



Cu(In,Ga)Se₂ absorbers from stacked nanoparticle precursor layers

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ABSTRACT

The following paper presents a processing route for Cu(In,Ga)Se₂ absorber layers that is based on nanoparticle dispersions which are applied by doctor blade deposition and converted with elemental selenium vapors. In particular, the preparation of the precursor layers is investigated by systematically assessing the influence of the stacking sequence of mono- and multi-metallic layers on sintering, elemental distribution and solar cell efficiency. By applying suitable stacking sequences, precursor layers with both local Cu-rich and over-all Cu-poor stoichiometry could be prepared that allowed improved sintering properties and modifications of the gallium gradient. Despite the still prevailing porosity of the absorber layer, solar cells with efficiencies exceeding 5% could be obtained.

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1. Introduction

Solar cells based on Cu(In,Ga)Se₂ (CIGS) absorber layers have shown the highest efficiency amongst all thin film technologies [1]. For record devices the absorber layer is typically deposited via co-evaporation method from the elements, allowing for the controlled deposition of high purity layers. Most research groups follow the “three stage process”: first, a (InGa)_xSe_y compound is deposited; this is followed by the deposition of Cu and Se until the film has an overall Cu-rich composition; and finally, In and Ga are added to bring the composition back to Cu-deficient [2,3]. The efficiency gain has been attributed to both electronic and structural reasons: the formation of a double Ga-gradient that exhibits enhanced solar light absorption due to a low minimum band gap, increased minority carrier collection at the back contact due to the introduction of a back surface field, and an improved open circuit voltage (V_{OC}) due to an elevated built in voltage at the front contact. Structurally, it was shown that the Cu-rich growth phase results in an improved grain size and morphology [2–6].

In contrast to that, a single graded absorber is typically obtained for selenization processes. The higher Ga/III content near the back contact is formed spontaneously due to different formation rates of CIS and CGS during a selenization process that is initiated from the top [6,7]. Overcoming this limitation, researchers have widened the absorber band gap at the surface by post sulfurization treatments, but highly reactive gases, i.e. H₂S, had to be utilized to ensure the anion substitution [8,9]. Selenization processes of sputtered or

printed precursor layers have gained wide attention at an industrial scale due to favorable large scale uniformity. Printing processes in particular excel with low capital investment, high throughput, and high material utilization. Both solutions and particle dispersions have been employed and have shown remarkable efficiencies up to 15.2% [10] and 17.1% [11,12]. However, toxic and explosive solvents or gases often have to be employed for complete dissolution or conversion/reduction of metal oxide particles.

In this paper, we present a process based on the conversion of hydroxide particles by selenium vapors. The chemical coordination of the particle and a deposition method of multiple “stacked” precursor layers with varying chemical composition allowed improved sintering and fabrication of a double Ga-gradient while omitting the use of H₂ or H₂Se/H₂S gases.

2. Experimenta details

Nanoparticles of hydroxides were synthesized using chemical means. The reaction product was dried to obtain fine powders of carefully controlled residual hydroxide content. Based on Hansen parameter studies, a polymeric dispersant of the AB copolymer type was selected. To formulate precursor inks, the powders were dispersed in butyl glycol acetate (BGA) by milling technique. The solid load in the dispersions was fixed to 20–25 wt.% with 15–20 wt.% dispersant relative to the solids. The particles exhibited a mass median diameter (D50) between 50 and 100 nm as obtained by dynamic light scattering method. Three individual nanoparticle inks based on Cu-, In-, and Ga-hydroxides were employed, allowing the stoichiometric adjustment of the final precursor layer by means of adequate mixing ratio or sequential processing. In the standard

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process, the composition was tailored to be $\text{Cu/III} = 0.80$ and $\text{Ga/III} = 0.25$, as confirmed by XRF measurements. The dispersions were deposited by knife coating technique on molybdenum coated glass slides heated to 80°C , with a substrate to knife distance of $50\ \mu\text{m}$, and a blading speed of $50\ \text{mm/s}$. The obtained precursor film was dried at 200°C for 3 min and subsequently selenized in a two-temperature zone selenization furnace as previously described [13].

For multilayer deposition, the drying and deposition step was repeated three times with varying precursor inks at a reduced substrate to knife distance of 20, 20, and $10\ \mu\text{m}$. The selenization time at 550°C was 35 min. Selenized films were treated by KCN etching step to remove any residual Cu–Se binary phases and then coated by a $\sim 50\ \text{nm}$ thick buffer layer of CdS that was deposited by chemical bath deposition. The solar cell was finalized by RF-sputtering of a i-ZnO/ZnO:Al window layer and mechanical scribing to $9\ \text{mm}^2$ cell area. The current voltage characteristic was then measured at simulated AM1.5 solar irradiation under standard test conditions.

Morphological and compositional analyses were conducted using X-ray fluorescence spectroscopy (XRF) from a rhodium target at 45 kV, powder X-ray diffraction (XRD) on a Siemens D5000 diffractometer with Ni-filtered Cu-K α radiation, scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) on a Hitachi S-4800, time-of-flight secondary ion mass spectroscopy (ToF-SIMS) by a ION-TOF TOF.SIMS 5 ION-TOF using Bi $^+$ as the primary ion for the analysis (25 kV, 1 pA, $100 \times 100\ \mu\text{m}^2$) after a two second sputter cycle with O $^{2+}$ for the depth profile analysis (2 kV, 400 nA, $300 \times 300\ \mu\text{m}^2$). Inductively coupled plasma mass spectrometry measurements (ICPMS) were performed with an Agilent 7500cs ICPMS with Merck ICPMS single element standards (0.1–10,000 $\mu\text{g/l}$). In-situ XRD was carried out using a PANalytical X'Pert Pro MPD system in grazing angle geometry at an incident angle of 10° . The substrate heating at 5°C/min was done with an Anton-Paar XRK 900 heating chamber. Surrounding Se pellets, a Se top layer as well as a graphite dome covering the sample ensured sufficient Se supply during the measurement. The graphite dome, however, contributed to the obtained diffractograms with additional carbon reflections (PDF No. 26-1079).

3. Results and discussion

3.1. Morphological comparison of stacks and mixtures

Hydroxide nanoparticle inks were used in this study to omit the need of H $_2$ reduction while being able to achieve complete conversion by means of elemental Se vapors. This concept was proven by EDX measurements of selenized films that resulted in stoichiometric amounts of selenium with no detectable amounts of residual oxygen and carbon (dried precursor: C = 15 at.%, O = 60 at.%, selenized film: C = 0 at.%, O = 0 at.%). Absorber layers from these mixed precursors, however, appeared porous with small grain size and micro cracks, as seen in Fig. 1a.

While a copper-rich growth phase is commonly used in vacuum deposition of CIGS to improve grain growth, less research has been carried out for nanoparticulate precursors. To mimic the idea of a copper-rich growth phase while keeping an overall Cu-poor stoichiometry to avoid shunting Cu–Se segregations, a multilayer approach was studied. In the latter, a locally Cu-rich layer in form of a Cu-precursor film was surrounded by a top and a bottom layer of mixed Ga and In precursors. In comparison to results from mixed particle precursors, it is apparent in Fig. 1b that the morphology significantly changed. Cross-section SEM images reveal a porous intermediate layer at the position of former Cu-precursor. While top-view SEM pictures indicate improved sintering of the top layer, large grained segregations of CuInSe $_2$ and Cu $_{2-x}$ Se – as confirmed by EDX – appear on the surface. It should be noted that the overall stoichiometry as obtained from ICPMS measurements from selenized precursors was $\text{Cu/III} = 0.80$, $\text{Ga/III} = 0.25$ for the mixture and $\text{Cu/III} = 0.74$, $\text{Ga/III} = 0.25$ for the stack, showing that improved sintering was feasible even though a lower Cu-content was present.

3.2. Reaction kinetics with in-situ XRD

To further elucidate the origin of morphological changes, in-situ XRD measurements have been conducted for both mixed and stacked precursors. Fig. 2 shows the temperature evolution of the respective

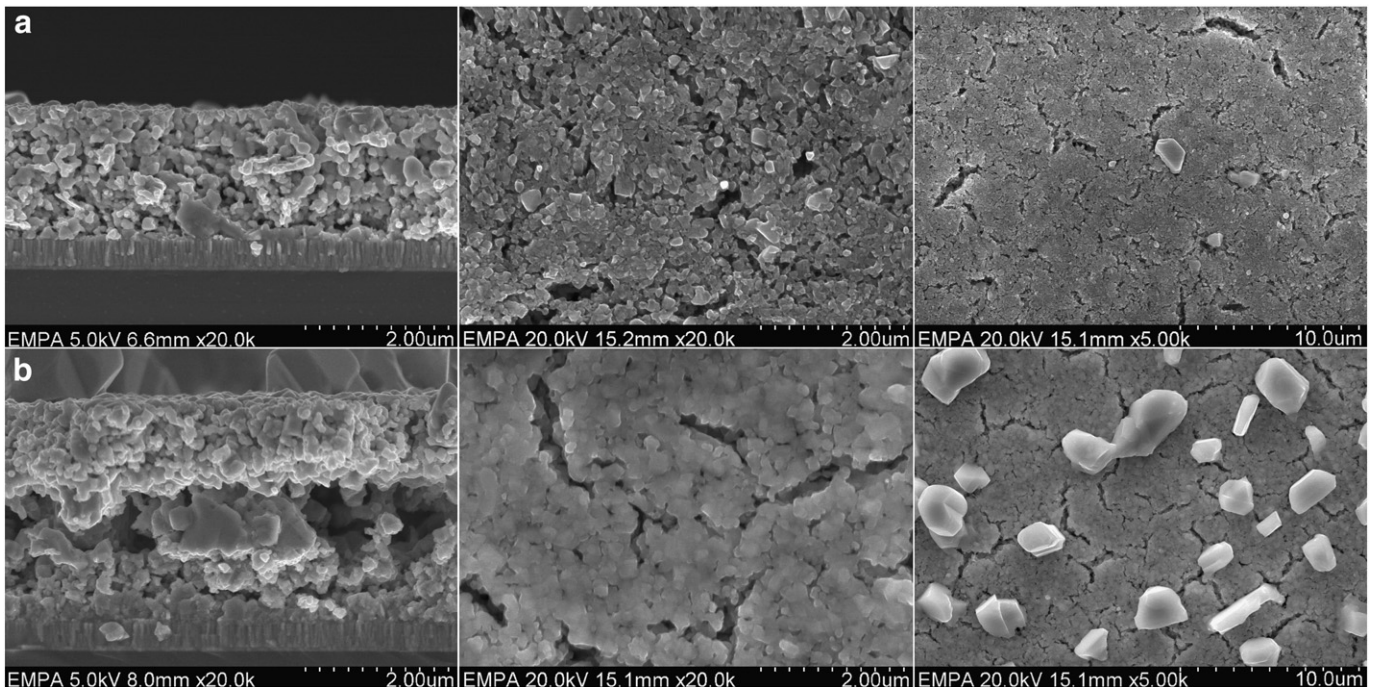


Fig. 1. Top-view and cross-section scanning electron micrographs of selenized precursor layers on Mo coated soda–lime glass substrates. Absorber from mixed metal precursors (a) results in porous morphology with small crystallites whereas absorbers from stacked precursor layers (b) exhibit the formation of a porous intermediate layer at the position of Cu-precursor. As the crystallites in the latter case increase, large grained segregations of CuInSe $_2$ and Cu $_{2-x}$ Se – as confirmed by EDX – appear on the surface.

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