicity issues (e.g., Cd), thereby potentially limiting these technologies in terms of future cost reduction and production growth. In order to develop a photovoltaic technology that is truly compatible with terawatt deployment, it is desirable to consider material systems that employ less toxic and lower cost elements, while maintaining the advantages of the chalcopyrite and CdTe materials with respect to appropriate direct band gap tunability over the solar spectrum, high device performance (e.g., > 10% power conversion efficiency) and compatibility with low-cost manufacturing. In this review, the development of kesterite-based  $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$  (CZTSSe) thin-film solar cells, in which the indium and gallium from CIGSSe are replaced by the readily available elements zinc and tin, will be reviewed. While vacuum-deposited devices have enabled optimization within the compositional phase space and yielded selenium-free CZTS device efficiencies of as high as 6.8%, more recently a liquid-based approach has been described that has enabled deposition of CZTSSe devices with power conversion efficiency of 9.7%, bringing the kesterite-based technology into a range of potential commercial interest. Electrical characterization studies on these high-performance CZTSSe cells reveal some of the key loss mechanisms (e.g., dominant interface recombination, high series resistance and low minority carrier lifetime) that limit the cell performance. Further elucidation of these mechanisms, as well as building an understanding of long-term device stability, are required to help propel this relatively new technology forward.

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## 1. Introduction

Photovoltaic (PV) electricity generation currently meets less than 0.1% of world-wide electricity demand [1], despite orders of magnitude higher potential, primarily because of the cost discrepancy between solar and more conventional carbon-based technologies. Within the PV arena, over 80% of the solar market is currently dominated by silicon-based technology [1,2], in part because of an entrenched and relatively mature silicon industry, as well as the attractive device stability and power conversion efficiencies offered by crystalline silicon (record efficiency for crystalline silicon cells is currently 25.0% [3]). However, crystalline silicon technology relies on an absorber with indirect band gap, thereby necessitating a thick layer to absorb an appreciable

fraction of the incident solar radiation (> 100  $\mu\text{m}$  assuming no light trapping incorporated within the cell design). Additionally, since grain boundaries are active as recombination centers in Si-based technologies, nominally perfect single crystal substrates are required to build highest efficiency solar modules, thereby contributing to higher cost.

By contrast, thin-film PV technologies rely on direct band gap materials such as CdTe,  $\text{CuIn}(\text{S,Se})_2$  (CISSe) and more generally  $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$  (CIGSSe). Because of the direct band gap (and corresponding high absorption coefficient of  $\sim 10^4\text{--}10^5 \text{ cm}^{-1}$ ), material utilization can be reduced, with 1–2  $\mu\text{m}$  layer thickness generally being enough to absorb most of the incident solar radiation. Reduced requirements for film crystalline quality (grain boundaries are less active as recombination centers [4]) also enable lower-cost routes to be employed for layer deposition. Both CdTe and CIGSSe technologies yield champion cell efficiencies of greater than 15% (16.7% for CdTe and 20.1% for CIGSSe—not far behind crystalline Si technology [3]) and module production with average module power conversion efficiency of greater than 10% [3]. For CIGSSe, module efficiencies of as high as 16% have been demonstrated on the laboratory scale [5]. Manufacturing production growth rates for both technologies are also impressive, with First Solar (CdTe) being the first manufacturer to achieve greater than 1 GW/yr production and also the first to achieve < \$1/W production (at \$0.76/W level as of August 2010) [6].

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Industrial production of CIGSSe-based modules is also expected to reach the GW level by 2011 [5].

Despite the promise of CdTe and CIGSSe, both technologies rely on elements that are scarce in the earth's crust [7,8]. The abundance of indium in the upper continental crust is estimated to be 0.05 ppm (compared with an abundance of 25, 71 and 5.5 ppm for copper, zinc and tin, respectively) [9]. Current world-wide production capacity for indium is of order 600 metric tons per year [10]. However, much of this capacity is required for transparent conductive coatings for the growing flat panel display industry. One estimate, based on current production trends, is that world-wide production of indium can support a CIGSSe production capacity of approximately 70 GW/yr, well below the desired TW level [7]. The abundance of tellurium is even lower (0.001 ppm) [9]. Although there is a great deal of uncertainty in the ultimate production capacity limitations for CIGSSe and CdTe manufacturing [7,8,11], depending upon whether recycling programs are instituted for In and Te, the ultimate thickness of the absorber layer, the achievable module efficiencies and on competition for raw materials with other technologies, if pervasive deployment were implemented for CIGSSe and CdTe photovoltaics, materials costs would likely impact competition with other technologies as production volumes increase. Besides the issue of abundance, the heavy metal cadmium has experienced resistance towards adoption in some countries because of the toxicity issue. One reason for this resistance is the mass cadmium poisoning incident in the early-to mid-20th century, in which cadmium-laden waste water from mining operations in the Toyama Prefecture in Japan resulted in an outbreak of a painful and sometimes fatal affliction commonly referred to as "itai-itai" (translated literally as "ouch-ouch") disease [12,13]. Given the above considerations, there is a need to identify thin-film materials that are composed of plentiful and less toxic elements, while still providing adequate device performance, in order to enable pervasive deployment of PV technology to meet ever growing energy needs.

While materials availability and toxicity are two considerations in the search for appropriate absorber layer compositions that might contribute, along with CdTe and CIGSSe, to the thin-film PV market, the material must fulfill several additional fundamental criteria in order to enable the two key targets for an efficient solar cell of: (1) effective absorption of incident photons to generate electron-hole pairs and (2) ability to collect the photo-generated charges before they recombine. Optimal absorption of the solar spectrum and generation of electron-hole pairs requires the appropriate choice of band gap. Theoretical considerations predict maximum power conversion efficiency in the 20–30% range for absorber materials with a band gap of between 1 and 2 eV (optimal overlap with the solar spectrum should occur for a band gap of 1.5 eV). A direct lowest energy band gap also provides a large absorption coefficient ( $\alpha > 10^4 \text{ cm}^{-1}$ ) for photons with energy greater than the band gap. A direct band gap thereby allows effective absorption in a chalcogenide layer thinner than a few microns, thus reducing significantly the materials needs, in comparison with indirect band gap materials such as crystalline silicon. The ability to rely on a thin absorber layer also relaxes to some extent the constraint on the diffusion length (essentially the average distance photo-generated carriers diffuse before recombination), which poses in silicon technology costly requirements for materials purity and crystal quality. Nevertheless, in addition to an appropriate direct band gap semiconductor, the desire for a material with a relatively large photo-generated carrier lifetime (or long diffusion length) is a second target in identifying appropriate absorber materials for highest efficiency devices.

The need to concurrently address the requirements of appropriate size direct band gap and carrier lifetime, along with the need for a conveniently deposited material that has low toxicity and

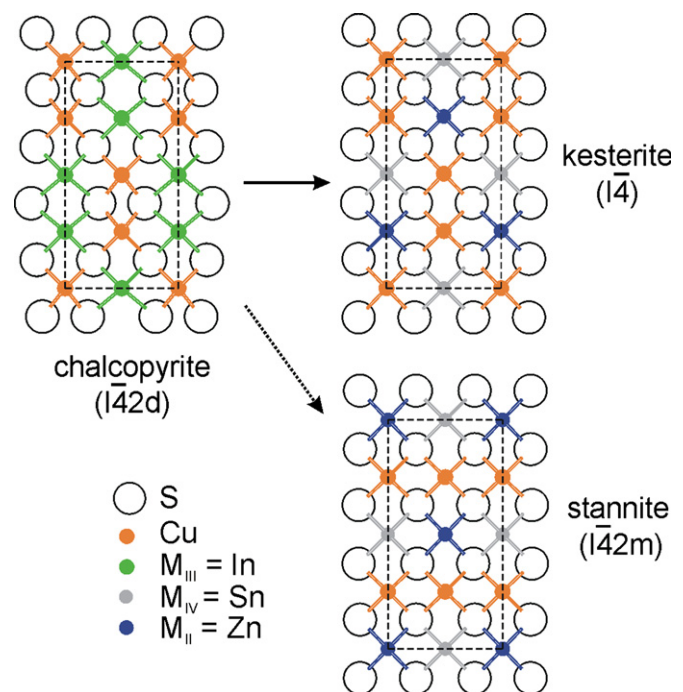
readily available elements, has led to a recent shift of research focus towards the kesterite-related family of thin-film chalcogenide materials.

## 2. History of kesterite-related PV materials

### 2.1. Kesterite-related compounds and structures

Chalcogenide compounds with a  $\text{Cu}_2(\text{M}_{\text{II}})(\text{M}_{\text{IV}})(\text{S,Se})_4$  ( $\text{M}_{\text{II}} = \text{Mn, Fe, Co, Ni, Zn, Cd, Hg}$ ;  $\text{M}_{\text{IV}} = \text{Si, Ge, Sn}$ ) stoichiometry have been of interest for many years because of their appearance as naturally occurring minerals and also suitable direct band gaps for application in solar cells and other optical devices [14–19]. The zincblende (or sphalerite)-related structures adopted by these compounds depend on the degree and type of metal cation ordering within the face-centered cubic (fcc) array of chalcogenide anions (with both metals and chalcogens adopting a tetrahedral coordination). One way of viewing these structures is by starting from the ternary chalcopyrite structure (Fig. 1),  $\text{CuM}_{\text{III}}(\text{S,Se})_2$ , and replacing the trivalent  $\text{M}_{\text{III}}$  ions with an equal number of divalent  $\text{M}_{\text{II}}$  and tetravalent  $\text{M}_{\text{IV}}$  metals. When the ordering of the metals is such that Cu and  $\text{M}_{\text{IV}}$  atoms alternate on the  $z=0$  and  $\frac{1}{2}$  ( $z$ =fractional coordinate along the long  $c$ -axis of the structure) planes and Cu and  $\text{M}_{\text{II}}$  atoms alternate on the  $z=\frac{1}{4}$  and  $\frac{3}{4}$  planes, this is known as the kesterite structure, whereas when  $\text{M}_{\text{II}}$  and  $\text{M}_{\text{IV}}$  atoms alternate on the  $z=0$  and  $\frac{1}{2}$  planes and only Cu resides on the  $z=\frac{1}{4}$  and  $\frac{3}{4}$  planes, this is known as the stannite structure. While the kesterite structure has the same basic Cu/S structure as chalcopyrite, the stannite structure requires some reorganization of the Cu sublattice.

Note that determining whether a structure adopts a kesterite or stannite structure is difficult to do without careful single crystal structural analysis or Rietveld-type analysis using X-ray and/or neutron diffraction data, which has not been completed for most of



**Fig. 1.** Schematic representation of the chalcopyrite structure (drawn with  $\text{M}_{\text{III}} = \text{In}$ ), and kesterite and stannite structures (drawn with  $\text{M}_{\text{II}} = \text{Zn}$ ,  $\text{M}_{\text{IV}} = \text{Sn}$ ). The unit cell boundaries are denoted with dashed lines and the space group for each structural type is also provided.

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