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Non-vacuum deposition of Cu(In,Ga)Se₂ absorber layers from binder free, alcohol solutions

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Abstract:

Non-vacuum methods for Cu(In,Ga)Se₂ (CIGS) absorber deposition have gained wide interest due to their inherent cost and energy saving potential. Here, a solution-based processing route for CIGS absorber layers is presented that employs binder-free solutions of metal salts in non-toxic, alcohol solvents. Despite the low-boiling-point nature of the employed solvents, a residual carbon-rich layer is observed between the CIGS and metal back contact. Based on comprehensive investigations by SEM, EDX/WDX, XRF, XRD, TGA, DTA and EXAFS, a formation reaction mechanism through intermediate metal-organic complexes is proposed. In this route, the CIGS layer is formed in selenium atmosphere via a gradual decomposition of the carbon-rich layer comprising carboxylic chelate complexes of metals. A compositional gradient occurs in the CIGS absorber whereas a significant amount of metals remains in the carbon-rich layer. The incorporation of Ga into CIGS is affected by the initial salt concentration and the selenization temperature. Fabricated solar cells exhibit active area efficiencies of up to 7.7% on 0.3 cm² area without AR-coating, which is amongst the highest reported efficiencies for solar cells from a solution process with non-explosive gases or solvents.

Keywords:

non-vacuum deposition, true solution, binder, CIGS, chalcopyrite, thin film solar cell

Abstract figure:

WDX line-scan of a solar cell with solution-processed CIGS absorber layer. Despite the use of low-boiling-point solvents, a residual carbon-rich layer is obtained. For the absorber layer, a compositional gradient from Cu- and Ga-poor at the surface to Cu/III = 1 and Ga/III = 0.2 towards the back contact can be detected. The carbon layer contains significant quantities of unreacted Cu and Ga. A formation mechanism for the observed carbon layer is proposed.

1. Introduction

Cu(In,Ga)Se₂ (CIGS) solar cells have demonstrated the highest conversion efficiencies of all thin film technologies at 20.3% [1]. Current state-of-the-art deposition methods for high efficiency cells are mainly based on vacuum methods, i.e. sputtering or co-evaporation from elemental sources. These techniques achieve a controlled deposition of high purity films, yet exhibit limitations during industrial scale-up and cost reduction. In that respect, non-vacuum methods offer several advantages due to their inherent low investment requirements, large area uniformity, high throughput, improved material utilization from 40-70% (evaporation/sputtering) to >90%, and potentially lower energy requirements.

Previous work, based on a printing method, has shown the potential of non-vacuum methods by yielding up to 14.5% efficiency solar cells from nanoparticle inks [2-4]. Production, stabilization, and toxicity of the nanoparticles, as well as their reduction and conversion, often involving explosive and/or toxic gases such as H₂ or H₂Se, have to be managed. True solution approaches that exhibit improved intermixing at a molecular level as compared to nanoparticles, yielded up to 13.6% efficiency by Mitzi et al. with highly reactive hydrazine solvent [5]. Using non-toxic solvents Kaelin et al. showed 6.7% efficient cells with ethyl cellulose as binder material that resulted in a carbon layer between absorber and back contact [6]. In order to avoid the carbon layer formation we previously investigated polymethyl methacrylate (PMMA) as an alternative binder material with improved decomposition properties. While no carbon layer was obtained, porous absorber films limited efficiencies to 3.1% [7].

In this paper, we investigate binder-free solutions from alcohol solvents that are capable of coordinating metal cations with carboxylic chelate complexes and prohibit hydrolysis, segregation, and metal loss during processing. The weak bonding nature

of the complex enables selenization by a mild selenization route employing elemental Se vapors.

2. Experimental

Unless stated otherwise, the precursor solutions were prepared by dissolving $\text{Cu}(\text{NO}_3)_2 \cdot 2.5 \text{H}_2\text{O}$ (99.99%, Sigma-Aldrich) with InCl_3 (99.99%, Alfa Aesar) and $\text{Ga}(\text{NO}_3)_3 \cdot x \text{H}_2\text{O}$ (99.999%, Alfa Aesar) in ethanol (ACS, Merck) and 1,2-propanediol (99.5%, Sigma-Aldrich). The molar ratio of Cu/In/Ga was 1/0.9/0.4 with a total molar metal concentration of 0.9 M. The mixture of solvents enables adequate adjustment of solubility, viscosity, wetting, and drying characteristics of the paste and was adjusted to be 25 %vol. ethanol and 75 %vol. 1,2-propanediol. The obtained viscous pastes were homogenized by constant stirring for a few days prior to deposition. Knife-coating with a substrate to knife distance of 50 - 60 μm was used to deposit wet films on molybdenum coated soda-lime glass substrates. The $\sim 600 \text{ nm}$ thick molybdenum layer was deposited by conventional DC-sputtering. The wet film was then dried in ambient atmosphere both under a heating lamp at 140°C and on a hot plate at 220°C for 2 minutes, respectively. Interference fringes on the dried precursor indicate a smooth morphology of the obtained films. The obtained precursor films are subsequently selenized in a two-zone temperature furnace with elemental Se vapors and N_2 carrier gas at a pressure of 10 mbar. The selenization temperature and time was 600°C for 20 minutes.

The CIGS absorbers were then processed to solar cells by applying a $\sim 50 \text{ nm}$ thick CdS buffer layer by chemical bath deposition (CBD), radio-frequency sputtering of a i-ZnO/ ZnO:Al window layer (TCO) and e-beam evaporation of Ni/Al/Ni grid lines. Prior to the CBD deposition a KCN etching step was applied to remove any potential binary Cu-Se phases. The solar cell area was then defined to 0.3 cm^2 by mechanical scribing. Current-voltage (I-V) and quantum efficiency (QE) measurements were performed under standard test conditions (AM 1.5G spectrum, 1000 W/m^2 , 25°C).

Compositional and structural characterization was conducted by energy dispersive x-ray fluorescence (XRF) from a rhodium target at 45 kV, x-ray diffraction (XRD) with a Siemens D5000 diffractometer with Ni-filtered $\text{K}\alpha$ radiation at 0.154 nm , and scanning electron microscopy (SEM) with energy dispersive x-ray spectroscopy (EDX) by a Hitachi S-4800. The average grain size was estimated from SEM pictures with the software Lince v2.31. For the wavelength dispersive x-ray spectrometry (WDX) line-scan measurement, a Hitachi SU-70 was used with an acceleration voltage of 5 kV to obtain surface sensitive information in the range of 100 nm . Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) measurements were performed with a Netzsch STA 409 CD thermo balance coupled to a Netzsch QMS 403 C Aeolos mass spectrometer. The temperature ramping was $5^\circ\text{C}/\text{min}$ with a gas flow rate of $50 \text{ ml}/\text{min}$ in synthetic air or nitrogen. Extended X-ray absorption fine structure spectroscopy (EXAFS) was used as a sensitive technique for probing atomic coordination chemistry of a selected metal element in the precursor layer, Ga in this case. The Ga K-edge EXAFS measurements of the dried

precursor films were performed at the microXAS beamline from the Swiss Light Source. The spectra were collected in fluorescence mode, in air, and at room temperature, using an X-ray beam of 0.6 mm² in size. Data normalization treatment and fitting procedures were carried out using Athena/Artemis software packages [8].

3. Results and Discussion

3.1. Composition and stoichiometry of selenized precursors

Low-boiling-point alcoholic solvents without binder components – $T_B(\text{ethanol}) = 78^\circ\text{C}$ and $T_B(1,2\text{-propanediol}) = 188^\circ\text{C}$ [9] – were used in this study. Two precursor solutions were prepared with varying metal concentration of 1.4 M and 0.9 M. The cross-section and top-view scanning electron micrographs are shown in Fig. 1. As also manifested by the XRD reflection pattern, crystalline grains of phase pure CIGS can be obtained for both concentrations. Despite lower molarity from Fig. 1a to 1b, average grain size increased from 880 ± 200 nm to 1450 ± 520 nm. The cross-section SEM reveals the formation of an additional layer between Mo and CIGS layer that is comprised of 40 - 60 at.% carbon, as confirmed by EDX. This carbon-rich layer decreases from about 1100 nm to 700 nm with decreasing molarity, even though the same amount of organics was added to the solution. Also, it was seen that the ratio of 1,2-propanediol in total solvent could be altered from 100 %vol. to 5 %vol. with negligible change in carbon layer thickness. The complete removal of 1,2-propanediol resulted in porous, carbon free layers with low amount of CIGS phase. Thus, it is suggested that 1,2-propanediol forms an intermediate compound with the precursor metals that helps in the CIGS formation process, however, might lead to the formation of a residual carbon layer.

Fig.1. Top-view and cross-section scanning electron micrographs of selenized precursor layers on Mo coated SLG substrates. As confirmed by EDX measurements, a carbon-rich layer (C = 40 - 60 at.%) is obtained between absorber and Mo back contact. As the molarity of metals in the precursor paste was lowered from 1.4 M (a) to 0.9 M (b), the average CIGS grain size increased and the thickness of the carbon-rich layer decreased.

Fig.2. X-ray diffraction patterns of the CIGS (220/204) reflection for varying selenization temperatures and precursor compositions. The inset and top-axis shows precursor and selenized absorber compositions, respectively. Better crystallinity and gallium incorporation can be obtained for higher selenization temperatures.

Highest efficiency CIGS solar cells are obtained with a band gap of around 1.2 eV which corresponds to Ga/III ratio of 0.3 [1]. An increasing gallium incorporation in the CIS crystal structure will lead to a progression to higher angles in 2θ . Fig. 2 shows XRD patterns of the CIGS (220/204) reflection for precursors with varying $x = \text{Ga}/(\text{In}+\text{Ga})$ ratios and different selenization temperatures 550 and 600°C. The precursor ratios were measured by XRF prior to selenization and ranged from $x = 0 - 0.6$. Comparing precursor and absorber composition, it becomes apparent that all absorbers contain significantly less gallium than was initially measured for the precursor. For a precursor stoichiometry of $x = 0.3$, an increase in selenization temperature from 550°C to 600°C resulted in a increased gallium incorporation and a more pronounced CIGS peak on XRD pattern.

Fig.3. WDX line-scan from a cross-section of a completed solar cell with non-vacuum deposited absorber layer. The normalized metal fractions of Cu, In, Ga are given in at.%. A compositional gradient in the absorber from Cu- and Ga-poor at the surface to $\text{Cu}/(\text{In}+\text{Ga}) = 1$ and $\text{Ga}/(\text{In}+\text{Ga}) = 0.2$ towards the back contact can be detected. The carbon layer contains significant quantities of unreacted Cu and Ga.

A line-scan of a solar cell cross-section was measured by WDX (Fig. 3) which allowed good resolution at low acceleration voltage of 5 kV and thus surface-

sensitive information in the range of 100 nm. The normalized metal fraction of Cu, In, and Ga for a solar cell with non-vacuum deposited absorber and efficiency of about 4 - 5% is shown in Fig. 3. This enables visualization of the compositional changes in the absorber layer. Starting from a Cu- and Ga-poor surface, the absorber becomes gradually more Cu- and Ga-rich and transitions to a composition of $\text{Cu}/(\text{In}+\text{Ga}) = 1$ and $\text{Ga}/(\text{In}+\text{Ga}) = 0.2$ towards the interface of the carbon-rich layer. Furthermore, a significant amount of Cu and Ga is detected in the carbon-rich layer. Cu and Ga are accumulating towards the absorber and Mo back contact, respectively. The Cu-poor surface is widely considered to be beneficial [10] and may have been obtained with KCN etching in this case. For two-step processes, a Ga-gradient towards the back contact is commonly observed and the resulting back-surface field considered beneficial for device performance [11,12]. The lower reactivity of Ga as compared to In can be used to explain the gradient [13], in addition to a lower diffusivity of Ga from the precursor layer as indicated by the high Ga content in the residual carbon-rich layer. The finding of unreacted Ga in the carbon layer is in agreement to previous XRD measurements showing an offset in Ga incorporation between absorber and precursor (Fig. 2).

3.2. Proposed reaction mechanism

To understand the formation of the carbon-rich layer in more detail, TGA and DTA measurements were conducted. In-situ mass spectrometry allowed volatile phases to be traced during the heat ramp up. Three model experiments with one representative cation – Cu^{2+} – were set up with various solutions and heating atmospheres to illustrate the effect of the oxidizing anion (NO_3^- vs. Cl^-) and oxidizing atmosphere (air vs. N_2), i.e. a solution of 1.5 M CuCl_2 (97%, Riedel-de Haen) in 1,2.-propanediol in N_2 (Fig. 4a), and solutions of 1 M $\text{Cu}(\text{NO}_3)_2$ in 1,2-propanediol in both N_2 (Fig. 4b) and synthetic air (Fig. 4c). Volatile species of mass 18 (Fig. 5a), mass 30 (Fig. 5b), and mass 44 (Fig. 5c) were simultaneously recorded.

TGA and the corresponding differential thermogravimetric curve (DTG) of Fig.4a show a single-step mass loss from 175 - 195°C with an endothermic character as seen by DTA. The main accompanied mass-fractions with weight losses are mass 18 - H_2O (Fig. 5a), mass 44 (Fig. 5b), and mass 30 (Fig. 5c) which are thought to stem from the decomposition of propanediol into hydroxymethyl group and acetaldehyde. This is to be expected and corresponds to the reported evaporation and decomposition of propanediol ($T_B = 188^\circ\text{C}$). From the molarity of solution the initial copper weight was calculated and compared to the residue (Fig. 4a inset). The observed increase in weight can be explained by the presence of copper chloride residues [14].

Fig. 4. TGA, DTG and DTA plots for solutions of 1,2-propanediol with CuCl_2 or $\text{Cu}(\text{NO}_3)_2$ in different atmospheres of N_2 or synthetic air, as indicated in the graphs. While for chlorides only a single mass drop from solvent evaporation is observed, the TGA/DTG of nitrates shows multiple weight losses in three steps. The formation and decomposition of a complex between oxidized propanediol and Cu-ions is suggested.

Fig. 5. In-situ mass spectrometry of mass recorded during the TGA measurements in Fig 4. Masses of 18, 30, and 44 correspond to volatile H_2O , NO/HCHO , and $\text{CO}_2/\text{CH}_3\text{CHO}$, respectively. Reaction mechanisms are proposed as indicated by the Roman numerals.

The behavior changes from a single-step to a three-step transition when the chloride anion is substituted by nitrate (Fig. 4b). While, similar to Fig. 4a, a mass loss appears at 188°C , Fig. 4b is differentiated by the occurrence of a second mass loss at lower temperatures around 150°C . Unlike the transition at 188°C , the character is exothermic (as seen by DTA) and accompanied by a loss in NO , CO_2 and H_2O . This indicates a possible oxidation reaction, where the nitrate ion oxidizes propanediol species into carboxylate anions. Moreover, a third mass loss is visible in TGA and DTA curves between $280 - 300^\circ\text{C}$ that involves the evolution of CO_2 . The amount of

residue is 4 % higher than the initial Cu amount and could be a mixture of organic residue and Cu.

Changing the ambient gas from N₂ to synthetic air (Fig. 4c) results in the equivalent transitions as obtained in Fig. 4b. However, the third mass loss is shifted to slightly lower temperatures, i.e. 270 – 275°C, and an exothermal peak stemming from the oxidation of Cu is visible in DTA. The weight of residue was increased by 7% of the initial Cu amount due to the formation of copper oxides.

Based on these measurements we propose the following reaction mechanisms:

I: Oxidation of propanediol by nitrate anions [15,16]:

II: Carboxylate complex formation [17]:

III: Decomposition of propanediol [18,15]:

IIIa:

IV: Decomposition of complex [16,17]:

We propose that similar reactions I-IV take place for all metal species, i.e. Cu^{2+} , In^{3+} and Ga^{3+} , in the process of drying and selenizing the Cu-In-Ga precursor. Nitrate ions in the initial solution and ambient oxygen and heat during the drying step promote the oxidation of propanediol into carboxylic anions. The formed metal carboxylate complexes decompose in Se containing atmosphere according to reaction IVa, and liberated metal species react with elemental Se to yield the CIGS layer.

To further prove this concept and reveal the nature of organometallic compounds present in the precursor layer, EXAFS technique was employed for probing the local atomic coordination of one representative metal element, Ga in this case. Fig. 6 presents the measured and fitted EXAFS oscillations of the Ga K-edge in (a) k -space, as well as in (b) R -space. Only the first nearest neighbor shell containing oxygen atoms has been considered in the fit. The best fit has been obtained for a number of 5.41 oxygen atoms, situated at 1.9595 Å from the Ga atoms. This atomic local environment for Ga is very similar to the Ga carboxylic chelate complex, where the Ga atoms are surrounded by 6 oxygen atoms at 2.01 Å.

Fig.6. (a) Normalized Ga K-edge EXAFS spectrum measured in fluorescence mode on the precursor films. The dotted lines represent the range of Fourier transformation, 2.2 – 12.0 Å⁻¹. (b) Pseudo radial distribution function around the Ga atoms. The dotted lines represent the range of inverse Fourier transformation, 1 ÷ 2.3 Å.

3.3. Solar cell performance

Absorber layers, prepared by the described deposition method, were processed to solar cells of 0.3 cm² size and their J(V) (Fig. 7) and QE(λ) (Fig. 8) were measured.

The highest efficiency obtained on active area and without anti-reflection (AR) coating was up to 7.7% (Fig. 7) which is amongst the highest reported efficiencies for CIGS absorbers from a solution process with non-explosive gases and/or solvents. The low series resistance is particularly noteworthy given the still prevailing carbon-rich layer between absorber and back contact. The significant amounts of Cu and Ga in the carbon-rich layer (Fig. 3) might improve the conductivity. From the cut-off at high wavelengths in $QE(\lambda)$ (Fig. 7) a band gap of 1.05 eV was calculated which corresponds to a still low Ga content of $Ga/(In+Ga) = 0.08$. This is in good agreement with XRD measurements (Fig. 2) of a precursor composition of $Ga/(In+Ga) = 0.3$ which was employed for this cell. The plateau between 540 - 760 nm and insetting losses for wavelengths higher than 800 nm suggest an absorber thickness of about 500 nm [19], which is also confirmed by SEM cross-section pictures.

Fig.7. Current-voltage measurement of a solar cell with non-vacuum deposited CIGS absorber layer. An active-area efficiency of up to 7.7% was obtained on 0.3 cm² area without AR-coating.

Fig 8. Active area $QE(\lambda)$ measurement of 7.7% efficient solar cell without AR coating indicates an absorber band gap of 1.05 eV.

4. Discussion & Conclusion

Residual carbon layers stemming from the binder material ethyl cellulose have been reported in the literature before [6,20,21]. Although numerous beneficial influences of ethyl cellulose such as adjustment of paste rheology, reduction of metal evaporation and segregation, preferential oxidation medium, and possible reduction of back contact recombination have been described in literature, TGA studies have shown that ethyl cellulose cannot be fully decomposed when heated in inert atmosphere to elevated temperatures [22]. Metal-organic complexes can have similar beneficial influences in that they stabilize the metal salts and avoid hydrolysis, segregation and evaporation prior to the conversion into CIGS. This enables paste preparation and deposition even at ambient conditions. Propanediol solvent can form strong chelate complexes with metal cations, and is known to fully decompose in both O₂ and inert atmosphere [16,17]. To form a homogeneous precursor solution and avoid oligomerization and precipitation of polymeric species, 1,2-propanediol instead of 1,3-propanediol is preferred [17,23].

A mechanism is proposed in which carboxylic anions coordinate metal species to form chelate complexes which later decompose to liberate metals to form the CIGS absorber film in the presence of selenium atmosphere.

TGA and DSC measurements indicate that carboxylic acids can be formed via an oxidation of propanediol by nitrate anions at temperatures around 150°C. These acids can then coordinate surrounding metals by carboxylic chelate complexes. For the case of Cu^{2+} , it was found that the complex decomposition takes place at around 280 - 300°C. This is a suitable temperature range given that released metal species can readily react with elemental selenium to form intermediate selenide phases. The formation of carboxylate complexes was proven by EXAFS for the Ga metal atoms.

For the employed processing conditions, SEM cross-section pictures with EDX analysis revealed a remaining carbon-rich layer between CIGS and Mo back contact. WDX measurements of this layer showed significant amounts of Ga and Cu that suggests an incomplete decomposition of complexes. A compositional gradient in the absorber layer with a Cu-poor surface and more Ga incorporation towards the back contact was also visible. This may be attributed to the differences in the respective metal reactivity with selenium [13] and different stability of metal complexes [24,25]. Comparison of XRD and XRF measurements confirmed lower Ga incorporation in the absorber than provided by the initial precursor. Higher selenization temperatures could improve crystallinity and Ga incorporation in CIGS.

Conclusions

CIGS layers were formed via the gradual decomposition of a carbon-rich precursor layer composed of metal carboxylate complexes. The formation of complexes was assisted by in-situ oxidation of suitable solvent molecules, i.e. 1,2-propanediol, capable of forming carboxylate chelate ligands upon oxidation. Despite the remaining carbon-rich layer, low band gap of 1.05 eV and CIGS absorber thicknesses of only 0.5 μm , conversion efficiencies of up to 7.7% were obtained. Further efficiency improvements could be expected with thicker absorber layers and an increased Ga incorporation. Although the carbon layer seems to provide an adequate electrical contact between the CIGS and the metal contact, its complete decomposition is desirable, which could be possibly achieved by selecting more thermally labile carboxylate ligands.

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