

## Chapter

# Solution-Processed Chalcogenide Photovoltaic Thin Films

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## Abstract

Chalcogenides-based thin film solar cells are great competitors to beat high efficiencies as silicon solar cells. The chalcogenides that have been commonly used as absorber materials are CIS, CIGS, and CZTS. They present some advantages of having a direct and tunable band gap, high absorption coefficient and respectable efficiency to cost ratio. Solution processable deposition approaches for the fabrication of solar cells attracts a great deal attention due to its lower capital cost of the manufacturing than the vacuum-based techniques. In this chapter, we detail the use of a low-cost method of deposition for the chalcogenide thin films by spin-coating and spray-coating, which is already widely employed in several fields of industries.

**Keywords:** chalcogenides, solar cells, spin-coating, spray

## 1. Introduction

Currently, the photovoltaic market is based on silicon solar cells with conversion efficiency of 15–22%. However, chalcogenides-based thin films solar cells are great competitors of silicon technologies. Among of all photovoltaic thin films, chalcogenide solar cells present some advantages of having a direct and tunable band gap (1.0–2.5 eV), high absorption coefficient ( $>10^4 \text{ cm}^{-1}$ ) and respectable efficiency to cost ratio [1]. Devices containing  $\text{CuInGa}(\text{S},\text{Se})_2$  (CIGS) recently recorded a 23% efficiency [2] and it becomes possible to PV modules based on that chalcogenide thin film to have already entered the market at similar or even lower costs than traditional silicon modules [3]. Despite this high efficiency level, the CIGS-based PV technology has not yet attained its full potential. If all loss mechanism were addressed at the same time, the theoretical maximum 30% could be technically feasible. The reported highest efficiency for CIGS thin film solar cell is based on vacuum process for coevaporating the elements and depositing the absorber layer. However, vacuum-based methods are quite expensive, which creates cost and technological barriers to produce low-cost photovoltaic modules [4]. Therefore, some approaches have been investigated for further improvements, as well as, to develop cheaper strategies for the absorber layer.

Solution-processed techniques have been extensively studied to deposit chalcogenide thin films applied to the second-generation solar cells. The characteristics of the precursor solutions are fundamental to perform the deposition and have an important role in the resulting film. The solution composition, concentration

of constituents, viscosity, and solvent will influence on the film adherence onto substrate, grain growth, and most importantly, on the solar cell efficiency.

The solution processable deposition of chalcogenides absorber layer, such as CIS ( $\text{CuIn}(\text{S},\text{Se})_2$ ), CZTS ( $\text{Cu}(\text{Zn},\text{Sn})(\text{S},\text{Se})_2$ ), and CIGS compounds for the fabrication of solar cells attracts a great deal attention due to its lower capital cost of the manufacturing than the vacuum-based approaches, high production rate, ability for roll-to-roll production, compositional uniformity over large areas, and high material utilization [5, 6]. Several solution processed methods are already commonly used for chalcogenides film deposition, such as, electrodeposition [4], spin coating [7], ink jet printing, electrophoretic deposition [8], etc.

Among the solvents used to prepare solution-processed high-performance solar cells reported in literature are water ( $\text{H}_2\text{O}$ ), dimethyl sulfoxide ( $\text{C}_2\text{H}_6\text{OS}$ ), hydrazine ( $\text{N}_2\text{H}_4$ ), methanol ( $\text{CH}_3\text{OH}$ ), dimethylformamide ( $\text{C}_3\text{H}_7\text{NO}$ ) [9]. The solvent used in the precursor solution must be environmental-friendly, being able to dissolve the salts used as source of the chalcogenide cations and the compounds that are the source of the chalcogens, and not contribute to impurities in the film [10].

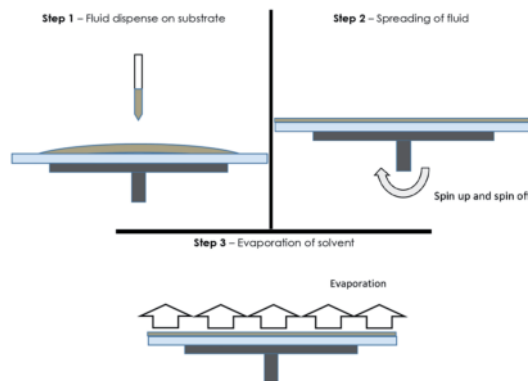
This chapter discusses the two most reported techniques used to prepare the world-record efficiencies of solution-processed chalcogenide solar cells: spin-coating and spray-coating. The fundamental characteristics of the solutions, regarding the physical chemical properties of the solvents, and the important characteristics of the deposition methods will be discussed.

## 2. Absorber layers deposited by spin-coating

The spin coating is a technique to deposit thin films on flat substrates. It has been very utilized on the fabrication of films in thickness range of micrometer to nanometer. This makes it attractive to prepare solar cells, on a manufactory point of view, mainly at laboratorial scale.

The process to produce thin films with this method can be resumed basically in three steps (**Figure 1** represents a schematic diagram of the steps), respectively; fluid dispense on the substrate, spreading of fluid (spin up followed by spin off) and evaporation. The solution dispensed spreads over the substrate surface by the centrifugal force and, at last, the evaporation forms the film.

The viscosity of the fluid dispensed ( $\eta$ ), density of volatile liquid ( $\rho_A$ ), evaporation rate ( $m$ ), and angular speed of the spinning plate ( $\omega$ ) are the main factors that



**Figure 1.**  
*Steps of spin coating technique.*

affects the layer thickness, the following equation represents the variation of the thickness in function of this parameters [11]:

$$h = \left( 1 - \frac{\rho_A}{\rho_{A0}} \right) \cdot \left( \frac{3\eta \cdot m}{2\rho_{A0}\omega^2} \right)^{1/3} \quad (1)$$

where thickness is  $h$ . These factors and possible contaminants (oxygen, humidity, solvent traces, etc.) can also influence on the roughness and the uniformity of the film [12].

Spin coating is a fast and low-cost process. The feasibility of the process is due to cheap material required, comparing to vacuum-based coatings, since a spinning plate is much cheaper than vacuum system [12]. In addition, this method allows the use of a wide range of particle diameters, which means that the method can be utilized for different applications. On the solar cells, smaller particles diameters mean more grain boundaries, and consequently, loss of charge carrier [13].

Otherwise, it is important to note that at the spin coating process, there is an expressive material wastage, since only 2–5% of the material stays on the layers, while 95–98% drops out of the layer [14]. Another disadvantage is that this technique does not form uniform layers over a large area and it does not have roll-to-roll capability [15]. Lastly, there is a difficulty at the production of multilayers devices with this method.

The spin coating has a good cost effective, mainly at laboratorial use, to produce thin and uniform films. Anyway, it is indispensable to consider the advantages and the disadvantages before using this method to conclude if this is viable.

Since the success of the deposition of  $\text{Sn}(\text{S,Se})_x$  films using hydrazine-based solution, this method has been applied to fabricate highly efficient devices. CIGS thin film was deposited by spin coating using a hydrazine-based solution containing the chloride salts of the cations and thiourea [16]. Hydrazine is a solvent that has been used to prepare molecular inks to deposit highly pure films for highly efficient solar cells. The current world record efficiency for a solution-processed solar cell is hold by a device containing CIGS deposited via hydrazine-based solution (12.6% for a CIGS solar cell) [17, 18]. Hydrazine is used to dissolve elemental metals and binary compounds, as SnSe to produce kesterite solar cells [19]. It has also been used to prepare precursor solutions containing  $\text{Cu}_2\text{S}$  e  $\text{In}_2\text{Se}_3$  to deposit  $\text{CuIn}(\text{S,Se})_2$  thin films [20]. The advantage of using hydrazine is because it is a poor coordination solvent. During thermal treatment, hydrazine decomposes in small molecules ( $\text{H}_2$ ,  $\text{NH}_3$  and  $\text{N}_2$ ) which easily leaves the film without keeping residues. The absence of carbon or oxygen in hydrazine structure avoid organic impurities which compromise the solar cell efficiency [21]. However, hydrazine use is limited because it is highly toxic irritant, highly reactive and easily catch fire [12]. Because of that, hydrazine-free solutions have been studied to unexpected dangerous reactions.

Alcohols are a green, less toxic, and low-cost alternative for deposition solutions. Methanol-based solution containing the chloride salts of the cations and thiourea, as sulfur source, have been used to deposit CIGS films. The cation acetate salts are more recommended rather than the nitrate and chloride-based salts to form absorber layers with a minimum of residues.

Alcoholic solutions have also been used to prepare inks with butyldithiocarbamic acid (BDCA) as the sulfur source instead of thiourea to deposit CZTS solar cells with 6% conversion efficiency. Ethanol-based solutions with BCDA to dissolve

binary oxides  $\text{Cu}_2\text{O}$ ,  $\text{ZnO}$  and  $\text{SnO}$  to deposit CZTS films [20]. Ammonium thioglycolate has also been used to dissolve metallic oxides as an environmentally friendly alternative [10].

The cations and thiourea complexes with dimethyl sulfoxide (DMSO) or dimethyl formamide (DMF) to prepare molecular inks to deposit chalcogenide absorber layers [22]. This combination acts stabilizing the desired oxidation state of the metals in the resulting film [10]. Thiourea binds to the cations and avoid their evaporation during annealing [23, 24]. DMF and DMSO also dissolves selenourea to prepare the selenide compounds [9].

Beyond the salt-based precursor solutions and molecular inks, nanocrystals inks have also been used to deposit chalcogenide absorber films. CZTS solar cells fabricated using a nanoparticle-based solution have presented a maximum of 10.2% conversion efficiency, which is close value to the efficiency for a device prepared using hydrazine. The synthesis of the nanocrystals typically consist of oleylamine solution of the cation salts (chlorides or acetylacetonate) [13, 25], and a hot injection of sulfur oleylamine solution. Dodecanethiol and hexanethiol are alternatives to oleylamine [20]. Dichlorobenzene has also been used to dissolve sulfur. Dichlorobenzene is not recommended to prepare Se-based chalcogenides because of the Se low solubility in this solvent [25]. After separation and purification, the nanocrystals are dissolved in an organic solvent such ethanol, hexane, chloroform, or toluene to prepare the nanocrystal inks.

The combination of molecular and nanocrystal inks is known as hybrid ink [20]. A hybrid solution prepared by dispersing  $\text{Cu}_2\text{SnS}_3$  nanocrystals in a solution containing Zn and propylmercaptan to obtain a hybrid solution applied to deposit  $\text{Cu}_2\text{ZnSnS}_4$  thin films. The hybrid solution-based CZTS solar cell presented a PCE of 5% and  $V_{oc}$  of 440 mV [20]. Solvents may leave residues trapped in the film. The time and temperature for annealing and sulfur/selenization are not only essential for crystal growth but must also remove all the possible residues left by solvent and other organic [5, 26].

Although the CIGS devices prepared by vacuum-based techniques present values of efficiencies of  $\sim 23\%$ , the efficiency of a spin-coating deposited  $\text{CuIn}(\text{S,Se})_2$  solar cell is similar to the efficiency of a  $\text{Cu}(\text{Ga,In})(\text{S,Se})_2$  device fabricated in the same condition. In addition, the efficiency of a CZTS solar cell is the same as for a device fabricated by vacuum techniques. This evidences that spin-coating is an inexpensive alternative to fabricate highly efficient devices. The efforts for developing inks using environmentally friendly solvents, metals and chalcogen precursors, decreasing the residues in the films are fundamental to approximate the photovoltaic characteristics of a solution-processed device to the characteristics of the expensive vacuum-based solar cells (**Table 1**).

Absorber	solvent	$V_{oc}$ (V)	$J_{sc}$ ( $mA\ cm^{-2}$ )	FF (%)	PCE (%)	Ref.
$\text{Cu}(\text{In,Ga})(\text{S,Se})_2$	hydrazine	0.623	32.6	75	15.2	[16]
$\text{Cu}(\text{In,Ga})\text{S}_2$	methanol	0.787	17.0	62	8.3	[27]
$\text{CuIn}(\text{S,Se})_2$	ethanol	0.561	27.6	65	10.1	[28]
$\text{CuIn}(\text{S,Se})_2$	DMF	0.512	36.9	71	13.4	[9]
$\text{Cu}_2\text{ZnSn}(\text{S,Se})_2$	DMSO	0.457	36.0	65	10.7	[29]
$\text{Cu}_2\text{Zn}(\text{Sn,Ge})(\text{S,Se})_2$	DMF	0.583	33.6	56	11.0	[9]

**Table 1.**

*Photovoltaic parameters of highly efficient chalcogenide solar cells fabricated by spin-coating.*

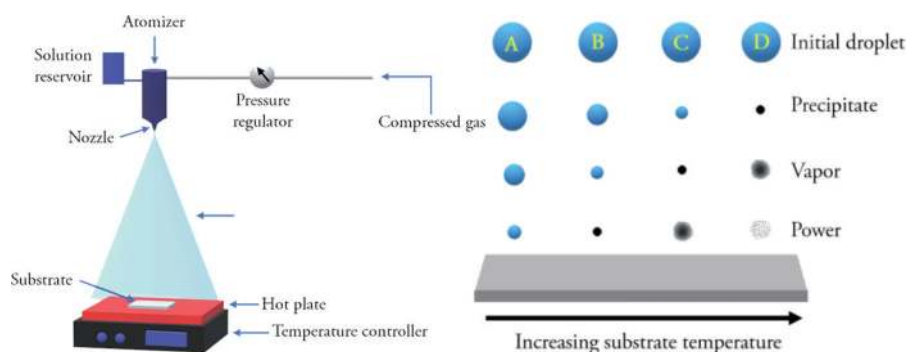
### **3. Spray-coating: a low-cost technique for chalcogenide solar cells**

In general, the success of the deposition of a thin film by spray-pyrolysis depends mainly on three factors: the composition of the precursor solution, the atomization and droplet transport process and the substrate temperature [30]. The control or modification of these parameters directly impacts the quality of the obtained film. Considering the production of the precursor solution, it can be composed of inorganic salts or organometallic compounds dissolved in aqueous or organic solvents, respectively.

The choice of the precursor reagent and solvent is an important step, since it will define the maximum concentration of salt that can be used and will directly affect the process of formation and transport of the aerosol in the atomization step [30]. The use of aqueous solvents and inorganic salts are the most used reagents, since they have lower degree of toxicity and environmental pollution than organic solvents and organometallic compounds. In addition, it has been observed that the use of alcoholic organic solvents can lead to carbonaceous impurities that are harmful to the photovoltaic device. They affect the growth of crystals in the film and acting as barriers for extracting loads, leading to low values of open-circuit voltage ( $V_{oc}$ ) and fill factor (FF) of the solar cell [31, 32]. A common approach in the production of precursor solutions for deposition of copper-based chalcogenides thin films, such as CIS and CIGS, is to prepare aqueous solutions stocking the chloride or nitrate salts of the metals of interest, and the sulfur source, which is normally the thiourea. The concentration of the sulfur precursor is usually 5 to 10 times more concentrated than metallic salts. The excess of the sulfur has a compensatory role due to losses during deposition, and when using molybdenum substrate, it prevents the formation of oxides of this metal [33, 34]. These solutions are diluted and mixed to obtain the final precursor solution, the concentration of each component in the final solution must be varied in order to assess the influence of each metal on the chemical and physical properties of the obtained films. Solar cells with a CIGS absorbing layer obtained by spray-pyrolysis using this approach in the preparation of the precursor solution have achieved 5 to 10% efficiency [31, 35].

The typical atomizers used for depositing chalcogenides films are the pneumatic and ultrasonic. The aerosol formation mechanism is quite different between the two models, while in the pneumatic the aerosol is formed by the action of a pressurized gas, in the ultrasonic, the aerosol is produced by ultrasonic waves generated by a piezoelectric component that is in contact with the solution, the formed aerosol is transported to the substrate surface by a carrier gas [36, 37]. Although ultrasonic atomizers are more expensive and complex than pneumatic ones, these atomizers have better control of average droplet size and the rate of aerosol formation is independent of the flow rate of the carrier gas. The efficient control of the droplet size distribution is important due to its influence on uniformity of the deposited film [38]. The two types of atomizers mentioned are also differentiated by the atomization rate and the initial speed of the drops, because as the pneumatic works with a pressurized gas carrier, both the atomization rate and the velocity of the droplets are much higher [30, 39]. In pneumatic spraying, the main factor to be tested is the pressure of the carrier gas, since the distribution of the average size of the droplets and the initial velocity of the droplets, as well as the rate of aerosol formation are directly linked to this factor. On the other hand, when using an ultrasonic atomizer the main factor to be monitored is the atomization frequency, since the distribution of the average droplet size is defined by this parameter [40]. When choosing carrier gas, one must consider whether it is reactive or not. Oxidizing gases, such as  $O_2$ , should be avoided, as they can react with the precursor metals in the pyrolysis phase,





**Figure 2.** Schematic illustration of thin film deposition by spray-pyrolysis and the effect of increasing substrate temperature on the spray-pyrolysis deposition.

leading to the formation of unwanted oxides. In this sense, inert gases such as  $N_2$  or Ar are the most suitable for depositing chalcogenides by spray-pyrolysis [41].

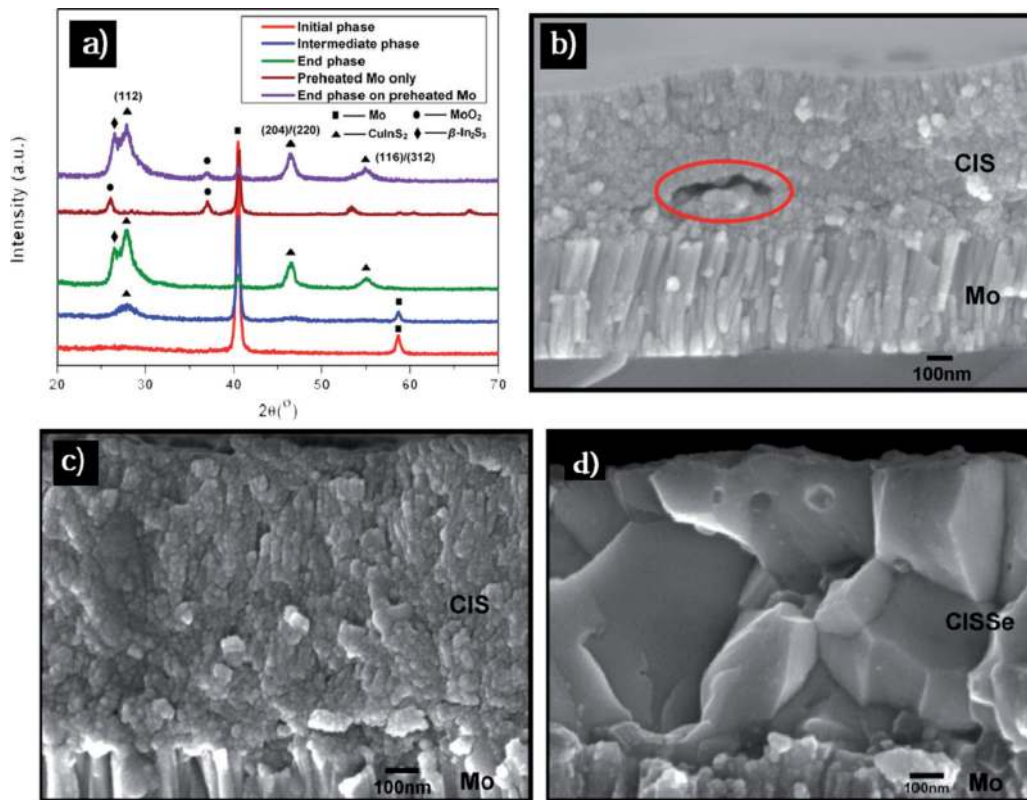
Among the several factors that must be taken when depositing thin films by spray-pyrolysis, the substrate temperature is pointed out as the most important parameter [38]. Many stages of the thin film deposition process depend directly on the substrate temperature, among which are: droplet spreading, solvent evaporation and salt decomposition and compound formation. All these steps are important for obtaining the compound with the desired chemical and physical characteristics in the form of a homogeneous thin film. **Figure 2** summarizes the effects of increasing the temperature on the deposition process [30, 38, 39]. At low temperatures, the solvent still does not evaporate and the droplets of the precursor solution collide with the substrate and undergo decomposition (process A). At intermediate temperatures the solvent evaporates completely during transport, reaching the substrate in the form of a dry precipitate which then decomposes (process B). From intermediate to high temperatures, the solvent evaporates, and the solid precipitate is formed, but before reaching the substrate the precipitate melts and vaporizes, leading to chemical vapor deposition (CVD) (process C). Finally, at high temperatures (process D) the vapor phase formed after melting the precipitate decomposes to form the compound powder, which is deposited on the substrate. In this context, the processes A and D are not indicated for chalcogenides deposition, because the films obtained are often rough or the form of poorly adherent powder [38]. Thus, temperatures where processes B or C can occur ( $300^\circ$  to  $450^\circ\text{C}$ ), are the most suitable for the deposition of thin films of chalcogenides such as CIGS and CZTS.

**Table 2** shows the parameters used in the spray-pyrolysis deposition of absorber layers of copper-chalcogenide thin film from aqueous precursor solutions and the parameters obtained in the solar cells. As can be seen, most of the chalcogenide films are deposited using pneumatic atomizer, this reflects the simplicity and cost-benefit of this type of system. Other points to note are the prevalence of the use of  $N_2$  as a carrier gas, and the flow rate that varies between  $0.25$  and  $3\text{ ml min}^{-1}$ .

Mo-coated glass is among the most used substrates for depositing chalcogenides for PV applications. However, the preheating temperatures of the substrates required in the spray-pyrolysis process are high enough ( $T \geq 200^\circ\text{C}$ ) for the formation of Mo oxides. The oxide layer can lead to loss of charge carrier collection efficiency and worsen the adhesion of the film that will be deposited later. The solution found by Ho and colleagues [31] was to deposit the CIS layer with a gradual increase in substrate temperature from  $120^\circ\text{C}$  to  $300\text{--}350^\circ\text{C}$ . The XRD patterns shown in **Figure 3a** indicate that in the initial phase of deposition (red line) with temperatures between  $120$  and  $150^\circ\text{C}$ , in the intermediate phase with temperatures

Deposition parameters				Solar cell parameters					Ref.		
Absorber	Atomizer	Gas carrier	ultrasonic frequency (Hz)	Rate flow (mL min <sup>-1</sup> )	Substrate temperature (°C)	Atomization gas pressure (MPa)	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA cm <sup>-2</sup> )	FF (%)	PCE (%)	Ref.
CIGSSe/ CdS	PSP	N <sub>2</sub>	—	—	300–350	0.4	0.62	24.29	69.84	10.55	[35]
CZTS/CdS	PSP	Ar	—	3	220	0.2	0.41	10.07	33.0	1.4	[41]
CZTS/In <sub>2</sub> S <sub>3</sub>	PSP	N <sub>2</sub>	—	1.2	450	0.1	0.43	28.27	47.07	5.54	[42]
CIGSSe/ CdS	USP	—	—	—	430	—	0.64	27.43	61.93	10.89	[43]
ACZTSSe/ CdS	PSP	—	—	—	380	—	0.67	18.5	57.6	7.14	[44]
CIGSSe/ CdS	PSP	N <sub>2</sub>	—	3	280	0.4	0.37	27.3	50.6	5.14	[45]
CCTS/CdS	USP	—	—	—	280	—	0.21	22.0	—	1.14	[46]
MCZTS/ CdS	PSP	N <sub>2</sub>	—	—	450	—	0.67	17.2	59.34	6.73	[47]
ACZTSSe/ CdS	PSP	N <sub>2</sub>	—	—	350	—	0.34	36.95	55.92	71	[48]
ACZTSSe/ CdS	PSP	N <sub>2</sub>	—	2	280	0.5	0.47	29.41	60.0	8.28	[24]

**Table 2.** Atomizer parameters used in the spray-pyrolysis deposition of some copper-chalcogenides and the parameters obtained in solar cells.



**Figure 3.** (a) XRD patterns of the CIS films deposited by spray-pyrolysis at different substrate heat stage. (b) Cross-section SEM image of CIS film deposited on the preheated substrate. (c) Cross-section SEM image of CIS film deposited with gradual substrate heating. (d) CISSe film after heat treatment and selenization processes. Adapted with permission from [31]. Copyright (2014) American Chemical Society.

between 150 and 250°C (blue line) and the final phase with temperatures between 250 and 350° (green line) there were no characteristic peaks of  $\text{MoO}_2$ . On the other hand, in the films in which the Mo substrate was preheated between 300 and 350°C (violet line), peaks related to  $\text{MoO}_2$  were found. **Figure 3b** and **c** show the scanning electron microscopy (SEM) images of films deposited with preheating and gradual heating, respectively. As can be seen, the CIS film deposited with preheating was less uniform and with pores at the CIS/Mo interface. The formation of Mo oxides is identified as the main cause of film malformation. Finally, most of the chalcogenides thin films deposited by spray-pyrolysis require a thermal treatment after their deposition, this is essential to increase the crystallinity, as shown in **Figure 3d**, and by means of sulfurization or selenization serves also for the stoichiometric improvement of S or Se deficient films.

#### 4. Conclusions

Solution-processed chalcogenide thin film solar cells have already reached similar efficiencies to the ones prepared by using vacuum techniques. Spin-coating and spray-coating are inexpensive alternatives to fabricate highly efficient devices. The progress in the field since the hydrazine-based solution to deposit chalcogenide led to the development of environmentally friendly and low-cost molecular inks, nanocrystal inks and hybrid inks. Although solution-processed CIS and CZTS solar cells are equally to or more efficient than the vacuum-based devices, many improvements need to be done to put solution-based CIGS solar cells on top of the



efficiency charts. Spin- and spray-coating are undoubtedly more advantageous for the process of solar cells fabrication, and more efforts are still needed to develop inks using environmentally friendly solvents, metals and chalcogen precursors. It is still needed to work on decreasing the residues in the films to eliminate any possible site of recombination. Optimization of these techniques will be essential to the scalability of the fabrication of the highly stable and highly efficient solar cells.

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## **Conflict of interest**


The authors declare that there is no conflict of interest.

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