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Processing and Characterization of Vacuum-Free CuInSe₂ Thin Films from Nanoparticle-Precursors using Novel Temperature Treatment Techniques

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ABSTRACT

The objective of this work is the processing and characterization of a dense CuInSe₂ solar-cell-absorber-layer based on nanoparticulate precursors. Bimetallic copper-indium- and elemental selenium-nanoparticles were synthesized by wet-chemical processes and then dispersed in organic solvents as nano-inks. These inks were then printed into different layer-stacks on a molybdenum coated float-glass-substrate via doctor-blading. The temperature treatment to transform these layer-stacks into dense CISE thin films was investigated, using a face-to-face technique and mechanically applied pressure or the repetition of coating and annealing. All absorber layers were characterized with SEM, EDX and XRD. Dense, coarse grained CuInSe₂ layers with a thickness $\approx 7 \mu\text{m}$ were formed and the application of mechanical pressure shows potential to reduce thickness and sinter together the nanoparticles to large grains of ca. $3 \mu\text{m}$ in size. The face-to-face-annealing ensured keeping a stoichiometric ratio of $(\text{Cu}+\text{In}) / \text{Se} \approx 1$, and can help reducing the content of oxides, even when the annealing is performed in ambient atmosphere. With a repetition of coating and annealing, dense CISE layers could be produced at low temperature of only $350 \text{ }^\circ\text{C}$.

Keywords: CuInSe₂, solar cell absorber, nanoparticles, vacuum-free, face-to-face annealing, uniaxial pressure

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Introduction

Thin-film solar cells have promising properties as saving material and production costs and allowing flexible or semi-transparent solar cells when compared to crystalline silicon. Solar cells based on $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_y\text{S}_{2-y}$ (CIGSSe) achieved an efficiency of 21.7% [1] which top tier amongst all thin-film solar cells. The state-of-the-art procedure resulting in these best efficiencies is the co-evaporation of the elements onto a heated substrate to form CIGSSe [1,2]. Another route is a two-step stacked elemental layer and thermal annealing process [3,4]. First Cu-In-Ga layers are deposited by sputtering and Se by thermal evaporation, followed the annealing and sulfurization in H_2S atmosphere. Both process routes involve vacuum technology and high temperatures as well as dangerous and toxic chemicals like H_2Se and H_2S , which require additional efforts and costs for safe handling and waste disposal.

An alternative production route is the wet chemical synthesis of nanoparticles like metallic copper-indium [5,6], selenium [7,8], copper selenide [9] and indium selenide [10] which requires no vacuum or high temperature steps. These particles can be spin coated or doctor bladed on a substrate to form CIGSSe during subsequent annealing at lower temperatures than in the stacked layer process [11,12]. This work shows the progress in the manufacturing and densification of a CIGSSe absorber layer

using nanoparticles and different heat treatment techniques.

Experimental

Cu-In Nanoparticle Synthesis

Copper chloride (CuCl_2) (97%, Sigma Aldrich), indium chloride (InCl_3) (99,99%, Alfa Aesar), sodium borohydride (NaBH_4) (99%, Fluka), tetraethyleneglycol (TEG) (99%, Alfa Aesar) were used as received without further purification. All syntheses were performed under ambient conditions.

Bimetallic copper-indium nanoparticles were synthesized as described in previous work [5,6,13]. CuCl_2 (1 mmol) and InCl_3 (1.12 mmol) were dissolved in 150°C hot TEG to serve as a precursor solution. A reducing agent solution was prepared separately, dissolving NaBH_4 (14.84 mmol) in 10°C pre-cooled TEG. Both solutions then were dropped together in a third beaker at room temperature under vigorous stirring using an *Ismatec REGLO Digital MS-4* peristaltic pump and immediately formed a black precipitate. To remove excess BH_4^- and terminate the bubbling alcoholysis, acetone was added to the beaker 10 min after the reaction was finished. The nanoparticles were isolated by centrifugation and washed several times with iso-propanol (IPA) and stored being dispersed in IPA or toluene in small flasks.

Se Nanoparticle Synthesis

Sodium sulfite (Na_2SO_3) ($\geq 98.0\%$, dehydrated, Sigma Aldrich), Se powder ($\geq 99.5\%$, Sigma Aldrich), polyvinylpyrrolidone (PVP, 10000 g/mol,

Fluka Analytical), hydrochloric acid (HCl) (Merck, 37% fuming) and trisodium-citrate (Merck, dehydrated) were used as received without further purification.

The Se nanoparticles were fabricated from a 0.127 mol/l Na_2SeSO_3 precursor solution [7,8], which was prepared by dissolving Na_2SO_3 and Se powder in 80 °C hot deionized water under vigorous stirring and using a water cooled reflux condenser. After 24 h the precursor solution could be used for the Se-NP synthesis. To stabilize the nanoparticles a 1.35 mmol/l PVP solution was prepared in the reaction flask and trisodium citrate (2.38 mmol) was added as acidic buffer. Then 25 ml of the Na_2SeSO_3 precursor solution were mixed into the stabilizing solution and HCl was added successively in 5 ml steps until the pH reached a value of ≤ 0.5 . The solution immediately turned from clear to an orange-red murky color in every performed synthesis. After 1 h of stirring the nanoparticles were isolated by centrifugation, pH neutralized with 1 M NaOH solution and washed several times with pre-cooled deionized water. For storage the particles were concentrated and dispersed in IPA or toluene, constantly stirring in small flasks.

Processing of Absorber Layer

The substrates for all samples were 75 x 25 mm² float glass slides that were coated with 500 nm molybdenum by DC sputtering. Cu-In and Se nanoparticles were coated on the substrates by doctor blading. Typically 120 μl of a nano-ink were injected into the film applicator with a height of 200 μm and the blade was

moved with a velocity of 10 - 12 mm/s. After evaporation of the solvent, the next layer was applied, resulting in layer stacks.

The heat treatment was performed on a hot plate in ambient atmosphere at 350 - 430 °C. All samples were annealed using a second uncoated float glass slide for face-to-face sealing of the layer stacks to limit the Se loss and oxidation of the nanoparticles. Moreover an external uniaxial mechanical pressure was applied to the face-to-face sandwiched nanoparticle films by using different weights.

Figure 1 depicts the schematic of layer stack and face-to-face procedure with external pressure.

Characterization

The morphology of the processed thin film layers and their element composition (with EDX) were examined using a *JEOL 6400* scanning electron microscope. Phase analysis was performed using a *Panalytical Empyrean* X-Ray diffractometer (XRD).

Results and Discussion

Face-to-face annealing with application of uniaxial mechanical pressure

The main goal of this work is to produce a dense and homogeneous CISE absorber layer with a thickness of about 2 - 5 μm from nanoparticle inks. To achieve a closed layer on the Mo substrate the nanoparticles have to be coated repeatedly to relatively thick stacks until no Mo is shimmering through the film. Since the heat treatment was

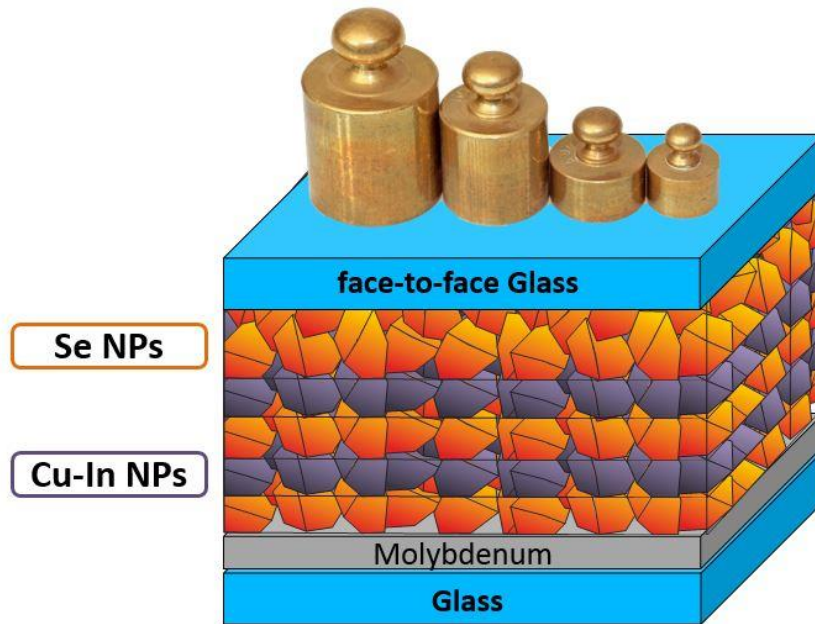


Figure 1: Schematic of the examined samples, showing the Cu-In and Se nanoparticle stack on Mo coated float glass and the face-to-face sealing with application of external pressure.

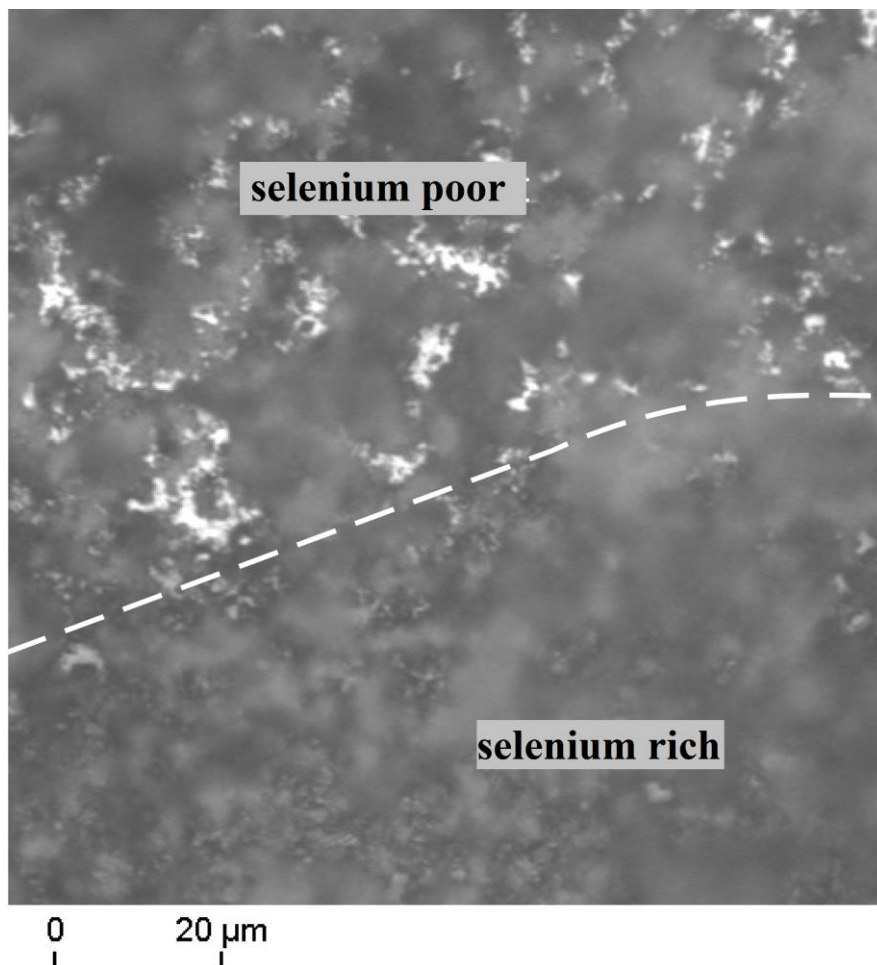


Figure 2: SEM top-view of the CISE layer after annealing. The boundary of the face-to-face glass can be seen in morphology and selenium content, determined with EDX.

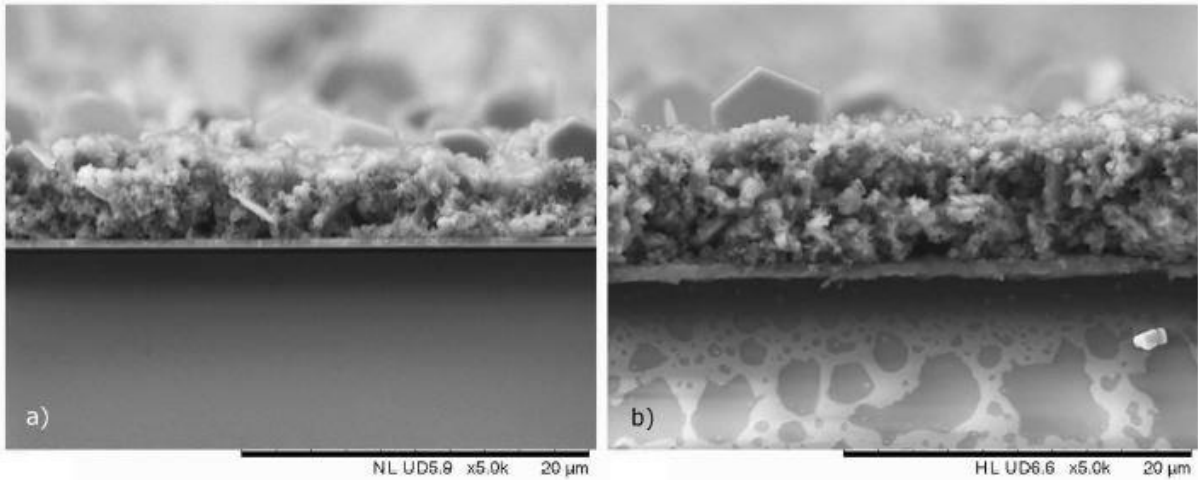


Figure 3: SEM cross-section images of two samples prepared with the same amount of particles and annealed at 350 °C. Left: Sample a) was exposed to 0.2 kg external weight during annealing which condensed the film to 5.3 μm. Right: Sample b) annealed with same parameters but without external pressure, the layer thickness is 8.2 μm.

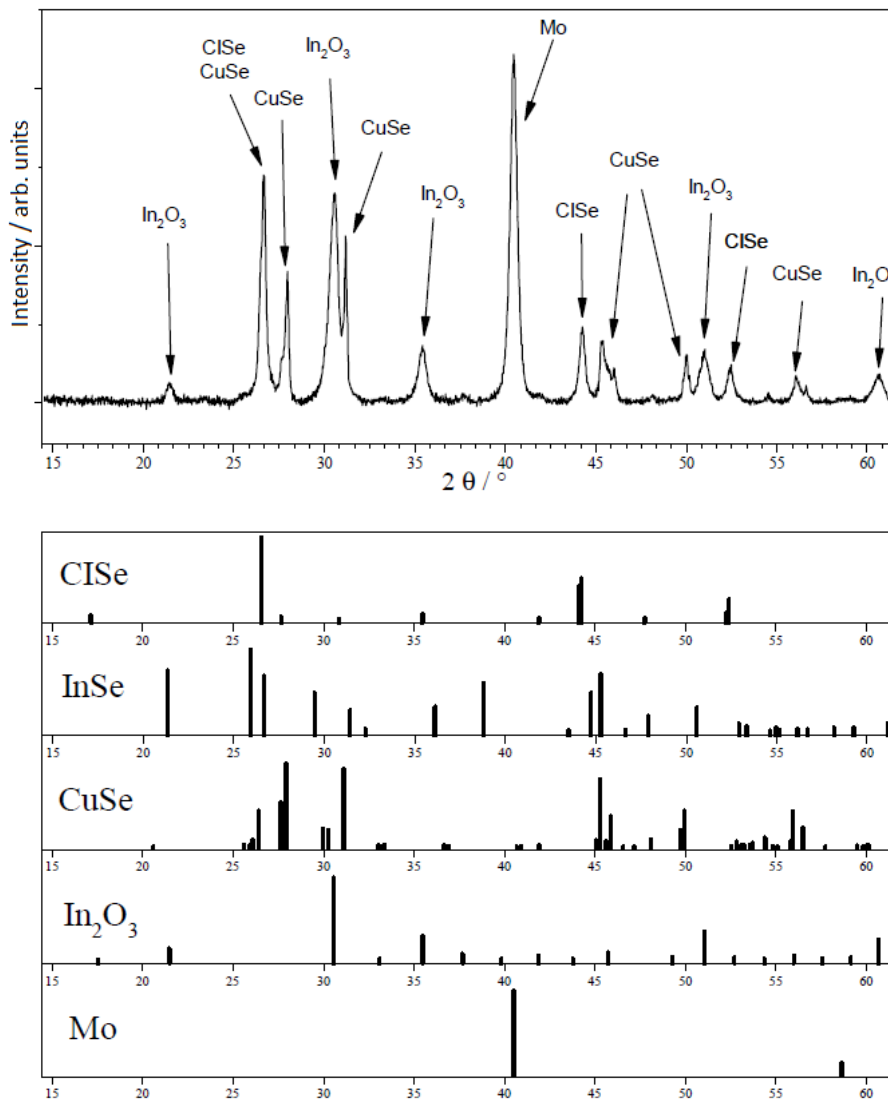


Figure 4: XRD measurement of the ClSe film after face-to-face annealing at 350 °C on a hotplate in ambient conditions.

performed in ambient conditions, and not in selenium atmosphere, the face-to-face method proved useful to limit the loss of Se. Figure 2 shows an SEM image of the boundary area of the face-to-face glass. The boundary can clearly be seen in the difference of morphology and Se content, which was determined with EDX. The covered part shows a closed layer with almost balanced (Cu+In)/Se ratio, whereas the CISE layer is Se poor in the uncovered part and shows holes, where the Se evaporated.

Furthermore, as the stacks thickness was about 10 μm before and after annealing, some experiments with mechanical pressure on the face-to-face glass were conducted to condense the films. Figure 3 shows the cross-section SEM images of two samples, which were deposited with the same amount of particles under the same conditions. Sample a) was annealed with an additional weight of 0.2 kg on top of the face-to-face glass slide, whereas sample b) had no external pressure applied. It can be seen that the film is condensed from 8.2 μm to 5.3 μm by the uniaxial pressure and also the porosity seems reduced. Clearly visible, and confirmed by EDX and XRD (figure 4), are CuSe flakes on the surface that are a sign of unfinished reaction, most likely due to the hotplate not reaching the necessary temperature for complete CISE transformation [14] and oxidation of indium, as seen in figure 4 as well.

To condense the particle film even more, higher uniaxial pressure, achieved with larger weights, was applied. Also the

temperature was raised to 430 $^{\circ}\text{C}$ to improve CISE formation. Figure 5 shows the SEM top-view of the sample processed with 1.2 kg external weight for 8 min at 430 $^{\circ}\text{C}$ on a hotplate. Clearly visible are flat and compressed areas at a higher level next to uncompressed valleys. Most likely these areas were at a lower level after the deposition and the weight did not press as strong, or not at all, on these lower parts. This shows that it is important to have a low surface roughness after deposition and to apply the uniaxial pressure as homogenous as possible over the complete surface area. With an additional weight of 5.2 kg dense, 3 μm diameter grains were observed which look similar to absorber layers from sputtered stacked elemental layers, as can be seen in comparison in figure 6. This shows the great potential of adding weight to the face-to-face annealing. The pressure on the glass slide helps the nanoparticles sintering together to form large grains. However as shown in figure 6, there are still nanoparticulate areas that did not sinter together as well as their neighboring grains, for the same reason as before, the inhomogeneous application of pressure due to surface roughness of the thin film after the coating.

Moreover the larger weights prevent selenium loss even better than face-to-face annealing without additional weight, resulting in the proper (Cu+In)/Se ratio of ≈ 1 . Figure 7 shows XRD measurements of CISE films after face-to-face annealing with different external weight. It can be seen, that the amount of In_2O_3 is

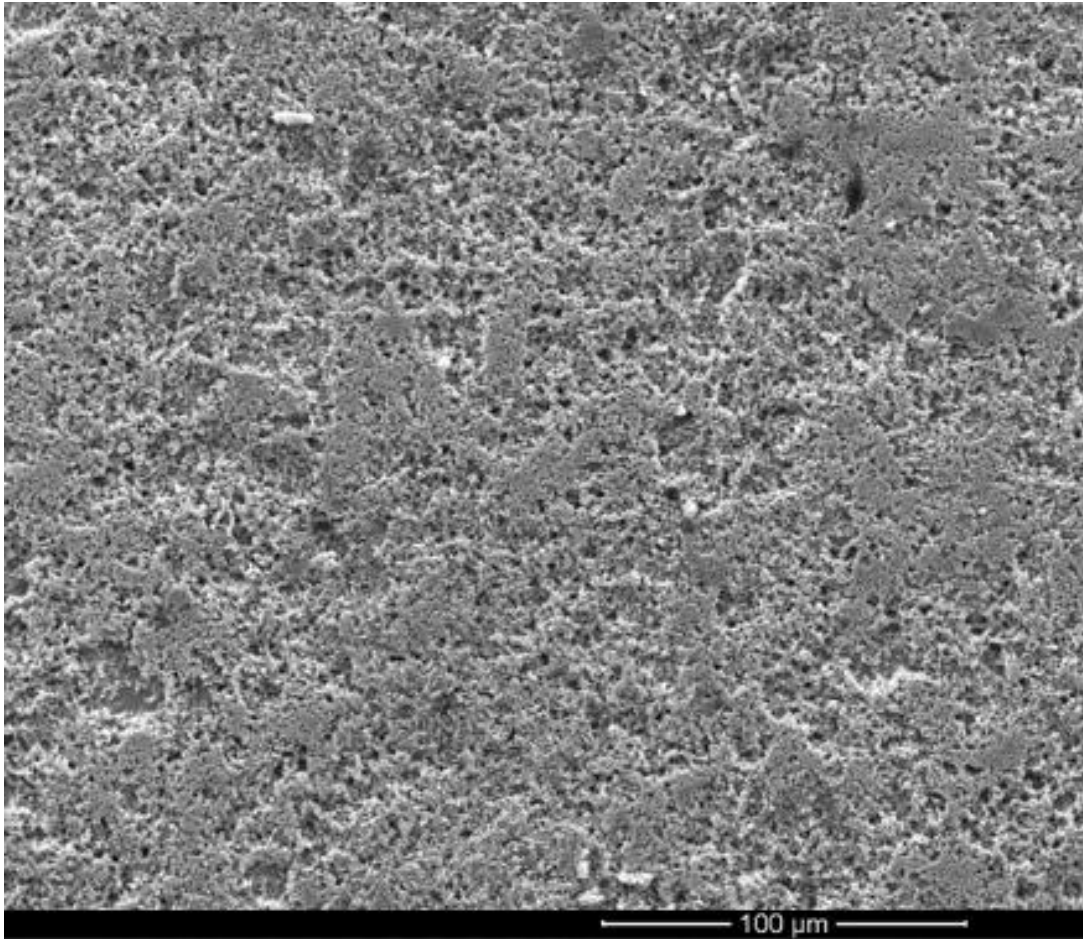


Figure 5: SEM top-view image of sample processed with 1.2 kg external weight for 8 min at 430 °C on a hotplate, showing flat and compressed areas next to uncompressed valleys.

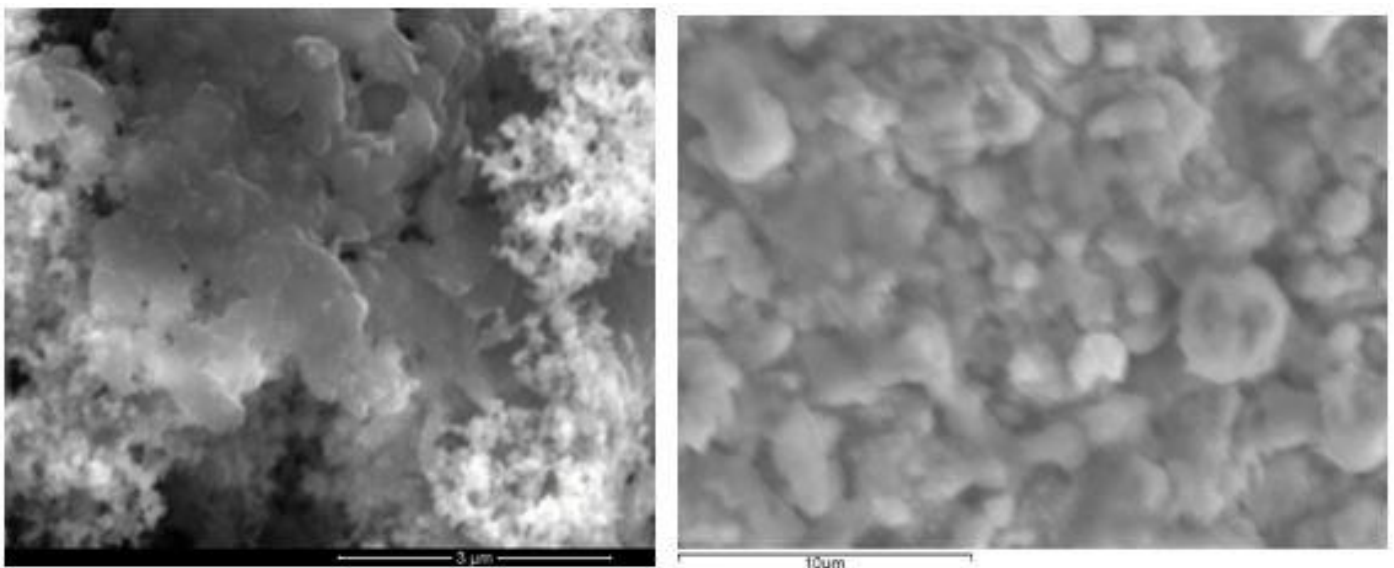


Figure 6: SEM top-view image of sample processed with 5.2 kg external weight for 8 min at 430 °C on a hotplate (left) showing dense, 3 μm diameter CIGS grains which look similar to absorber layers fabricated with sputtered precursors at 550 °C for 15 min (cf. right image).

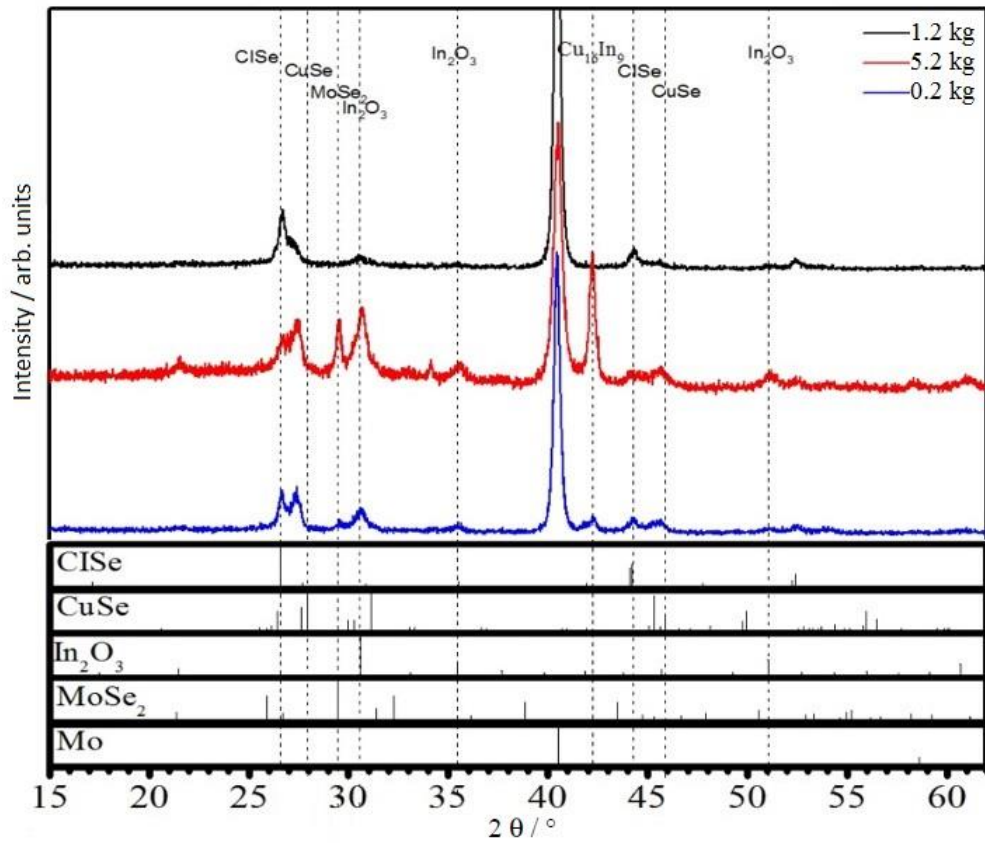


Figure 7: XRD measurement of the CISE films after face-to-face annealing with different external weight at 430 °C on a hotplate in ambient conditions.

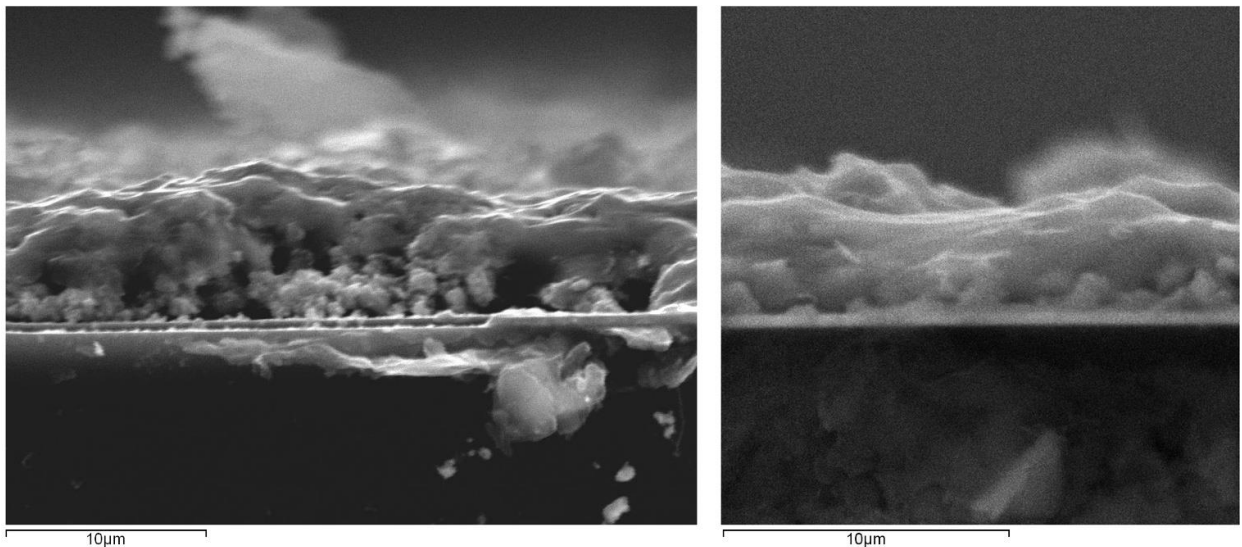


Figure 8: SEM cross-section images. Left: Characteristic double-layer CISE after face-to-face annealing at 350 °C on a hotplate showing a dense coarse grained top layer and a porous fine grained bottom layer. Right: Dense coarse grained single-layer CISE manufactured by repetition of coating and face-to-face annealing at the same temperature, whereas the first annealing process was held for 5 min and after the second coating for 20 min.

significantly reduced by using 1.2 kg weight compared to 0.2 kg, leaving the indium to transform into CISE and with this also reducing the CuSe content. The sample with 5.2 kg shows oxides again after the face-to-face glass broke due to the pressure, as well as unused Cu-In phase due to selenium loss. However in this experiment it can be seen, that a MoSe₂ phase has been formed, which would be desired in a CISE solar cell. So it seems worthwhile to use a large weight, but the pressure has to be applied carefully.

Repetition of coating and annealing

Previous experiments mostly resulted in a double layer structure of CISE where a fine grained CISE layer is next to the back electrode and a dense coarse grained CISE layer on top of the fine grains, also shown in the cross-section figure 8 left. By coating Se- and Cu-In nanoparticle inks on top of already annealed CISE films a uniform dense layer could be achieved, as depicted in figure 8 right. Both temperature treatments were performed at only 350 °C, the first one lasting 5 min and the second one 20 min. The first annealing was kept short on purpose, so that the Cu-In and Se particles would react to mostly binary selenides and a few CISE grains [14]. After the second coating the layer stack from CuSe, InSe, CISE, Cu-In and Se was annealed for longer times to form the uniform and dense CISE layer as depicted in figure 8 even at 350 °C. The mixture stack shortens the diffusion paths as well as provides larger surface area for

the reaction to take place and provides more supply of the elements for the CISE grains to grow.

Conclusions

In this work different annealing processes were examined to form a CuInSe₂ absorber layer from nanoparticulate precursors. The application of uniaxial pressure during annealing of Cu-In and Se precursors was performed by adding external weights on top of the face-to-face lids. 0.2 kg of external weight showed the potential to condense the nanoparticle layers by ca. 35 %. Applying larger weights like 5.2 kg helps with the sintering of the nanoparticles to larger grains with the diameter of about 3 µm that resemble strongly the absorber layers formed from sputtered precursors. The nanoparticle films should have a surface roughness as small as possible after the deposition and the pressure should be applied as homogenous as possible. Also raising the temperature can help with the formation of denser layers but is not necessarily needed. By repetition of coating and annealing dense and uniform CISE absorbers could be manufactured at temperatures as low as 350 °C. The first temperature treatment was kept short, and freshly deposited Cu-In and Se nanoparticles surrounded the CISE grains, CuSe flakes and InSe particles from the first annealing. During the second annealing a dense CISE layer is formed assisted by short diffusion pathways, larger surface area and supply of the elements.

Acknowledgements

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