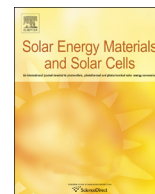




ELSEVIER

Contents lists available at SciVerse ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Recent trends in direct solution coating of kesterite absorber layers in solar cells

Y.E. Romanyuk^{a,*}, C.M. Fella^a, A.R. Uhl^a, M. Werner^a, A.N. Tiwari^a, T. Schnabel^b, E. Ahlswede^b^a Laboratory for Thin Films and Photovoltaics, Empa—Swiss Federal Laboratories for Materials Science and Technology, 8600 Dübendorf, Switzerland^b Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg (ZSW), 70565 Stuttgart, Germany

ARTICLE INFO

Keywords:

Kesterite
Cu₂ZnSn(S,Se)₄
CZTS
Non-vacuum deposition
Direct solution coating
Thin film solar cell

ABSTRACT

This review describes a specific group of non-vacuum methods for depositing kesterite solar cell absorbers, which we refer to as *direct solution coating* (DSC). These methods work by coating a layer of precursor-containing *solution* on the surface of a substrate followed by appropriate thermal processing to yield the desired kesterite Cu₂ZnSn(S,Se)₄ phase. General aspects, challenges and future prospects of the DSC are discussed in detail. Two research highlights are presented in which kesterite layers are processed from solutions of metal salts in simple non-toxic organic solvents to yield up to 7.5% efficient solar cells.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Kesterites – the family of compounds comprising Cu₂ZnSnS₄ (CZTS), Cu₂ZnSnSe₄ (CZTSe) and associated alloys – are certainly one of the most intriguing absorber materials for thin-film solar cells today. They may offer low-cost manufacturing starting from abundant and non-toxic materials, provided that the optoelectronic characteristics of kesterite solar cells are better understood and can be further improved [1,2]. Kesterite thin films can be prepared by a variety of deposition methods resulting in different material qualities and solar cell efficiencies. The current record efficiency of 11.1% is reported for a Cu₂ZnSn(S,Se)₄ (CZTSSe) absorber processed with a mixed solution-particle approach in hydrazine solvent [3]. Other notable results include 9.3% efficiency for CZTSSe by co-sputtering with post-annealing in SnS and S [4], 9.15% for CZTSe by co-evaporation [5], 8.4% for CZTGeS₂ sintered from nanoparticle inks [6], 7.3% for CZTS by electroplating metal precursors with post-sulfurization [7], and recently, 7.5% for CZTSSe processed from a metal salt solution in dimethyl sulfoxide (DMSO) followed by selenization [8]. Several recent reviews summarize the state of the art in non-vacuum processing of kesterites [1,9], the current understanding of the defect physics [10], as well as general aspects of the emerging kesterite solar cell technology [1,2,11,13].

CZTSSe can only be a reasonable alternative to the established Cu(In,Ga)Se₂ (CIGS) technology if the cell efficiencies reach nearly the same values, i.e. in the range of 20% in the laboratory. Lower efficiencies are acceptable only if the overall cost per watt is significantly lower. As the cost of the absorber material contributes only a minor part in today's vacuum-based CIGS solar module manufacturing and system costs, the replacement of the expensive indium and gallium must also be accompanied by a cost-effective and simple production route. This means low cost precursor materials and high throughput processing methods have to be combined for development of high efficiency CZTSSe solar module production. It is hence very encouraging that the rapidly progressing CZTSSe technology already achieves similar efficiencies for devices processed with both traditional vacuum and for non-vacuum approaches.

In this paper we focus on the specific group of non-vacuum deposition methods that work by coating a layer of precursor-containing *solution* on the surface of a substrate followed by appropriate thermal processing to yield the desired kesterite phase. We refer to this group of methods as *direct solution coating* (DSC) in analogy with the expression “direct liquid coating” seen in publications from the IBM group e.g. [9], or the often used expression “chemical solution deposition” (CSD) [14]. There are several reasons why we would like to limit our considerations only to the direct coating of solutions:

- This approach offers all advantages of non-vacuum deposition such as the possibility to use low-cost and high-throughput equipment, low wastage of raw materials, high uniformity of

* Corresponding author. Tel.: +41 58 765 4169; fax: +41 58 765 1122.

E-mail addresses: yaroslav.romanyuk@empa.ch, yaroslav.romanyuk@gmail.com (Y.E. Romanyuk).

- layer properties over large area and finally, potential deployment of large-scale production with low capital investment.
- In contrast to the other popular solution-based techniques for kesterites such as chemical bath deposition (CBD) [15,16], electrodeposition (ED) [7], successive ionic layer absorption and reaction (SILAR) [17], and spray pyrolysis [18,21] which imply a slow growth of the kesterite phase during the actual deposition step, the DSC techniques such as spin-, spray-, dip-, knife-, and curtain-coating, as well as printing techniques like ink-jet, flexography, and gravure allow fast coating of the wet layer with low wastage of the precursor solution.
 - As compared to nanoparticle-based inks, solutions offer the following benefits: (i) no need for pre-synthesized nanocrystals; (ii) readily available, cheap metal salts with high purity and long storage time; and (iii) reproducible processing with a homogeneous intermixing of constituent elements on the molecular level.

It is important to note that the nucleation of nanoparticles can also occur in an initially homogeneous precursor solution leading to the formation of a colloid sol, especially if the solution constituents favor condensation and redox reactions. This fact blurs out the clear division between true solution and colloidal dispersion approaches. In this paper we will focus on homogeneous precursor solutions prepared without any pre-synthesized nanoparticles, not excluding the possibility of the in-situ formation of colloidal aggregates.

The DSC approach obviously has its own challenges and limitations. The most critical issues are: (i) the absolute need for a high-temperature annealing step, preferably in a chalcogen-containing atmosphere; (ii) the adequate chemical coordination of metal species in coated precursor layers to prevent undesirable metal segregations and metal losses during a subsequent thermal treatment; (iii) unwanted effects associated with the drying of a wet film such as increased layer porosity, cracking and delamination; (iv) possible contamination with solvent elements and unwanted residuals of the initial precursor solution. Here we present a critical assessment of the most important aspects of the DSC and describe two research highlights in which kesterite layers are processed from solutions of metal salts in simple non-toxic organic solvents to yield up to 7.5% efficient solar cells.

2. General aspects of DSC of kesterites

The DSC of kesterites involves several steps starting from solution formulation and finishing with high-temperature annealing to yield the desired crystalline CZTS(Se) layer. Fig. 1 represents a typical DSC procedure that includes the preparation of precursor solution, coating of a wet film, drying, and a final annealing step for chemical reaction and crystallization. It is important to note that coating and drying steps can be repeated to obtain multilayer structures. This is often required to build up layer thickness, but also can be used for improving layer homogeneity and creating intentional compositional gradients in the multilayer precursor coating. During each step, a variety of parameters have to be controlled as discussed below in the individual sections.

2.1. Solution formulation

2.1.1. Solvent

The solvent is one of the most critical components and is often used to name a particular DSC approach in the scientific community, e.g. “hydrazine route” or “DMSO route”. Two primary requirements on the solvents are: (i) to dissolve Cu-, Zn-, Sn-, and, if possible, chalcogen-containing compounds, and (ii) not to leave

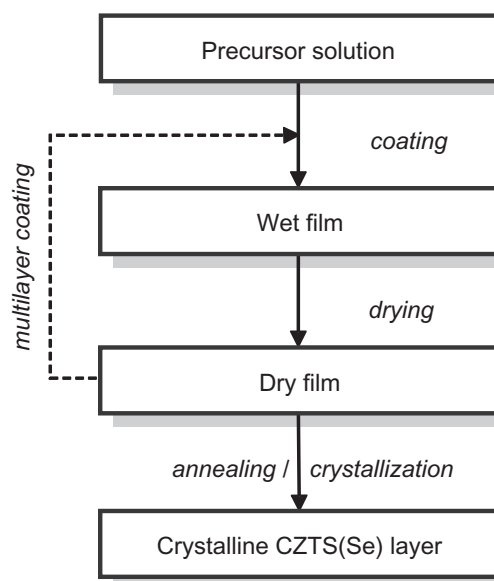


Fig. 1. Processing steps in direct solution coating of a kesterite layer, including a possibility of multilayer coating.

any detrimental impurity elements in the CZTS(Se) layer after the annealing step. There are many secondary factors that should be considered such as surface tension, volatility, reactivity, toxicity, and cost. Only polar solvents have been used for the DSC of kesterite due to the ionic nature of the metal compounds to be dissolved. An ideal solvent for DSC should be able to coordinate metal cations in the precursor solution by forming soluble complexes which, however, should fully decompose during the heat treatment without leaving unwanted impurities.

Water is certainly the cheapest, safest and most environmentally friendly solvent. There is, however, only one report of water being employed as the solvent for spin-coating water-ethanol solution of metal salts and thiourea to obtain CZTS layers on glass substrates [22]. Many salts of Cu and Sn readily hydrolyze in water and thus induce high solution acidity ($\text{pH} < 2$) that can corrode not only the molybdenum-coated substrate but also certain metallic parts of the coating equipment. Water molecules coordinate metal cations only weakly, so that hydrated salts of Cu, Zn, or Sn release water upon the drying step well below $300\text{ }^\circ\text{C}$. Handling of dried metal salt precursors under ambient conditions is problematic, because anhydrous salts of Cu, Zn, and especially Sn are hygroscopic and therefore intensively intake the moisture from air resulting in re-crystallization and undesired segregations. In addition, salts of Sn(IV) can easily evaporate upon annealing or even during drying (e.g. SnCl_4 has a low boiling point of $114\text{ }^\circ\text{C}$), which leads to a decrease of Sn content if no additional stabilizers are used. Two other issues with water as the solvent are the high surface tension, often leading to poor wetting, and its tendency to introduce oxygen impurities.

Hydrazine (N_2H_4) is the carbon- and oxygen-free compound that can be considered as an ideal solvent because it dissolves metal chalcogenides and elemental chalcogens (sulfur and selenium) and excludes the introduction of any detrimental impurity elements by decomposing cleanly into N_2 , NH_3 , and H_2 . Another important feature of hydrazine is its strong reducing action that prevents any metal oxidation [9]. The hydrazine route was developed by the IBM group [23] to achieve the current highest efficiency of 11.1% for a CZTSSe absorber [3]. The IBM hybrid route foresees, however, the formation of ZnS(Se) nanoparticles because of the low solubility of ZnS(Se) in N_2H_4 . Since this hybrid approach is beyond the scope of this review we refer the interested reader to

Download English Version:

<https://daneshyari.com/en/article/6535975>

Download Persian Version:

<https://daneshyari.com/article/6535975>

[Daneshyari.com](https://daneshyari.com)