

Development of CuInS₂-based solar cells and modules

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ABSTRACT

Starting from a small area cell published in 1993, CuInS₂ technology has been continuously improved with respect to performance and manufacturability. Major milestones include successful preparation by rapid thermal processing, a monolithically integrated module test structure on a 5 × 5 cm² substrate, implementation of an industrial pilot line, incorporation of gallium for higher open circuit voltages and better performance and demonstration of Cd-free devices. Phase formation, reaction pathways and interdiffusion mechanisms have been investigated and modelled as have been electronic and device properties such as current transport. This review summarizes the most significant aspects of development and our current understanding of the technology.

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1. Introduction

CuInS₂ (CIS) is one of the chalcopyrite compounds used as absorbers in thin film solar cells and modules. Its technology and properties are in many aspects comparable to those of the more widely researched Cu(In,Ga)Se₂ (CIGSe) or Cu(In,Ga)(S,Se)₂ (CIGSSe) compounds. There are, however, also differences that lead to advantages in terms of large-scale production. The development efforts have therefore early on been aimed at transferring research results to what we believe are processes suited for mass production. In our previous review of CIS [1] we described the establishment of a lab-scale stable baseline process for monolithically integrated module test structures on a 5 × 5 cm² substrate. The CIS absorber is prepared using annealing metal precursors in the presence of sulphur vapour (reactive rapid thermal processing). The other components are the same as in typical CIGSe modules, *i.e.*, glass substrate, sputtered Mo back contact, CdS buffer layer (chemical bath deposition) and sputtered ZnO/ZnO:Al transparent front contact. The perceived maturity of the lab baseline had triggered the implementation of an industrial pilot line by the company SULFURCELL, where the technology was to be scaled up directly (without intermediate formats) to 120 × 60 cm² modules.

Since then SULFURCELL has demonstrated successful pilot production and is currently ramping up production in a new facility designed for a 35 MWp/a production capacity [2]. Researchers meanwhile have been focusing on improving the scientific foundation of the technology. The main emphasis has been on

topics related to production throughput and yield as well as product quality and certification. They include analysis of reaction kinetics and phase formation, morphology and micro structure, quality assessment and process monitoring [3] for the former and device long-term and meta-stability [4] for the latter. Of equal importance has been the work aimed at possible next generation products, *e.g.*, investigating concepts for increased efficiency, Cd-free devices, and wide band-gap transparent solar cells.

2. Modification of CuInS₂ by doping and alloying

Various efforts to tailor material properties by incorporation of additional elements have been carried out. The addition of zinc or magnesium [5] in small concentrations improves the open circuit voltage, but leads to a deterioration in photo current collection and at higher concentrations destroys the photovoltaic properties completely. Silver [6] was found to decrease the lateral conductivity of the film and leakage currents in devices. This can lead to significantly better cell performance under low illumination and minor improvements in fill factor and open circuit voltage under full illumination. Antimony diffusion caused a buried junction with reduced efficiency [7]. The effects of low energy implantation of hydrogen [8] were visible in Raman and photoluminescence spectra but the device results were not conclusive.

CIS has a band-gap energy E_g of about 1.5 eV, which is at or already slightly above the optimum value for single junction solar cells and the standard solar spectrum (AM 1.5). Incorporation of gallium increases the band-gap energy of the material, which – in this simple view – should decrease the cell performance. In practice, however, incorporation of gallium has evolved as the most consistent approach to improve the efficiency. In our initial

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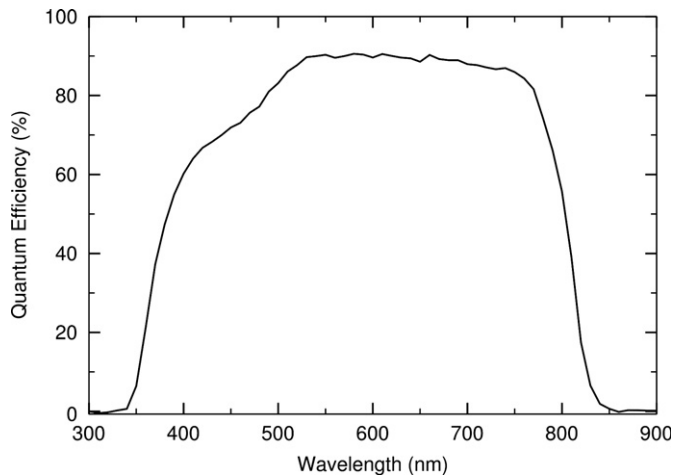


Fig. 1. External quantum efficiency of a MgF/ZnO/CdS/CIGS cell (data certified by ISE Freiburg).

work we had used various lab scale processes using evaporated metal precursors and rapid thermal processing in Ar/H₂S or conventional slow thermal processing in a sulphur beam. It was already observed in this work that the open circuit voltage as a function of the effective band-gap energy exceeds the linear dependency for the best cells and for small contents of gallium in the cell's active region. Therefore, the efficiency increased notwithstanding the inferior match to the solar spectrum. In an effort to examine the efficiency potential more precisely we switched to multi-source evaporation and achieved a confirmed efficiency of 12.3% [9]. After the CIS technology had been successfully scaled up we proceeded to study the incorporation of gallium in the baseline process. The complex reaction kinetics (see absorber film formation below) made this a challenging task; however reasonable process stability and a confirmed efficiency of 12.8% [10] have now been achieved. CIS cells have always shown excellent minority carrier transport and this property is preserved with the gallium incorporation as can be deduced from the quantum efficiency shown in Fig. 1. Efforts are already under way to transfer the technology to industrial production [11].

3. Absorber film formation

3.1. Multi-source evaporation

In contrast to the selenides, CuInS₂ and related films are usually prepared under Cu-rich conditions throughout or at least towards the end of the process. The reasons for this are discussed in our previous review [1]. The most straightforward preparation method is the simultaneous evaporation of the elements at constant rates onto a heated substrate. While this can result in reasonable film properties [12] it is not the optimum approach regarding complete segregation of the Cu_xS secondary phases to the surface. Walter et al. [13] proposed a modified recipe, where the evaporation of indium and sulphur in the first stage (typically at reduced substrate temperature) is followed by a second stage, where copper and sulphur are evaporated. An important feature of this process is re-crystallization of the film approximately at the point where the total Cu content of the film exceeds molecularity ($[Cu]/[In] > 1$). It is believed that this helps in driving the secondary phases to the surface. Re-crystallization was deduced *ex-situ* from samples quenched at various points in the process.

We have followed a similar approach for the preparation of Cu(In,Ga)S₂ (CIGS) [9]. Here, re-crystallization [14] is of even higher

significance because it not only establishes morphology and proper Cu_xS segregation to the surface, but also influences the gallium depth distribution. It results in a layered structure of CIS on top of CuGaS₂ (CGS), which is not necessarily desirable. The top layer contains just a little bit of gallium, which increases the band-gap energy by about 30 meV. The driving force for re-crystallization can be reduced by adding some copper already in the first stage and/or by eliminating the substrate temperature difference between the two stages. This results in a more homogeneous gallium depth distribution and the active region band-gap energy can be increased by up to 250 meV, which is relevant for the evaluation of top cells for tandem structures. The process was modified further in order to prepare films with band-gap grading towards the back as well as front surface, similar to that resulting from the three-stage recipe used for the best CIGSe cells [15]. While such band-gap grading could be achieved, a further increase in efficiency was not observed [16]. Another modification consisted of adding a third stage to the process to remove the Cu excess and related secondary phases [17]. This process eliminates the need for chemical etching of the secondary phases but goes against the general strategy to maintain Cu excess throughout the preparation. It therefore resulted in inferior device properties. Nevertheless, an efficiency of 9.3% could be achieved when films were annealed *in-situ* in sulphur and oxygen.

3.2. Reactive annealing

Film formation in the sequential processes (sulphurisation of metal precursors) has been investigated by quenching as well as *in-situ* analysis. We have evaporated precursors [18] but typically use sputtered precursors consisting of one layer of copper and one layer of indium. In early development sulphur was supplied by a Knudsen source; the precursors were heated using a conventional substrate heater and the process took from 10 min up to 1 h (conventional thermal processing, CTP). In the current process [19], sulphur powder and precursors are heated simultaneously by halogen lamps and the hold time is typically 3 min (rapid thermal processing, RTP). In gallium-free films the reaction sequence is very similar for evaporated and sputtered precursors, in CTP and RTP. It is also relatively straightforward [20]—copper and indium react quickly to form CuIn₂ during evaporation, sputtering or precursor storage. More Cu-rich phases such as Cu₁₁In₉ or Cu₁₆In₉ are formed when ramping up the temperature. Ideally, these phases react with the sulphur vapour to directly form a chalcopyrite compound without intermediate binary sulphides or CuIn₅S₈. Excess copper reacts first to form Cu₂S and, during cool-down, forms CuS if the sulphur pressure is sufficient. There are indications that Cu₂S formation triggers re-crystallization of the film, in analogy to what has been observed in multi-source evaporation. More recently, it has become feasible to study Cu_xS-induced re-crystallization in real time and *in-situ* [21]. Real time monitoring of domain size by X-ray diffractometry can be used to interrupt re-crystallization in different stages in order to further analyse intermediate states by *ex-situ* methods [22].

The addition of gallium to the precursor leads to significantly more complex reaction sequences and more significant differences between evaporated and sputtered precursors and among the different sulphurisation methods. However, we can still distinguish the following three distinct parts of the reaction sequence: alloying of precursors, incorporation of sulphur and re-crystallization. Two chalcopyrite phases, with compositions very close to CuInS₂ (at the surface) and CuGaS₂ (at the back contact), are typically formed during the second part. Some interdiffusion occurs in the third part resulting in the final gallium depth profile.

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