Chalcopyrite compound semiconductors for thin film solar cells
Susanne Siebentritt

Chalcopyrite semiconductors are used in thin film solar cells with the highest efficiencies, in particular for flexible solar cells. Recent progress has been made possible by an alkali post-deposition treatment. Other important trends are the development of tandem cells and of ultrathin solar cells. Recent progress has forwarded the understanding of off-stoichiometry and of bulk defects in these materials.

Addresses
Laboratory for Photovoltaics, Physics and Material Science Research Unit, University of Luxembourg, Luxembourg
E-mail address: susanne.siebentritt@uni.lu

Introduction
Cu(In,Ga)Se₂ is an alloy of CuInSe₂ and CuGaSe₂ which both crystallize in the chalcopyrite structure. It is a direct band gap semiconductor, used as absorber in thin film solar cells, which present a new generation of photovoltaic technologies. The advantages of thin film solar cells are low cost based on their low material and energy consumption, short energy pay back times, flexibility in design and light weight (see e.g. the White Paper on http://cigs-pv.net). Laboratory size solar cells have reached 22.6% of certified power conversion efficiency [1]. Commercial modules reach 16% efficiency (see Ref. [2] and the websites of various producers).

In the last three years there has been tremendous progress in efficiency based on an alkali post-deposition treatment. Even higher efficiencies are aimed at by the use of tandem solar cells based on thin film cells. Further progress has been made in the optical and the back contact design of ultrathin solar cells which use even less raw materials. The understanding of the role of off-stoichiometry and of defects has been expanded. These topics are discussed in detail in the following.

Alkali treatment
The last three years have seen a dramatic increase in the efficiency of Cu(In,Ga)Se₂ solar cells, based on a newly developed alkali treatment [3]. The role of sodium had long been recognised [4–6] and it had been thought that potassium has similar effects [7,8]. The potassium postdeposition treatment has led to a world record efficiency of 20.4% at that time [3], which is still the record efficiency of any flexible solar cell. The treatment is performed by depositing a small amount of alkali fluoride in the presence of Se pressure onto the surface of the film during cool down after growth [3], see Figure 1. Originally, the postdeposition treatment had been developed to introduce Na into Cu(In,Ga)Se₂ films grown at comparatively low temperatures. It was shown for these low temperature processes to be more beneficial than providing Na by a precursor [9]. The impeded annihilation of stacking faults in the presence of Na contributes to this observation [10]. Meanwhile the postdeposition treatment with K or heavier alkalis has been shown to be efficient for a low and high temperature processes and has led to a series of new record efficiencies [11–13]. Finally, it was found that treatment based on other heavier alkalis improves the efficiency even further, leading to the current world record efficiency of 22.6% [1]. An efficiency of 22.8% has been reported, but not certified, yet [13]. Alkali treatment also improves the efficiency in a full size industrial production process [14]. For absorbers prepared by a co-evaporation process, the treatment is done in-situ at the end of the process [1,3,14,15]. Ex-situ processes, where the alkali treatment is performed outside the deposition chamber were also shown to improve the efficiency [13,16–18]. It was found that the treatment is effective for sulphur containing absorbers based on Cu(In,Ga)(S,Se)₂ [13]. All these investigations found the improvement due to an increase in open-circuit voltage.

A large amount of research activity has been directed into understanding the effects of the alkali treatment. The main observations are: (i) the alkali treatment creates a layer of different composition at the surface and (ii) leads to an ion exchange within the whole absorber layer, which influences the electronic properties.

(i) The potassium treatment creates a completely Cu-depleted surface layer, which can be continuous [3,16] or structured [15], depending on the exact treatment conditions. The Cu-depleted layer was found to have a wider surface band gap than
A more radical approach to improving the efficiency is the use of tandem cells. In the past considerable effort has been extended to developing tandem solar cells based on wide gap and low gap Cu(In,Ga)Se$_2$ [30–34] or related compounds [35]. This effort has been hampered so far by the limited efficiency obtained with CuGaSe$_2$ solar cells: best efficiency so far has been 11.2% [36]. With the recent development of perovskite solar cells (see the review in this issue) tandems are now made with these cells as top cells [37–40]. An efficiency of 20.5% has been reached with a 4-terminal cell [40] and of 17.8% with a 2-terminal monolithically integrated minimodule (see press release at e.g. https://www.kit.edu/kit/english/pi_2016_133_record-for-perovskite-cigs-tandem-solar-module.php). These record efficiencies of the tandem devices are better than the efficiencies of the top or bottom device constituting the tandem cells.

The sulfide semiconductor Cu(In,Ga)S$_2$ covers the ideal band gaps for a top cell in a tandem application with CuIn(Ga)Se$_2$ or Si [41,42]. The field has been recently renewed by the development of a cell with efficiency above 15% based on higher substrate temperatures [43]. Open-circuit voltages above 970 mV have been achieved [44].

**Ultrathin cells**

Another current trend in Cu(In,Ga)Se$_2$ solar cells is to make the absorber thinner to save costly In. When the absorber thickness becomes lower than 0.5 μm the short circuit current decreases considerably [45,46]. Therefore optical confinement is needed. This is achieved by optimising reflection and absorption properties [46,47], by structures optimised for back side illumination [48,49] or by light trapping [50]. Light trapping can be achieved by using plasmonic structures: various approaches have been applied: Ag nanostructures at the back contact [51], at the surface of the cell [52], or at the surface of the absorber [53]. Generally a loss in open-circuit voltage is observed. Only one approach with plasmonic structures, has so far led to an actually improved efficiency compared to similar cells without nanostructures: SiO$_2$ nanoparticles at the back contact [54].

An additional challenge is posed by back surface recombination, which decreases current and voltage is ultrathin solar cells [55]. The recombination activity of the back surface seems to depend on the details of the preparation process and the cell structure: it has been observed to have only minimal influence in certain cases [56,57], whereas in others a serious reduction of the open-circuit voltage has been observed for absorbers thinner than 500 nm [45,58]. In any case an improved current collection is observed with passivated back contacts. Two approaches have been successful, based on insulating or conductive oxide layers. A non-conductive Al$_2$O$_3$ or SiO$_2$ passivation layer with point contact openings has been successful [58–62].
openings are achieved in a stochastic arrangement by CdS nanoparticles, which are etched after the oxide deposition [58–60], or in an ordered arrangement by electron beam lithography [61] or by plasma etching through a mask [62]. A structured layer has additional positive light trapping effects [62]. A conductive SnO2:F layer has also been demonstrated as a passivated back contact [63].

The best efficiencies obtained with ultrathin cells up to now are: 13.5% with a 385 nm thick absorber [60], 11.8% with a 240 nm thick absorber [61] and 9% with a 190 nm thick absorber [62].

Cu-rich chalcopyrite

All aforementioned Cu(In,Ga)Se2 solar cells are based on Cu-poor material, i.e. material with a substoichiometric Cu content. Solar cells based on Cu-poor material always show better efficiencies [64–66], although Cu-rich material shows the better semiconductor properties with lower defect concentrations and better transport properties [67]. It has also been shown that the phase transition between Cu-poor and Cu-rich material is essential for the stress release in the films during growth [68]. It has been long understood that the lower efficiency of Cu-rich solar cells is due to recombination at or near the interface, which limits the open-circuit voltage [64]. This recombination can be suppressed by an In-Se surface treatment [65] or by a potassium treatment [17]. In pure CuInSe2 solar cells (without Ga) the surface treatment leads to efficiencies of Cu-rich solar cells equal to Cu-poor ones [69], whereas in Ga-containing absorbers the surface treatment leads to an improvement of the open-circuit voltage, but not to a complete recovery of the values obtained in Cu-poor absorbers [66]. It was only recently understood that this difference is not in the first place due to a difference in interface properties, but to bulk properties of Cu(In,Ga)Se2: in pure CuInSe2 the quasi-Fermi level splitting, which is a measure of the open-circuit voltage an absorber could achieve, is higher in Cu-rich material than in Cu-poor [70,71], whereas in Cu(In,Ga)Se2 (with Ga) the quasi-Fermi level splitting is lower in Cu-rich material than in Cu-poor, already in the absorber without any interface [72]. It has been proposed that the difference is due to a deep GaCu antisite defect [73,74], which forms a less detrimental pair with copper vacancies in Cu-poor material.

Bulk defects

This observation shows once more that, although the interface is essential in the functioning of the solar cell, the bulk defects play an important role in the recombination behaviour. Furthermore they influence the electronic structure of the interface. A review of earlier work on grain boundaries and point defects and their role for doping and metastable effects can be found in Ref. [75]. Recently, progress has been made in determining the atomic structure of point defects; positron annihilation, which is sensitive to vacancy type defects, found the dominating vacancy defect in CuGaSe2 to be the Cu-Se double vacancy, whereas in CuInSe2 the double vacancy dominates only in Cu-poor material, whereas Cu-rich material contains single Cu-vacancies as the dominating vacancy type [76]. Cation related point defects have been detected by neutron diffraction in CuInSe2 [77] and CuGaSe2 [78]; in both cases Cu vacancies are found in Cu-poor material, in CuInSe2 additional InCu antisites account for the Cu deficiency, whereas in CuGaSe2 Ga interstitials were found. In Cu-rich CuInSe2 the only defect detected is the CuIn antisite, which is also present in Cu-poor material. It should be kept in mind that neutron scattering has a high detection limit for defects in the % range [79]. In fact, high defect densities have been observed in CuInSe2 [77], above 10^{20} cm^{-3}. Since experimental doping densities are in the range of 10^{15}–10^{17} cm^{-3} (see e.g. Refs. [21,27,80,81]), defects must compensate and neutralise each other. Possible is also neutralisation with other defect types that have not been observed in the neutron scattering study, like anion related defects. In Cu-poor Cu(In,Ga)Se2 thin films the presence of Na is essential to reach sufficient doping levels [6,80,82]. Neutron diffraction studies show that the addition of Na leads to a decrease of InCu antisite donors [83], which can explain the increase in p-type doping with the addition of Na. It has been theoretically predicted that while Na is likely to take interstitial sites, K is more likely to go on substitutional sites [84]. In addition to progress in the experimental characterisation of point defects, their theoretical description has evolved as well with the use of hybrid functionals in DFT.
calculations. A number of recent papers use hybrid functionals to calculate defect energies in the gap and their formation energies [85–88]. It is generally agreed that three more or less shallow acceptors exist, in agreement with photoluminescence studies [75,89–91]: the Cu vacancy $V_{\text{Cu}}$, the $\text{CuIn}$ antisite, and the In or Ga vacancy $V_{\text{In}}$ or $V_{\text{Ga}}$. Most calculations find that the In or Ga vacancy has a rather high formation energy [85,86,88] and it is thought to be unlikely the third acceptor. However, the luminescence associated with the third acceptor is rather weak (see e.g. Ref. [92]) and could thus still be due to the In or Ga vacancy. The shallow donor could be the Cu interstitial or the $\text{InCu}$ antisite. The Ga$_{\text{Cu}}$ antisite in CuGaSe$_2$ is proposed to be deep — see below. Our proposal for the energies of defects in the band gap, based on these experimental and theoretical results is given in Figure 2.

Deep defects play an important role for Shockley-Read-Hall recombination. One way to measure the influence of recombination is the determination of photocarrier lifetimes by time resolved photoluminescence measurements. Recently it was pointed out that the decay time of the photoluminescence signal gives information on the photocarrier lifetime only in special cases. In particular the measured decay time can be much longer than the lifetime due to trapping and detrapping effects [93]. The influence of detrapping effects can be detected by the temperature dependence of the decay behaviour [94]. The temperature dependent of the detrapping effect can be developed into a method to characterise the trap states themselves [95]. Besides affecting the doping density and the recombination behaviour, the electronic band structure is influenced by the details of the atomic structure: while the average bond lengths in Cu(In,Ga)Se$_2$ follow a linear Vegard’s law, it was found by X-ray absorption measurements, that the In-Se and Ga-Se bond lengths remain essentially constant throughout the whole composition range between CuInSe$_2$ and CuGaSe$_2$ [96]. This leads to a non-linear displacement of the anions, which contributes to the bowing behaviour of the band gap. In a combined optical and theoretical study it was shown that the stability of the band gap with varying Cu-content can be due to an interplay between anion displacement and Cu vacancies [79].

Besides point defects extended defects play an important role in the absorber. A recent review can be found in Ref. [97].

**Summary**

Considerable progress has been made on the technological side by improving efficiencies and reducing raw material. This was combined with progress in the fundamental understanding of the material. Both trends have fruitfully interacted and entailed each other.

**References and recommended reading**

Papers of particular interest, published within the period of review, have been highlighted as:

* of special interest
** of outstanding interest

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34. Dahan N, Jehl Z, Hildebrandt T, Greffet JJ, Guillermojes JF, Lincoln D, Naghavi N: Optical approaches to improve the photocurrent generation in Cu(In,Ga)Se2 solar cells with absorber thicknesses down to 0.5 mu m. *J Appl Phys* 2012, 112:7.

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