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Deliverable D2.4

Evaluation of different synthesis routes to obtain single phase low defect kesterite

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Partners	IREC, NU and UU-ASC
Authors	I.Forbes*, José Márquez*, C.Platzer Björkman♦ M. Neuschitzer† (* NU, ♦UU-ASC, †IREC)
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1 General introduction

Work package 2, concerns the “*Development of absorbers by PVD and chemical based processes*” with three partners hosting early stage researchers working on three different routes for kesterite absorber synthesis. NU, UU-ASC are primarily developing sputtering based PVD routes with IREC using their PVD technique as a reference to aid for the development of a low cost chemical synthesis (spray pyrolysis) process. Each partner hosts an early stage researcher, at NU, ESR2.1 will focus on the development of optimised sputtering processes for PVD growth of CZTSe that will later be extended to the sulfide and sulphoselenide absorbers. The focus for ESR2.2 at UU-ASC is sputtering (reactive) based methods for CZTS absorbers and ESR2.3 is developing both the PVD (conversion of sputtered, thick, precursor layers) and chemical strategies for the synthesis of CZTSSe absorbers.

A goal of the KESTCELLS project is to achieve device conversion efficiencies of 10% and the synthesis routes evaluated in D2.4 are those selected to produce material that is consistent with this goal. Within the context of thin film Kesterite absorber layers, the evaluation of synthesis routes that yield low defect material with a minimum of secondary phases will be evaluated and considered as meeting the low defect single phase requirement of this deliverable. The synthesis routes reported here are primarily sputtering based PVD techniques together with the chemical synthesis path being undertaken by IREC.

Deliverable 2.4 involves contributions from each workpackage partner. ESRs 2.1 and 2.3 were on secondment at EMPA for the 6-month reporting period the period prior to D2.4 and from WP3, ESR3.2 was on secondment at Northumbria during this period.

Synthesis routes based on sputtering are the basis of large-scale production of CIGS thin films solar cells. The technique has yielded laboratory scale CuInSe_2 (CISe i.e. CIGSe) devices with an efficiency 20.9% [1] and is the basis of the largest commercial CIGSe production companies, such as Solar Frontier in Japan and Miasole in USA [2]. The technique has been use by research groups over the last 20 years. Synthesis of $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) absorber layers using this method uses a variant of the 2-stage process, consisting in the sputtering of the Cu, Zn and Sn metals followed by a selenisation process but also includes processes that use one or more compound targets together with a subsequent annealing process.

2. Partner: NU - Development of CZTSe based absorbers by PVD processes

2.1. Introduction: summary of the variations of the 2 stages is presented in the following sub-section.

2.1.1. First Stage: Sputtering of Cu, Zn and Sn (CZT) metallic precursor.

Several groups have reported the sputtering of the metal precursors. IREC, sputter deposits “thick” stacked layers from elemental targets [3]. IMEC, the group reporting the best efficiency for the pure selenide, $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) solar cells, use precursors sputtered from alloy targets [4]. Northumbria University produces precursor layers by magnetron sputtering of Cu, Zn and Sn from 99.999% purity elemental targets onto Mo-coated soda-lime glass substrates on a rotating substrate table. The substrates pass underneath each target resulting in the formation of a mixed metal precursor. More information about the process can be found in the paper reported by Zoppi *et al* [5]. An example of CZT metallic precursor produced by this method can be observed in Figure 2.1

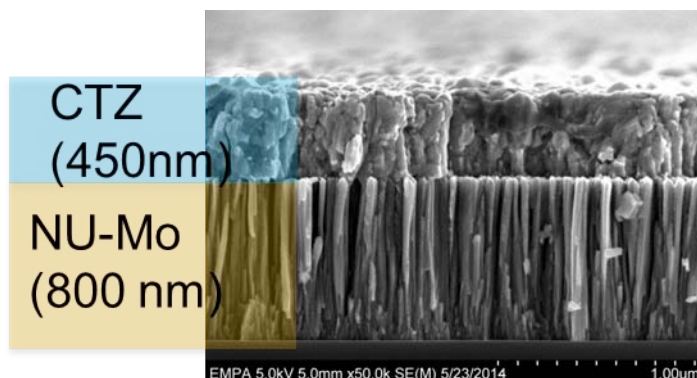


Figure 2.1. SEM cross sectional image of a sputtered CZT metallic precursor produced at Northumbria University

2.1.2. Second Stage: Selenisation of CZT metallic precursors.

The metallic precursors are converted into the absorber by reactively annealing in a Se atmosphere to form the CZTSe. Two Se delivery methods were tried by Northumbria University for D2.4. The standard process involved using a **thermally evaporated Se cap layer** on the precursors followed by heating, within a graphite box, using a tube furnace to temperatures above 500 °C. Details of this process were given in the Deliverable Reports D2.2 “Materials Data Correlated to: Evolution of Phases with Variation in Conversion Conditions and Precursor Composition” and D2.3 “Synthesis of thin films with systematic variation of stoichiometry (Cu-rich to Cu poor)”.

The alternative route evaluated consisted of adding separate **pieces of Se shot** to a graphite box within which uncoated precursor layers were located. The graphite box was introduced into a rapid thermal processing (RTP) system and converted using a 2-step ramp at temperatures of 500 °C after an intermediate dwell at 300 °C. A SEM cross-sectional image of CZTSe produced by this method can be seen in Figure 2.2.

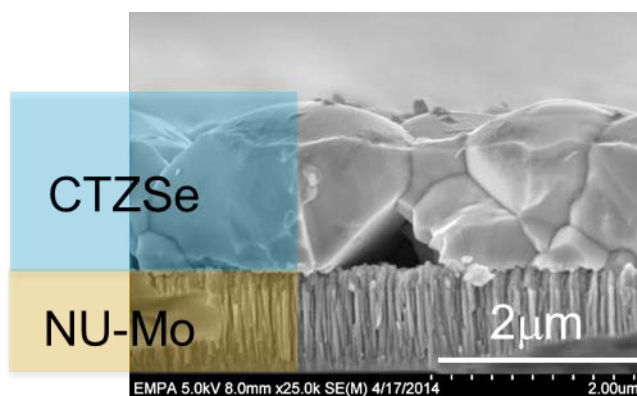


Figure 2.2. SEM cross sectional image of a CZTSe absorber layer produced by selenisation of a sputtered CZT metallic precursor using Se pellets as chalcogen source inside a graphite box and a 2-step conversion process.

(A range of similar techniques for the delivery of Se and converting into CZTSe are reported in the literature, and the NU technique can be considered as a variant of these routes. IREC, for example uses Se powder within a graphite box to convert the precursors by heating in a tube furnace [6]. Absorbers produced by IMEC, are synthesised by delivering Se via H_2Se (g) into an RTP reactor containing the precursors at temperatures of 470 °C [4]. However, H_2Se is highly toxic and was excluded as a route at NU and the technique used by IREC is the basis for reference absorbers reported in section 4.)



The stoichiometric region where CZTSe can be formed without the presence of secondary phases, is very small at temperatures around 400 °C [7]. Sputter deposition enables close control over the composition and the thickness of deposited films.

2.2. Synthesis routes for $\text{Cu}_2\text{ZnSnSe}_4$ absorber layers that minimise the presence of secondary phases.

Control of the composition was demonstrated in the deliverable D2.3. Films with three different compositions, defined as Cu-poor [$\text{Cu}/(\text{Zn}+\text{Sn}) = 0.84$], Stoichiometric [$\text{Cu}/(\text{Zn}+\text{Sn}) = 0.98$] and Cu-rich [$\text{Cu}/(\text{Zn}+\text{Sn}) = 1.11$], were produced. The Zn/Sn compositional ratio in three types of films was around 1.1. The compositions were measured by EDS and the experimental details are provided in deliverable report, D2.3.

CZTSe absorber layers were produced out of the set of precursors mentioned in the previous section using the thermally evaporated Se cap layer to introduce the chalcogen. XRD patterns of the absorber layers produced can be seen in Figure 2.3 (extracted from D2.3) where the formation of $\text{Cu}_2\text{ZnSnSe}_4$ is demonstrated for the three compositions tested. The work also showed for films with a slightly Cu-rich composition, the XRD patterns showed the presence of Cu_xSe secondary phases.

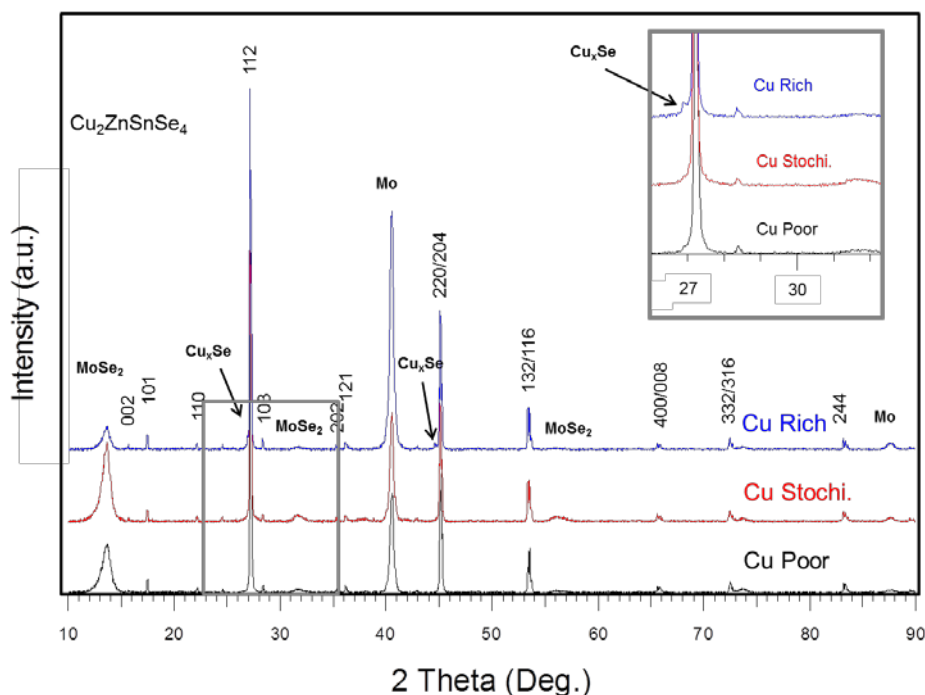


Figure 2.3. XRD patterns of the selenised Cu-Poor, Cu-Stoichiometric and Cu-Rich precursor films. The patterns indicate the presence of $\text{Cu}_2\text{ZnSnSe}_4$, and the formation of MoSe_2 in all the films. The peaks at 2-theta values of 27° and 45° for the Cu-Rich sample show the presence of Cu-Se binary phase (possibly CuSe or $\text{Cu}_{1.8}\text{Se}$). The inset shows a magnified section of the XRD pattern from 26° to 32.5° .

2.3. The performance of PVD CZTSe solar cells

In section 2.2 it was shown to minimise the presence of secondary phases it was necessary to produce precursors with compositions close to the stoichiometric CZTSe. However, at present, material with stoichiometric compositions does not necessarily lead to the best device performances. As reported in the literature and



observed in the current work, absorbers synthesised with composition Cu-poor $[(\text{Cu}/\text{Zn}+\text{Sn})\sim 0.8]$ and Zn-rich $[\text{Zn}/\text{Sn}\sim 1.2]$ gave the best efficiency (*N.B. a general summary of the relation of device performance with composition was reported by Delbos [8]*).

At NU, the best performing device was achieved by the selenisation of a 450 nm thick precursor layer synthesised as described in section 2.1.2. The process that yielded the highest performance devices involved was the Se shot chalcogen source. J-V characteristics and the EQE of the solar cells are shown in Figure 2.4. The compositional ratios of the precursor were $[\text{Cu}/(\text{Zn}+\text{Sn})=0.65]$ and $[\text{Zn}/\text{Sn}=1.1]$ measured by XRF. The precursor was converted by using an excess of Se pellets and heating to 500 °C inside a graphite box, in an AS-One RTP system (under static Ar at near atmospheric pressure). After the selenisation process, the compositional ratios of the absorber layer produced were $[\text{Cu}/(\text{Zn}+\text{Sn})=0.72]$ and $[\text{Zn}/\text{Sn}=1.3]$. (*Please note that Chen et al reported several reasons from a theoretic study of why to produce Cu-poor Zn-rich absorbers lead to better performance device [9]*.)

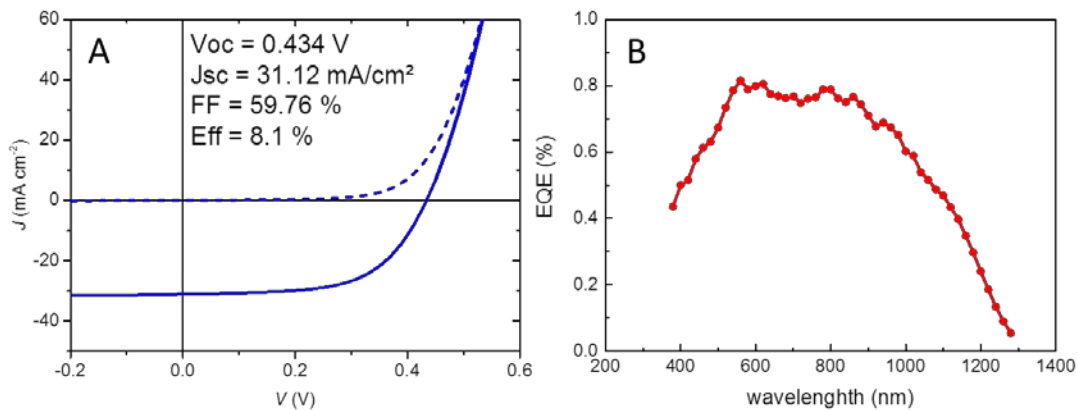


Figure 2.4. A) J-V characteristic and B) EQE of the best CZTSe solar cell produced by the methods described in this report.

2.4. Summary

It has been shown that by using sputtering to deposit metallic precursors onto rotating substrates, the composition of CZT metallic precursor layers can be controlled to minimise the presence of secondary phases in converted absorber layers. Two routes of delivering Se into the system to transform the CZT precursor into CZTSe absorber layers by 2-stage process are described. The CZTSe absorber layer which yielded the best device performance (8.1 %) had a composition very far from the stoichiometry of $\text{Cu}_2\text{ZnSnSe}_4$ $[\text{Cu}/(\text{Zn}+\text{Sn})=0.72]$ and $[\text{Zn}/\text{Sn}=1.3]$. The route used for the absorber layer synthesis involved conversion of sputtered metallic CZT precursors inside a graphite box using of Se pellets as chalcogen source. The graphite box was then heated up in an RTP system in a 2-step process involving a 300 °C first step for 5 minutes then 15 minutes at 500 °C to convert the precursors into CZTSe (dwell time and ramping rate are parameters that can also be varied to effect material quality). Whilst, use of an evaporated capping layer as a source of Se yields large area compositional uniformity in converted films (D2.2 and 2.3), using the current synthesis conditions, this chalcogen delivery method has not yielded devices performances that would indicate low defect material has been produced. This does not necessarily mean the route is not viable but does indicate that the conversion parameters require further investigation before a justifiable conclusion can be made.

2.5. References



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3. Partner: UU/ASC - Sputtering based methods for CZTS absorbers

3.1 Introduction

The synthesis route investigated at UU/ASC is based on sputtering of precursor films at low temperature followed by a rapid anneal in chalcogen atmosphere at high temperature. The advantage of this process is that precursor films with a very homogenous mix of all the four elements, (Cu, Zn, Sn and S) can be obtained in the first step. This allows for using very short annealing time in the second step and minimizes diffusion that could lead to extensive segregation of secondary phases in the second step. Several variations of the route are possible, in particular changing substrate temperature in the first or second step. In principle, a single step process could be obtained by using high substrate temperature during sputtering. However, due to the known decomposition of CZTS at high temperature in vacuum, this would require very high rates of Sn and S, not suitable for a high vacuum sputtering process. We therefore limit our process window to intermediate temperatures in the first step and do not investigate single stage sputtering.

The most critical aspects of our synthesis route, in order to reach high quality device material, are compositional control in the sputtering step, avoiding delamination in the annealing step and keeping high enough sulfur partial pressure for a given temperature in the annealing step. These three issues have been studied within the project leading to our current best synthesis route.

In summary, the best compositional control, i.e. best process stability was obtained using Zn and Sn metallic targets and CuS compound target. For this setup, the required sulfur content is obtained using an Ar:H₂S ratio of 1:1. Delamination and cracking of CZTS in the annealing step can be minimized by using an intermediate substrate temperature, in the current process around 180°C. Optimization of the annealing process showed the importance of providing enough sulfur. Annealing in graphite box at 560°C for 10 minutes gave the highest device efficiency of 7.9% (total area without antireflective coating).



Regarding secondary phase segregation, equilibrium phases according to the phase diagram are generally observed in the annealed CZTS films. Highest device efficiency is obtained for Cu/Sn around 1.9-2.0 and Zn/Cu+Sn around 0.36, i.e. slightly Zn-rich. ZnS segregation is expected for this composition and is indeed observed by UV Raman after annealing.

3.2 Compositional control in the sputtering step

Among the possible sputtering routes to deposit Cu-Zn-Sn-S films, reactive sputtering offers the possibility to vary sulfur content by controlling the amount of reactive H₂S in the plasma. Compound sputtering, either from CZTS target or binary sulfide targets can also give CZTS films with all elements, but with less flexibility in compositional variation. There are some challenges with the reactive sputtering process, since metal deposition rate will depend strongly on the amount of available reactive gas. Another issue is target evolution over time, both for compound targets and metallic targets in reactive sputtering. Even if this is not a main subject in this project, we were forced to deal with it in order to produce experimental series with controlled composition.

Before the start of the project, a two-target setup with Cu:Sn alloy target and Zn target was used. Even if some films and devices with good composition and device performance were made, the process stability was poor. The problem was a drift in Cu/Sn ratio from the alloy target in reactive sputtering over time. Initial film composition was below target composition in Cu/Sn ratio, and after some time switching to being above. By investigating the target surface, preferential loss of Sn and formation of thick layers of Cu₂S in areas with low erosion rate was concluded [1]. This can be explained by the high mobility of Cu and high reactivity with H₂S.

In order to avoid the compositional drift from CuSn alloy targets, the sputtering system was upgraded to three magnetrons. The first process investigated was with three metallic targets (Cu, Zn, and Sn). Due to flaking from the Cu target after reaction with the H₂S atmosphere, and formation of thick copper sulfide layers, this process was abandoned. However, reactive sputtering from metallic Sn was successful. As alternative Cu-source, a Cu₂S target was used instead of Cu. Evaluation of the process showed problems with arcing and cracking of the target surface. This could be related to the large thermal expansion of Cu₂S. Since CuS has smaller thermal expansion such a target was evaluated. Target behavior was good without arcing or cracking problems.

For reactive sputtering from three metal targets, or the Zn + CuSn targets, 100% H₂S was needed in order to reach full sulfur content in the films in our system. For the new process, with two metal and one compound target, overstoichiometric films were obtained using 100% H₂S. Recalibration led to our current process where 50% H₂S with 50% Ar is used (15 sccm Ar, 15 sccm H₂S). This process shows good stability with the exception of the Zn rate when switching from metallic to reactive sputtering. The Zn rate is about three times higher for initial reactive sputtering and stabilizes after several hours. Once the rate has stabilized, reproducibility is good. The exact reasons for the behavior of the Zn target are not known.

3.3 Avoiding delamination and cracking

Delamination or cracking of films can occur for many reasons such as volume changes, stress, difference in thermal expansion between film and substrate, formation of interface layers that are either soluble in subsequent etching or chemical bath processes or poorly adhesive due to their structure. In our process, a few clear trends have been observed regarding this issue. Sputtering with non-heated substrate gives cracking and sometimes delamination after annealing. By using slightly elevated temperature (180 °C), this problem is avoided. Further increase in substrate temperature to 300 °C gave no difference in peeling or film quality, and 180 °C was chosen as the standard deposition temperature.

Process parameters in the annealing step can also influence adhesion. Unfortunately, the results from variations in annealing temperature, sulfur content and annealing time are not conclusive. However, decent reproducibility regarding delamination was obtained for the optimized annealing process described below.

3.4 Optimization of the annealing step

Our annealing system consists of a tube furnace with a hot zone and a cold zone allowing fast ramping by moving the sample between these two positions. The samples are placed in a graphite box with additional elemental sulfur. A background pressure of argon is typically set to 300 mbar.



The precursor films after the sputtering step are highly disordered with a columnar crystalline structure best described as metastable cubic CZTS [2]. The appearance of non-equilibrium phases after low temperature sputtering was also seen for binary and ternary films sputtered in the same system [3]. During annealing step, the CZTS films crystallize into kesterite CZTS with small amounts of ZnS as shown by XRD and Raman (figures 3.2 – 3.4). The sputtered binaries and ternaries also crystallize into the equilibrium phases after annealing.

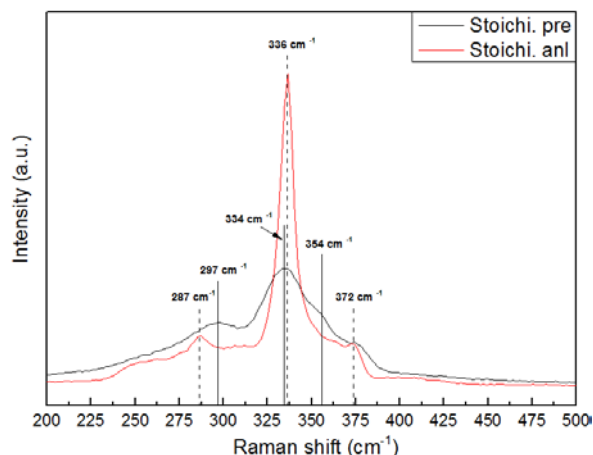


Figure 3.2 Raman spectra of the near-stoichiometric sample before and after annealing, measured by 532 nm excitation laser wavelength.

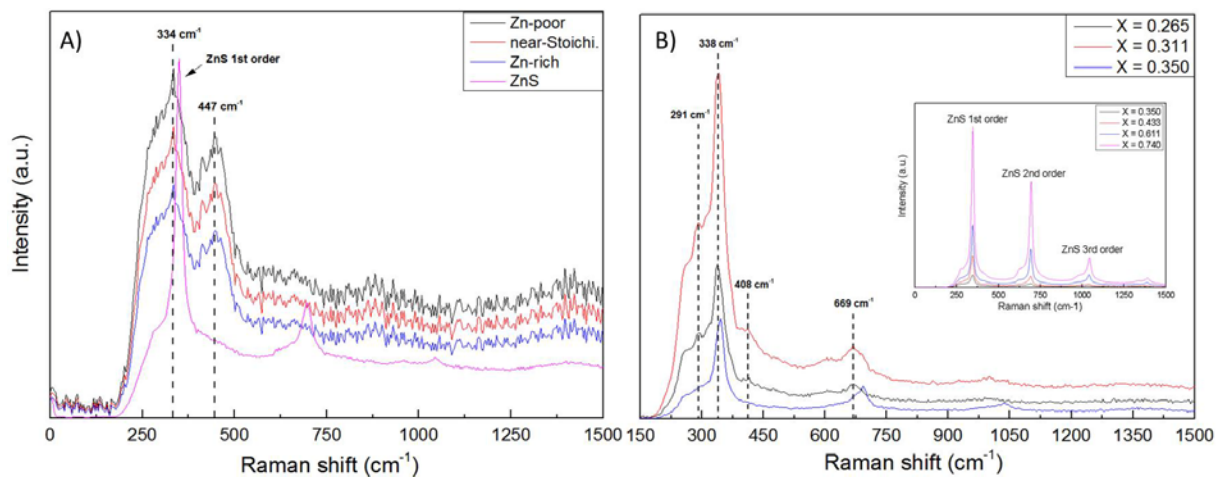


Figure 3.3 Raman spectra of CZTS samples measured by 325 nm excitation laser wavelength: A) before annealing; B) after annealing

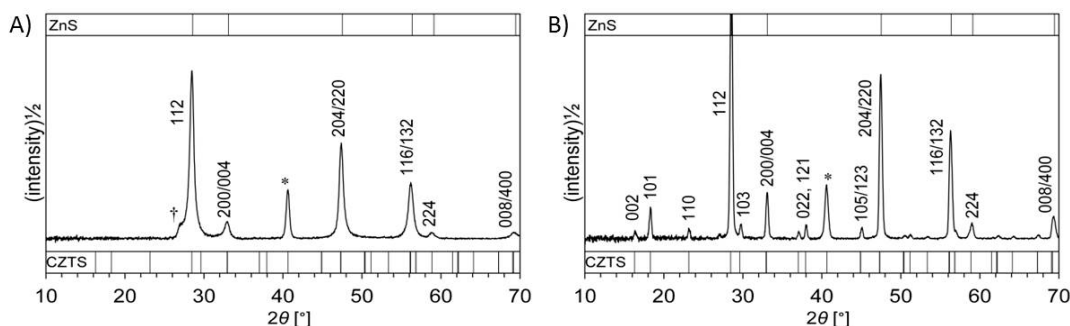


Figure 3.4. A) Grazing incidence XRD of precursor CZTS film deposited at 300 °C. B) The same precursor after annealing at 550 °C for 3 minutes. The composition of the film was Cu/Sn = 1.92, Zn/Sn = 1.31.

In optimizing the annealing step; temperature, time and pressure can be changed. However, since the graphite box is not impermeable to sulfur, prolonged annealing times cannot be used due to decomposition reactions at the front and back surfaces [4]. For an annealing temperature of 560 °C, annealing for 10 minutes with added elemental sulfur in the graphite box gave large grained films and the highest device efficiency, see table 3.1. In comparison, the same annealing process without any added sulfur, but with a glass plate placed on top of the sample to minimize the free volume gave reduced device performance, table 3.1. The reduced performance can be attributed to decomposition reactions at the CZTS surface, expected to result in secondary phase formation at this surface. However, neither Raman scattering nor XRD showed evidence for such phases. One explanation could be that the amount of secondary phases is below the detection limit. Another reason could be that defect formation at the surface, which cannot be probed by Raman or XRD, is responsible for the loss in device performance.

Table 3.1: Device parameters for annealing with sufficient (A) or insufficient (B) sulfur supply. Both anneals were performed at around 560 °C with an Ar background pressure of 300 mbar.

Anneal process	Efficiency (%)	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)
A: Graphite box with sulfur	7.9	667	19.6	60.0
B: Glass cover, no sulfur	3.0	596	9.2	54.9

3.5 Summary

In summary, the best synthesis route for Cu_2ZnSnS_4 based on reactive sputtering and annealing includes a sputtering process with good compositional control, tuning of substrate temperature to minimize delamination and annealing with sufficient sulfur supply. Good compositional control, i.e. best process stability, was obtained using Zn and Sn metallic targets and CuS compound target. For this setup, the required sulfur content is obtained using an Ar:H₂S ratio of 1:1. Delamination and cracking of CZTS in the annealing step can be minimized by using an intermediate substrate temperature, in the current process around 180°C. Annealing in graphite box at 560°C for 10 minutes with 20 mg of sulfur gave the highest device efficiency of 7.9%.

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4. Partner: IREC - PVD and Chemical based routes at IREC to synthesis kesterite absorbers

At IREC, two different routes are used to synthesise kesterite absorber material. The first of these is a 2-stage approach, consisting of physical vapour deposition of thick metallic precursor layers by DC magnetron sputtering followed by reactive thermal treatment under sulphur or selenium atmosphere. This approach allows easy and controlled compositional changes in the p-type kesterite absorber layers and ensures a smooth and homogeneous interface necessary for a good junction with the n-type buffer/window layer to build high performance heterojunction solar cells. The second route being developed at IREC is a non-vacuum process based on spray pyrolysis of chemical precursor solutions. This approach is especially interesting because it is a readily scalable technique, with low capital and operating costs and the potential to significantly reduce the cost of photovoltaic modules. In the following sections, the two processes are described in more detail and evaluated concerning their potential to produce single phase kesterite absorber material suitable for high performance solar cells.

4.1 IREC 2 step PVD based kesterite synthesis route

The starting point of this 2-stage method are Mo-coated soda lime glass substrates onto which a thin 10nm ZnO intermediate layer is deposited to prevent the decomposition of kesterite with the Mo back contact [1, 2]. On this substrate Cu/Sn/Cu/Zn metallic layers are subsequently deposited by DC-magnetron sputtering. By varying the metallic layers thicknesses it is possible to accurately control the composition of the absorber. The metallic composition of this precursor layer is determined by X-ray fluorescence measurements, which has been previously calibrated with inductive coupled plasma optical-emission spectroscopy. The second step consists of a reactive thermal conversion of the 5 cm x 5 cm metallic precursors in a graphite box, under selenium and tin containing atmosphere. A heating profile of 2 temperatures is used. First, a selenization takes place at 400 °C under Ar-flow keeping the pressure constant at 1.5 mbar for 15 minutes, followed by a higher temperature step at 550 °C for 15 minutes under static Ar pressure of 1 bar to improve the layer's crystallinity.

One main peculiarity of kesterite materials, used as photovoltaic absorbers, is that all high performances devices reported have a copper-poor and zinc-rich overall composition. This is due to the material's complex defect structure where intrinsic doping plays an important role [3–5]. This necessity of an off-stoichiometric composition and a narrow thermodynamically stable single phase region leads to the main problem when attempting to obtain high quality, single phase, kesterite absorber materials [3,5]. If secondary phases segregate on the surface chemical etching can provide a solution to remove them. At IREC a double etching using $KMnO_4$ in a H_2SO_4 -based medium, followed by subsequent etching in Na_2S is employed to remove possible unwanted ZnSe secondary phases formed during the annealing process [6].

The main parameters influencing the material growth are:

1. Precursor composition
2. Homogeneity
3. Thermal process

The PVD based 2-stage process allows an easy compositional control during the sputtering of the metallic precursor layers. Main challenge is the homogeneity of each layer, especially the deposition of smooth sputtered tin layers. Small compositional non-uniformities in the precursor layers can cause local secondary phase formations.



A 4 layer structure is employed with a thin Cu layer in the beginning to improve the subsequently deposited Sn layer. The pure metal precursor layers are very reactive, thus a conventional thermal process can be favourable for the final formation of kesterite as after the formation of binary and ternary phases the final thermodynamically stable phase will be kesterite. Rapid thermal processing can be more challenging due to Zn evaporation and kinetically limited conditions that can compromise the complete reaction of the precursors.

In Figure 4.1, Raman spectra measured with different excitation wavelengths of polycrystalline $\text{Cu}_2\text{ZnSnSe}_4$ thin film synthesized by the prior described 2-stage PVD route and after chemical etching are shown. The overall composition of this film is $[\text{Cu}]/[\text{Zn}+\text{Sn}]=0.77\pm 0.05$ and $[\text{Zn}]/[\text{Sn}]=1.21\pm 0.08$ (measured by X-ray fluorescence). The characteristic CZTSe peaks are indicated in the graph and no secondary phases are detected [7] at the surface. Devices build with these CZTSe absorbers using a CZTSe/CdS/i-ZnO/ITO heterostructure yield power conversion efficiency up to 8.3%, with high open circuit voltage (V_{oc}) values, which further confirms the high quality of the absorber material synthesized by this 2-stage PVD based method.

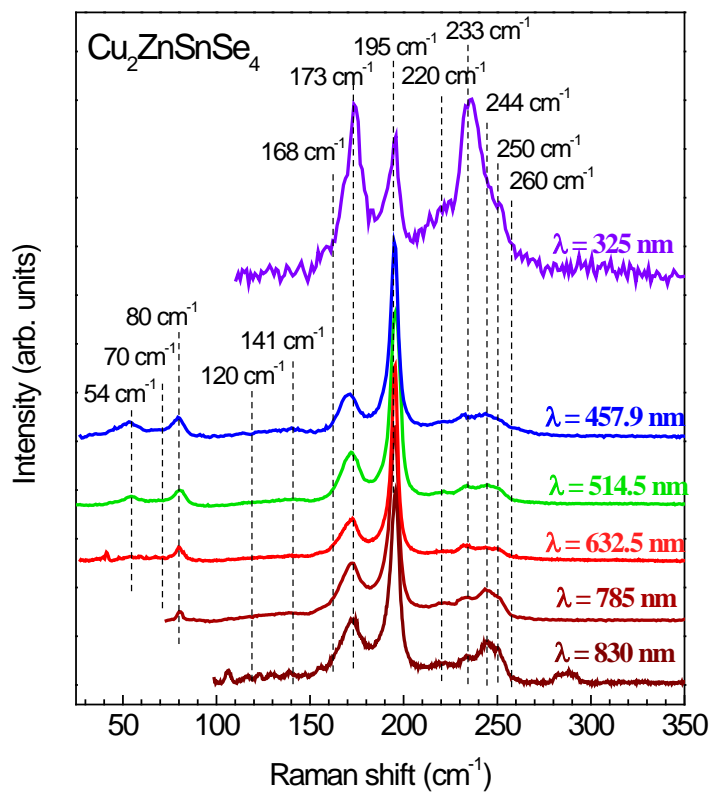


Figure 4.1 Raman spectra of polycrystalline $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) thin film measured with different excitation wavelengths with indication of the characteristic peaks. No secondary phases are detected.

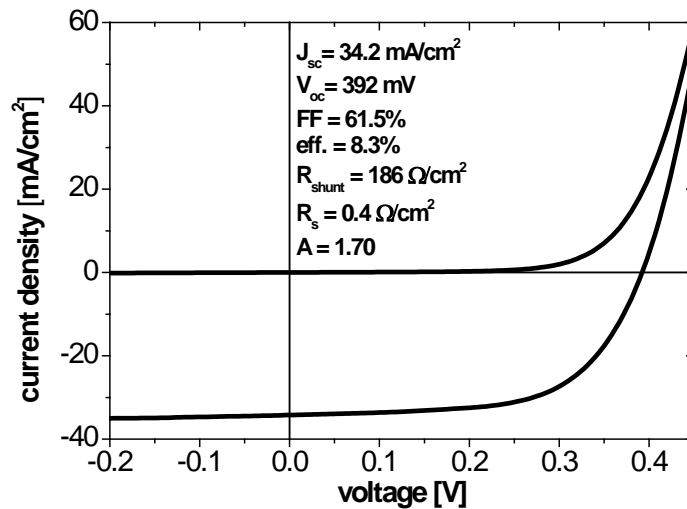


Figure 4.2 Dark and illuminated JV curves and device performance of PVD grown CZTSe absorbers used in CZTSe/CdS/i-ZnO/ITO heterostructure solar cell.

4.2 Chemical based routes to synthesise kesterite absorbers

Chemical non-vacuum based routes are especially attractive due to its low costs and scalability for industry. The current world record efficiency for kesterite based solar cells was obtained by a chemical process, however, that route uses highly toxic hydrazine as a solvent [4]. Nevertheless, non-toxic chemical approaches are showing promising efficiencies, up to 7.5% (excluding nanoparticle based chemical routes) [8,9]. At IREC, spray pyrolysis is investigated as the non-vacuum alternative to the more established PVD process [10]. In spray pyrolysis an aqueous precursor solution, of metal salts dissolved in deionized water, is sprayed onto a heated substrate. The small droplets of the atomized precursor solution start to evaporate on the way to the hot substrate, leading to a decomposition of the precursors and formation of a film. One of the most important parameters during spraying is the droplet size and size distribution both of which strongly influence the film morphology. In figure 4.3 as grown films using different pneumatic atomizer nozzles are shown, illustrating the importance of this deposition parameter for a surface morphology.

As-grown sprayed films need to be annealed under sulfur-tin, or selenium-tin, atmosphere and temperatures between 550 °C – 580 °C to increase the microcrystalline quality of the layer.

The same main parameters influence the material growth (as for the 2-stage PVD process):

1. Composition
2. Homogeneity
3. Thermal process

Adjusting the metal salt concentrations in the sprayed solution can be used to easily control the composition. Homogeneity inside the layer is good, however, the main problem occurs at the surface. The thermal processes that have been found to be most suitable for these spray deposited precursors are non equilibrium processes such as rapid thermal processing. These can be favorable because the thermal treatment is mostly use to promote grain growths within the well-mixed, as-sprayed, microcrystalline kesterite precursor layer.

Several investigations performed at IREC have shown that for the pure sulfur sprayed kesterite, ZnS is the main secondary phase and this is detrimental to cell performances, resulting in devices with efficiencies of 1.4% or less [10,11]. The major limitation of this interesting technique is the poor surface homogeneity and this is providing the main focus for the current research by improvement of the spray deposition process.

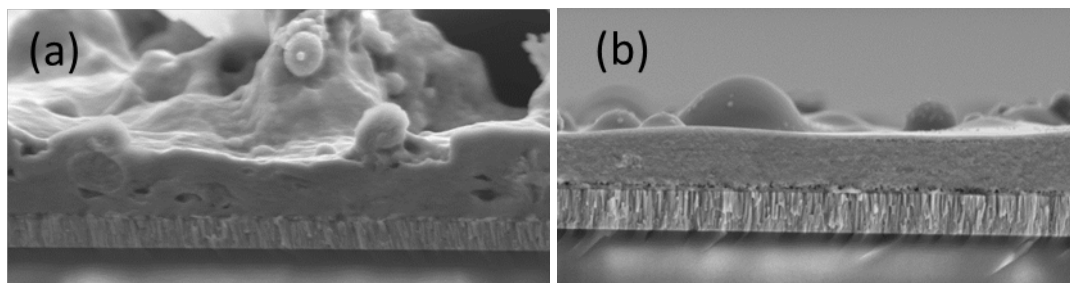


Figure 4.3 SEM cross-section of as grown sprayed films using different pneumatic atomization nozzles. Film sprayed with (a) nozzle producing larger droplet sizes (b) nozzle producing smaller droplet sizes.

4.3 Summary

A two-step PVD based approach consisting of the reactive thermal annealing under selenium atmosphere of sputtered metallic precursor layers allows obtaining single phase high quality device grade films resulting in CZTSe/CdS/i-ZnO/ITO heterostructure solarcells with up to 8.3% power conversion efficiency. Using Raman spectroscopy, CZTSe films with no secondary phases at the surface were confirmed. Chemical based routes offer an interesting low-cost alternative to PVD based methods. In the case of spray pyrolysis, much effort is focused in the improvement of the spray deposition setup itself, namely the atomiser nozzle to enable both a high quality material and a smooth interface both of which are needed for high device performances.

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5. Overall Summary

The work by the three partners within Work Package 2 has shown that PVD based processing based the annealing or conversion of sputtered precursor layers are each capable of yielding device quality absorber layers. Conversion of mixed metal precursors (NU) or stacked 4-layer metal precursors (IREC) as well as annealing of reactively sputtered $\text{Cu}_2\text{ZnSnS}_4$ layers, yield device efficiencies of ranging from 7.9 % to 8.3 %. The differences between efficiency values are partially explained by the difference in device areas produced at UU-ASC, NU and IREC (the devices produced by the latter two partners were significantly smaller than those produced by the former). However the main conclusions are that all-three synthesis routes show promise of achieving the target conversion efficiency of 10%. Although, the synthesis routes can be controlled, NU for instance, to produce near stoichiometric/single phase absorbers, currently the highest performance devices result from non-stoichiometric materials that exhibit secondary phases. The ability of each route to yield device quality Kesterite materials is critically dependent on the details of the deposition process and the subsequent conversion or annealing conditions. The non-vacuum process under investigation at IREC has shown promising results. At present the absorbers produced by this route contain secondary phases, particularly ZnS, but the economic advantages of non-vacuum technology and the control afforded by chemical solution based processes offers a path to achieve device quality absorber layers.