Ksterite thin films for photovoltaics: a review

S. Delbos^{1,2,3,a}

¹ EDF R&D, Institut de Recherche et Dveloppement sur l'nergie Photovoltaque (IRDEP), 6 quai Watier, 78401 Chatou, France

² CNRS, UMR 7174, 78401 Chatou, France

³ Chimie ParisTech, 75005 Paris, France

Received: 21 December 2011 / Accepted: 21 May 2012
Published online: 14 August 2012

Abstract In the years to come, electricity production is bound to increase, and $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTS) compounds, due to their suitability to thin-film solar cells, could be a means to fulfill the demand. After explaining the reasons of the sudden interest of the CIGS scientific community for CZTS solar cells, this paper reviews recent papers published on the subject of ksterites-based solar cells. After a description of crystallographic and optoelectronic properties, including CZTS crystalline structure, defect formation and metal composition, this review paper focuses on CZTS synthesis processes and device properties. Synthesis strategies, including one- or two-step processes, deposition temperature, binary formation control via atmosphere control and their effect on device properties are discussed.

1 Sustainability of photovoltaic industry

In the years to come, electricity production is bound to increase (from 17 PWh in 2009 to 28–34 PWh in 2035 [1]) and as a consequence the increased demand on fossil fuels as well as possible regulations on CO_2 emissions are bound to increase the wholesale electricity costs. On the other hand, the price-experience factor of 22% that was observed for the last 4 decades should stay at the same level or slightly below [2,3], leading to a decrease of photovoltaic (PV) electricity costs [2,4]. A first change of paradigm is now happening, because in some places like South Italy and other sunny/high electricity price regions [5], the price of retail electricity is higher than the cost of PV electricity (grid parity). A second parity, the “fuel parity”, will happen when the cost of PV electricity is lower than the marginal costs of operating fossil fuel based power plants [6]. According to deployment scenarios, this fuel parity could happen between 2020 and 2040.

The massive deployment of PV foreseen in years 2020–2040 could lead to 1.5 to 2.5 TWp of worldwide installed PV capacity in 2030, with a demand of 20–150 GWp/y and around 30% of the market taken by thin films [2,4].

The question of the sustainability of the production of 20–150 GWp/y of PV was raised by a few publications, and in particular the worldwide mining and refining capacity of a few critical elements could be the main problem of the photovoltaic industry in the years to come. Each

PV technology has one or more limiting elements, such as silver for crystalline silicon, indium and gallium for CIGS, Tellurium for CdTe, Ruthenium for dye-sensitized solar cells, silver and indium for thin-film silicon, germanium, gold, indium for III-V PV [7,8]. The chalcogenide technologies are particularly vulnerable to In, Ga, Te supply, which has been noted critical or near critical by the US Department of Energy [9] or the European Commission [10].

According to various authors, the production of PV modules could be limited below the demand reported earlier in this paper, as summarized in Table 1. Crystalline silicon PV seems suitable for supplying the demand, but one should keep in mind that the basic assumption used for the third and fourth column of this table is that all worldwide production of silver is used for crystalline PV. The fifth column shows the forecast 2030 demand for Ag, Te, In with respect to the 2008 production. It appears that the demand will grow enormously. If we focus on In, in 2030 the total demand (including PV and other uses) could be 3 to 7 times the 2008 production [10,11], whereas, as In is a byproduct of Zn extraction, the elasticity of the production with respect to demand is low. One author suggests that CIGS and CdTe technologies will not be impeded by resources problems, but he does not take the increase of other sources of demand for In and Te into account [12].

The sustainability of PV production is therefore a real question, and the development of a new PV technology based on abundant and preferably non-toxic elements would alleviate the pressure on all PV technologies in term of resources.

^a e-mail: delbos.sebastien@gmail.com

Fig. 1. Evolution of the record efficiency for CZTS solar cells. See Table 2 for the references.

Table 1. Production limitations of the PV technologies [7, 8, 10–12, 129].

PV technology	Limiting element	Max installed capacity based on the limiting element reserves (1.5–2.5 TWp demand)	Max yearly production based on annual production of limiting material (20–150 GWp demand)	Ratio (demand 2030/2008 production) of limiting element
c-Si	Ag	5–15 TWp	305 GWp	20
CdTe	Te	0.1–0.8 TWp	2.3–40 GWp	50
CIGS	In	0.1–0.6 TWp	13–26 GWp	3
Dye-sensitized solar cells	Ru, In (TCO)	0.06–0.9 TWp	2.2 GWp	n.a.

2 Advantages of CZTS

Recently the CIGS scientific community started to work on $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTS), and the enthusiasm was kindled by the fast increase of record efficiency of CZTS-based solar cells, from the 2009 record of 6.7% [13] to 2011 record of 10.1% [14], as shown in Figure 1. CZTS has numerous advantages that could lead to its massive use as an abundant, non toxic, low cost absorber for thin-film photovoltaic solar cells:

- it is a compound whose intrinsic point defects lead to *p*-type semiconductor behavior;
- it has a direct bandgap and an absorption coefficient $>10^4 \text{ cm}^{-1}$, which is suitable for thin film photovoltaics applications [15–17];
- its band gap has been predicted [18] to be 1.0 eV for $\text{Cu}_2\text{ZnSnSe}_4$ and 1.5 eV for $\text{Cu}_2\text{ZnSnS}_4$ and evidences of the bandgap tunability have been found via the variations of V_{OC} [19], as well as direct measurements of the variation of the bandgap between 1.0 eV for $\text{Cu}_2\text{ZnSnSe}_4$ and 1.5 eV for $\text{Cu}_2\text{ZnSnS}_4$ [20–24]. The band gap of CZTS can also be tuned by incorporation of Ge, Ge-containing materials having smaller bandgap than their Ge-free counterparts [25]. This tunability is of particular interest for the manufacturing of absorbers with a band gap between 1.1 and 1.5 eV, which allow theoretical efficiencies higher than 30% [26];
- its crystallographic structure can accept some shifts from the stoichiometric composition [27];
- it includes Zn and Sn which are respectively produced in quantity 20 000 and 500 times bigger than In [28];
- it is possible to make CZTS solar cells just by replacing CIGS by CZTS in CIGS solar cells, and such solar cells yielded efficiencies up to 10.1% [14, 29]. The knowledge gathered on back contact, buffer layers and window layer by CIGS scientists can therefore be used and adapted for CZTS solar cells. Nevertheless, for high efficiency solar cells the processes used for CIGS solar cells will need to be tuned. The buffer layer, in particular, will have to be tailored in order to adjust the lattice-matching, the valence and band offsets with CZTS;
- the grain boundaries (GB) seem to have the same beneficial properties for CZTS as for CIGS, such as enhanced minority carrier collection taking place at the GB [30].

3 Crystallographic and optoelectronic properties

This paper is focused on synthesis processes of CZTS, and thus will only briefly address the crystallographic and optoelectronic properties. For more information on crystal and band structure and defects in ksterites, the reader can find a recent review dedicated to these topics here [31].

3.1 Crystalline structure

In the literature $\text{Cu}_2\text{ZnSnS}_4$ and $\text{Cu}_2\text{ZnSnSe}_4$ (as well as $\text{Cu}_2\text{ZnGe}(\text{S},\text{Se})_4$ [32]) are described by the structural models of two natural minerals: stannite (space group $I-42m$) [33–35] and ksterite (space group $I-4$) [33]. These crystal structures are very close, in both structures the cations are located on tetrahedral sites but their distributions on planes perpendicular to the c -axis are not the same. In addition, the position of the chalcogen atom is slightly different in these structures [33–35].

- ksterite: $(\text{Cu} + \text{Sn}) / (\text{Cu} + \text{Zn}) / (\text{Cu} + \text{Sn})$, chalcogen in position (x, y, z) , Figure 2;
- stannite: $\text{Cu} / (\text{Zn} + \text{Sn}) / \text{Cu}$, chalcogen in position (x, x, z) .

In the rest of the paper, “ksterite” will be used for the crystallographic structure, and “ksterites” will be used for $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ compounds that are crystallized in ksterite type structure. X will be used for the chalcogens S and Se when an effect or properties can apply to both of them (for example $\text{Cu}_2(\text{S},\text{Se})$ will be noted Cu_2X).

Due to their structural similarities, ksterite and stannite are very difficult to distinguish by X-Ray Diffraction and Raman spectroscopy, and it is necessary to use neutron diffraction [36, 37] to tell them apart. According to ab initio calculi, the most stable crystalline structure is ksterite [38–42] and one study by ab initio calculation even suggests that all observations of stannite structure for CZTS compounds were due to partial disorder in the I-II (001) layer of the ksterite phase [32]. Recent neutron diffraction [37] and anomalous diffusion [43] characterizations show that CZTS crystallizes in the ksterite structure, and synchrotron X-Ray experiments show that this structure is dominant for temperature $< 876^\circ\text{C}$ (transition to a sphalerite cubic structure) [37].

The structural difference between $\text{Cu}_2\text{ZnSnS}_4$ and $\text{Cu}_2\text{ZnSnSe}_4$ is not clear. It seems that the Se compound has larger lattice parameters as well as higher electric conductivity than the S compound [20]. Concerning mechanical and thermo-physical properties of CZTS, no experimental data are available, but ab initio simulations were performed [44, 45].

Sulfur ksterites have XRD peaks very close to those of ZnS and Cu_2SnS_3 [36], and Raman spectroscopy is necessary to tell them apart [46]. Nevertheless, it is not possible to have a quantitative determination of the secondary phases by Raman. For such purpose, XENAS has been used [47].

Fig. 2. $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ compound in ksterite structure, according to [33].

3.2 Intrinsic point defect formation

The ksterite structure allows for several types of point defects which make discrete energy levels appear, allowing p-type doping. As in the CIGS materials, the doping is obtained by stoichiometry variations and not by extrinsic doping. Nevertheless, according to ab initio calculi, the ksterite structure is less tolerant to these variations than the chalcopyrite structure [39, 48–51]. According to point-defect measurements, the ksterites are susceptible to higher carrier recombination than chalcopyrite [52]. Measurements of the deep defects of CZTS are reported here [53].

Generally, the Sn-Se bond is much stronger than the Zn-Se and Cu-Se bond, leading to a high formation energy of V_{Sn} [51]. Contrary to CIGS, the accepting defect the most easily formed is not V_{Cu} but Cu_{Zn} [39, 49, 54, 55]. Nevertheless some authors suggest the contrary [52, 56, 57]. Zn_{Cu} substitutions occur at the 2c site and Cu_{Zn} at the 2d site [36, 58] (see Fig. 2). The accepting defects are easily formed, leading to difficult n-type doping [54]. The easy formation of Cu_{Zn} accepting defects also leads to low charge separation, a drawback that could be overcome thanks to the type-II band alignment of the CZTS/CdS interface [49]. The most active recombination centers are expected to be Cu_{Sn} (In_{Cu} for CIGS), and the lack of defect complex ($2V_{\text{Cu}} + \text{In}_{\text{Cu}}$ for CIGS) is thought to lead to the higher defect concentration observed [59].

3.3 Metal composition

The single phase composition region is much narrower for CZTS than for CIGS. According to the Tallinn team, single phase CZTS monograin powders can be synthesized only from a precursor mixture comprising metal ratios of $\text{Cu}/(\text{Zn} + \text{Sn}) = 0.92\text{--}0.95$ and $\text{Zn}/\text{Sn} = 1.0\text{--}1.03$ [60]. Nevertheless, a Rietveld refinement of anomalous dispersion measurements revealed a $\text{Cu}/(\text{Zn} + \text{Sn}) = 0.97$, and $\text{Zn}/\text{Sn} = 1.42$ composition for ksterites crystals [43], suggesting that the single phase composition region is not as narrow as the Tallinn team suggests.

Until now, only Zn-rich and Cu-poor materials gave high efficiency (see Fig. 3), as was already noted by the Nagaoka team [61]. In Zn-rich growth conditions, the ksterite structure is tolerant to stoichiometry deviations

Fig. 3. Composition map of the best CZTS solar cells. The diameter of the circles is proportional to the conversion efficiency. See Table 2 for the references.

by zinc excess and copper lacking [61–64], in the form of Zn_{Cu} and V_{Cu} vacancies [51, 65], but high Zn content also leads to structural disorder [66].

3.4 Bandgap measurement

Absorbance measurements are not suitable for extracting the bandgap values, because the absorption coefficient derived from spectrophotometric data on thin films is determined by defect absorption and by measurement accuracy limitations [66]. In particular, ZnSe [67] and Zn-caused disorders [66] lead to incorrect bandgap determination when it is determined from absorbance measurements. PL measurements now confirm that the bandgap of $\text{Cu}_2\text{ZnSnSe}_4$ is indeed around 1.0 eV at room temperature [68], whereas before that publication the measured band gap was around 1.5 eV. Suitable methods for measurement of CZTS bandgap are PL, TR-PL and EQE measurements.

4 Synthesis strategies

4.1 One-step or two step processes for thin films

For CIGS, the deposition techniques used to be classified as vacuum and non-vacuum techniques. For CZTS, the same approach was also used in a review [69]. Nevertheless, for CZTS, this classification is not accurate, because recent works showed that low-cost deposition does not mean low-cost solar modules [70], and because of the problematic of binaries control during CZTS synthesis (see next paragraph). We therefore decided to classify the processes into one-step or two-step processes:

- Two-step processes, where the needed elements are first incorporated during an ambient temperature process, followed by an annealing step. The chalcogen can be incorporated into the precursor or during the annealing step. These processes allow the use of fast and low-cost techniques for precursor deposition. Until now, and contrary to the CIGS, two-steps processes yielded the best efficiencies (more than 10%) [14]. IBM works on three such processes, the hybrid solution-particle technique [14], electrodeposition [71] and co-evaporation [72]. Other teams investigated numerous other deposition techniques, such as codeposition by evaporation, sputtering, OA-CVD (Open Atmosphere Chemical Vapor Deposition), nanoparticles, sol-gel (see Tab. 2).
- One-step processes, where all the elements are incorporated simultaneously. This type of processes yields the better results for CIGS, but until now it was not the case for CZTS. The best efficiency until now is 9.15% by coevaporation [73]. Only a few groups published significant results in terms of solar cell efficiency: NREL [73], Tallinn University [74], HZB [75]. Other groups tried reactive sputtering and pulsed laser deposition (PLD) (see Tab. 2). The method of Tallinn University also introduces a huge difference in cell architecture, where 50 μm CZTS monograins are synthesized in molten KI, wrapped in the buffer layer and attached to the substrate by epoxy glue [76].

These processes are different, but the two types of processes (one-step and two-steps) reached high efficiencies ($>9\%$). Until now, it does not seem that one or the other is intrinsically better, because, as we will see in the next paragraphs, the key point is temperature and atmosphere control during the one-step deposition or annealing step.

Table 2. Synthesis methods for CZTS solar cells.

Synthesis method	Chalcogen and method of insertion	η (%)	I_{sc} (mA/cm ²)	V_{oc} (mV)	FF (%)
Spin-coating of metal-chalcogen colloids in a hydrazine solution, 540 °C thermal treatment [14, 29, 64, 130, 131]	S, Se (in the colloids) S/(S+Se) $\sim$ 0.4 S/(S+Se) $\sim$ 0.03	10.1 [14] 10.1 [29]	31 39	517 423	64 62
Coevaporation of metals and Se, three-stage process [73]	Se during coevaporation, 40 �/s	9.15 [73]	37.4	377	65
Coevaporation of metals and cracked S on low-temp (150 °C substrate) followed by 5 min anneal at 570 °C at atmospheric pressure [72, 120] Coevaporation of metals followed by 540 °C with S, 5 min [94, 103]	Pure sulfur, coevaporated. Mix of coevaporated S and Se (7.5%) [121]	8.4 [72]	19.5	661	66
Monograin solar cells with S/Se gradient [74]	CZTSe monograin ($\sim$ 50 �m), SnS ₂ annealing causing a 0.1–2 �m S diffusion.	7.4 [74]	18.4	720	60
Monograin cells [19, 23, 76, 132]	Sn _{0.75} , Se _{0.25} [76]	7.3 [23]	19.9	696	58
Sequential electrodeposition [71, 133–141]	585 °C in S/N ₂ for 12 min	7.3 [71]	22	567	58
Blade-coating of CZTS nanoparticles in hexanethiol. Best efficiency (7.2%) after light-soaking. 6.8% with Cu ₂ ZnSn _{0.3} Ge _{0.7} (S _{0.5} , Se _{0.5}) ₄	S in the colloids, Se thermal treatment (20 min 500 °C)	6.7 [142] 6.8 [25]	30.4 21.5	420 640	52 49
Cosputtering of ZnS, SnS, Cu [13, 65]	3 h at 580 °C with H ₂ S	6.7	17.9	610	62
Stacked deposition of ZnS (sputtering) / Cu (evaporation) / Sn (evaporation) [106]	30 min in Se atmosphere	6.0	31.5	390	49
Stacks of evaporated metals [17, 113], 6.1% with Cd buffer, 5.8 with Cd-free buffer. Variation with evaporation of ZnS, Sn, Cu [100]	Sulfurization	5.8	15.8	618	60
Open-Atmosphere Chemical Vapor Deposition (OA-CVD). Spray pyrolysis of metal-oxide precursors [143]	520–560 °C for three hours in 5 vol% H ₂ S balanced with N ₂ .	6.0	16.5	658	55
Coevaporation of Cu, Zn, Sn, Se [98]	Thermal treatment in the presence of Sn and S	5.4	20.0	497	54
Sol-gel: metals and sulfur in ethanol [144]	Annealing under N ₂ +H ₂ S (5%) atmosphere at 530 °C for 30 min	5.1	18.9	517	53

Table 2. Continued.

Synthesis method	Chalcogen and method of insertion	η (%)	I_{sc} (mA/cm ²)	V_{oc} (mV)	FF (%)
Sputtering of Cu/ZnSn/Cu [108]	Annealing 30 min 560 °C	4.6	15.4	545	55
Metallic precursors in alcohol [99]	Thermal treatment in Se atmosphere	4.2	23.2	305	55
Metal chlorines in dimethyl sulfoxide [145]	Thiourea in solution and Se atmosphere, 500 °C	4.1	24.9	400	41
Fast coevaporation (~20 min) of Cu, Sn, ZnS [75]	Cracked sulfur during evaporation	4.1	13.0	541	60
Cosputtering of Cu, Sn, Zn [146]. Variations with Cu/Sn, Zn and Cu/Sn, ZnS [147, 148] and with Se thermal treatment [149]	S in sealed glass tube	3.7 [146]	16.5	425	53
One-step electrodeposition of metals [16, 62, 85, 104, 150–153]. One-step electrodeposition (including sulfur) [154–157]	H ₂ S in Ar at 550 °C for the record. Other techniques includes S in Ar, H ₂ S in Ar, S in N ₂ , Se and H ₂	3.4 [62]	14.8	563	41
Reactive cosputtering of Cu, Zn, Sn in H ₂ S/Ar [30]	50% H ₂ S / Ar mixture at 5 mtorr	3.4	12.4	428	64
Sequential sputtering of Cu, Zn, Sn [158]	Se vapors at 500 °C for 30 min	3.2	20.7	359	43
PLD from CZTS based on sintered Cu ₂ S, ZnS and SnS ₂ . N ₂ thermal treatment at 500 °C during 1 h [159–162]	S in the CZTS pellets	3.14	8.8	651	55
Sol-gel solution (metals/methoxyethanol) [91, 163]. Nanoparticles on flexible Al foil, ZnS as buffer layer [118]	H ₂ S 3% in N ₂	2.23	10.2	529	42
Successive ionic layer adsorption and reaction S (SILAR) [164, 165] (measurements at 30 mW/cm ²)	1.85	3.2	280	62	
Sequential e-beam evaporation of Cu, Zn, Sn [166]	S vapors for 2h at 560 °C	1.7	9.78	478	38
Reactive sputtering from Cu ₂ ZnSn target [167, 168]	H ₂ S plasma	1.35	9.52	0.343	41
Chemical bath deposition of SnS, ZnS, Cu ion exchange [169]	H ₂ S at 500 °C for 2 h	0.16	2.4	210	31
Evaporation from a quaternary source [170]		0.36

Fig. 4. SEM cross-section of CZTSe films grown at the same temperature and constant deposition fluxes, except Cu rates were adjusted to produce only (a) Cu-rich growth or (b) Cu-poor growth [59].

Other methods of synthesis that did not produce solar cells include: cosputtering of Cu, Sn, Zn followed by annealing in a hot tube in presence of H_2S [77], dip-coating in a methanol solution followed by annealing at 200 °C in air [78], CZTS nanoparticles in oleylamine [79], chemical bath deposition [80], sputtering of a sintered mix of $CuSe$, ZnS , and SnS_2 [81].

4.2 CZTS formation

Similarly to CIGS, CZTS needs temperature between 500 and 600 °C to be synthesized. Nevertheless, the chemical reactions are not yet completely understood, even if a reaction path was proposed [82]. There are successive reactions taking place in the bulk of the layer between the elements leading to binaries, ternaries and finally the quaternary.

At room temperature, only metal binaries can form, for example Cu_6Sn_5 [83], Cu_5Zn_8 [84], Cu_3Sn and $CuZn$ [85]. At higher temperature, between 200 and 450 °C, metal-chalcogenide binaries such as CuX , Cu_2X , and SnX form [86–88], and for temperature >450 °C, Cu_xX binaries then react with Sn to form Cu_xSn_yS [80]. At higher temperature (between 550 and 580 °C [71,85,86,89]), and for longer annealing time (~8 h) or one-step deposition at 500 °C [73,83], ZnX reacts with Cu_2SnX_3 to form Cu_2SnZnX_4 according to the equation proposed by [82]:

In order to control which reactions take place during the annealing step of a two-step process, it is necessary to closely monitor the temperature of the layer, because, for example, too fast an annealing can lead to liquid Sn bubbles formation, preventing the formation of large grains [90]. For processes using elemental sulfur or selenium, fast annealing (a few minutes) is possible, whereas for processes using H_2S , which is less reactive than elemental sulfur, a long annealing time (2–3 h) is necessary for

the binaries to react completely and to form large grains of CZTS [91,92].

For one-step processes, Cu-rich growth conditions are needed at the beginning of the reaction in order to foster growth of large grains [73,93], as shown in Figure 4. Nevertheless, for both processes, the finished layer must be Zn-rich (see part 4.3), and in particular Cu_2X -free [60] in order to get high photovoltaic efficiencies. If the layer is not Cu_2X -free at the end of the synthesis process, the subsequent cyanide etching leads to possible voids and defects [89]. If Zn-rich growth conditions are used, ZnX formation is promoted [48,49].

Therefore, for one-step processes it is necessary to adapt the rate of deposition of each element with respect to the reaction path, as well as control deposition temperature, because higher temperatures can also increase grain size [59]. For two-step processes it is necessary to closely monitor growth conditions, and in particular prevent Cu_2X formation and increase ZnX reaction with Cu_2SnS_3 .

4.3 Atmosphere control

Unfortunately, contrary to CIGS, the elements involved in CZTS synthesis are prone to evaporation and sublimation. Zn sublimates at 430 °C [94], $SnSe$ at 350 °C [88], SnS at 370 °C and Sn evaporates at 460 °C [95,96]. Moreover, high temperatures promote CZTS decomposition, according to the chemical equilibrium between CZTS and solid and gaseous binaries [97,98].

If this equilibrium is displaced towards the right member, ZnX , SnX and X formation and losses will occur, leading to a Cu_2X -rich layer, increasing layer resistance and preventing good photovoltaic efficiencies (see 5.6). It is therefore of the utmost importance to prevent CZTS

decomposition as well as binaries losses. The key to that result is atmosphere control.

The equilibrium of equation (2) can be displaced towards CZTS by saturating the atmosphere in one of the right-side members of the equation [93,97]. It is possible to counteract SnX evaporation by introducing gaseous SnX during the thermal treatment [98], or by increasing the partial pressure of the chalcogen [99], by performing the chalcogenation in a small closed volume [100], or by using a cap on the precursor layer during annealing [101]. If the annealing takes place in a H_2 atmosphere, Zn loss can be prevented by using ZnS as a precursor [102]. Continuous evaporation of Zn towards the substrate prevents the decomposition of CZTS in a coevaporation process [73]. It also seems that the presence of MoX_2 at the back contact pushes the reaction towards the right member [103].

If atmosphere control is not good, annealing time is the next best lever on CZTS decomposition, because if CZTS is synthesized and cooled rapidly, only a small quantity of binaries will be lost. One paper compared slow and fast annealing [104]. It concluded that fast annealing is better than slow annealing because many different secondary phases were found with slow annealing, without more explanation. Nevertheless, in this case slow annealing could be linked to a badly controlled reaction atmosphere, leading to CZTS decomposition into binary and ternary phases.

Concerning the key point of atmosphere control, strategies of synthesis should be slightly different for one-step or two-step processes. For two-step processes, there seems to be two stages during the annealing step: one short (a few minutes) step of CZTS formation, and one longer (up to a few hours) step of grain growth. The control of the atmosphere should be very accurate in the second step, and the reaction atmosphere could also be completely different from the first step [93]. Fortunately, it is quite easy and inexpensive to design annealing equipments that provide good static atmosphere control (that is to say, equipments where nothing can either go in or go out). Nevertheless, vapor injection is more tricky, as it requires carrier gas, pressure measurements, leading to an equipment resembling an evaporator.

For one-step synthesis, atmosphere control is not so easy, because reaction chambers are designed for controlling the deposition rate and not the partial pressure of each element. In order to prevent CZTS decomposition and binaries losses, Sn and chalcogen deposition rate should remain high during the cooling phase, in order to counteract Sn loss [73].

4.4 Composition gradient

The composition gradient either created by a variation of the rate of deposition of each element in a codeposition or by stacked elements, has an influence on CZTS film properties, because of Cu diffusion, Sn loss and chemical mechanisms of formation.

Concerning Cu, its diffusion can create voids at the back contact. Two-step processes, especially when the

precursor layer is a codeposited metal layer or stacked metal layers with Cu as first layer, are subject to these voids [89,103]. Secondary phases are observed, preventing the total formation of CZTS [105].

As explained in the previous paragraph (see Eq. (2)), Sn evaporates if the atmosphere is not well controlled. Nevertheless, the loss of Sn could also be prevented by having the Cu layer on top [63,93].

Concerning the reaction mechanism, for stacked metals, it is beneficial to have Cu and Sn in close contact for the formation of large CZTS grains [106]. If they are separated by Zn or Zn(S,Se), the reaction between copper chalcogenides and tin chalcogenides, which is necessary to form Cu_2SnX_3 [82], could be inhibited [107]. For stacked metals, Cu on top seems to foster formation of Cu_xS , which may result in larger grains and denser films [108]. For one-step processes, high Cu content at the beginning of the deposition promotes the formation of large grains [73].

Concerning the composition gradient,

- for two-steps processes, the Cu must not be deposited first, and Cu and Sn should be in close contact. The possible combinations for stacks are therefore Mo/Zn(X)/Cu/Sn or Mo/Zn(X)/Sn/Cu. The codeposition seems also possible, but with a Cu-poor composition near the back-contact;
- for one-step processes, the layer must be Cu rich at the beginning of the deposition in order to promote the growth of large grains.

4.5 Sodium

Sodium seems to have the same effects on CZTS as on CIGS: it promotes the growth of larger grains, enhances conductivity and has a significant effect on film morphology, as was demonstrated by SLG / borosilicate substrate comparison and dipping in Na_2S [109,110]. Nevertheless, contrary to CIGS, Na was not detected by XPS at the surface, meaning that the Na diffusion in CZTS is smaller than in CIGS [111].

4.6 Device properties

CZTS devices are similar to CIGS devices. The architecture is usually SLG/Mo/CZTS/CdS/*i*-ZnO/ZnO:Al, as presented in Figure 5. Calculation showed that CdS has a suitable band offset with CZTS [112] and until now, the most efficient solar cells were obtained with a CdS buffer layer. Oxidation of the CZTS absorber by dipping in deionized water [13] or O_2 annealing [73] before deposition of CdS seems to improve efficiencies. As for CIGS, reducing the time between absorber synthesis and CdS deposition to the minimum is of the utmost importance [106].

A few variations of the architecture are known, especially on the buffer layer. Pure ZnS does not seem to be a suitable buffer layer because of too high a band offset [112], but good results were obtained with Zn(S, O, OH) by Solar

Fig. 5. Classical architecture for CZTS solar cells.

Frontier [113]. Nevertheless for such a buffer layer the optimal composition of the absorber layer seems to be less Zn-rich ($\text{Zn/Sn} \sim 1$) [113]. Other architectures were proposed: SLG/Mo/CZTS/a-Si/ITO [114], a superstrate architecture (glass/FTO/CZTS) [115, 116], another superstrate (glass/FTO/TiO₂/In₂S₃/CZTS/Mo) [117], a flexible substrate (Al foil/Mo/CZTS/ZnS/i-ZnO/ITO/Al-Ni) [118].

The literature is still quite poor concerning device properties, because very few high-efficiency devices were synthesized yet. The IBM team started to investigate this field [14, 72, 119, 120] concluding that their devices were limited by the recombination at absorber/buffer interface, minority carrier lifetime and Schottky-type barrier in the back contact, which appears to be caused by secondary phases and/or MoS_x interfacial layer between CZTS and Mo [121].

Concerning the absorber / buffer interface, it seems that the surface of the CZTS is Cu-poor, similarly to CIGS [111], or even Cu-free [122]. The KCN etching, which is also used in CIGS processes to remove binaries from the surface, seems to etch Cu preferentially and Sn in a lesser extent [93]. It seems also beneficial for removing Cu₂X that increase the resistivity of the layer [123]. This causes a widening of the bandgap without type inversion, which could be an easy way to tailor bandgap alignments [124, 125]. It seems also that the electronic structure of a Sn-depleted surface is not favorable for the formation of well working *p-n* junction [74, 93]. The Conduction Band Offset, about 0.4–0.5 eV, is somewhat above the optimal range of 0–0.4 eV and may contribute to lower *J*_{sc} and fill factor in the CZTS devices [126]. Better lattice matching between absorber and buffer could limit recombination at the interface, and using different buffer with smaller lattice such as In₂S₃ or Zn(S, O, OH) could improve the efficiency of the devices [127, 128].

Concerning the back contact, ZnX was observed at the back contact [59, 106], as shown in Figure 6, and it seems that increasing the ZnX content strongly impairs efficiency [47]. It was nevertheless speculated that ZnS could be less detrimental than previously thought [72], acting as a simple “dark” material. Binaries losses that occur during annealing makes Cu₂X to diffuse towards the rear of the cell, could lead to a Cu₂X/MoX₂ mix, leading to high resistance at the back contact.

Concerning minority carrier lifetime, it might not be such a problem, because as in CIGS and CdTe, grain boundaries collect minority carrier and provide a current pathway for them to reach the *n*-type CdS and ZnO layers [30] and for coevaporated absorbers, high minority carrier diffusion length was measured (several hundreds

Fig. 6. CZTSe with ZnSe segregation at the back contact [59].

of nm [72]). Nevertheless, it seems that grain boundaries are Cu-rich, which could increase recombination rates and thus diminishing *V*_{OC} [29]. Cu-rich absorbers were found to have lower *V*_{OC} than Cu-poor ones [60], probably in relationship with Cu₂X formation. Longer minority carrier lifetimes were measured in low band gap materials, such as CZTSe, than in high band gap devices [29]. The difference between *E*_g in eV and *V*_{OC} in V, called *V*_{OC} deficit, can therefore be decreased by diminishing the band gap as well as tightly controlling the formation of Cu₂X or its removal by KCN etching.

For high efficiency, it is important to focus both on absorber quality and on interfaces between the absorber and the back contact and buffer. The Cu_xX binaries control seems to be a key point for both absorber and interface quality. Fortunately, the CIGS community has a strong experience on such problems, and hopefully it will be possible to optimize these interfaces much faster than for the CIGS.

5 Conclusion

The problematics encountered by research teams working on CZTS-based solar cells were presented and discussed. The field of CZTS solar cells is young, and until now it is difficult to point to certainties. Nevertheless, it seems that these assumptions start to be viewed as “common knowledge” in the community:

- CZTS has kesterite structure;
- the bandgap is tunable between 1.0 eV (Cu₂ZnSnSe₄) and 1.5 eV (Cu₂ZnSnS₄);
- the synthesis atmosphere must be controlled carefully;
- binary formation control is a key point for high efficiency devices;
- Zn-rich materials yield better results (when using a CdS buffer layer).

Nevertheless, there are numerous questions still, such as:

- what are the crystalline defects, how are they formed; what role do they play in the structure;
- what is the reaction path to CZTS, how to control binaries formation;
- what is the role of sodium during growth.

More and more scientists from the CIGS community work on CZTS solar cells. The problems encountered in CZTS solar cells are quite similar to the ones of CIGS solar cells, and similar methods can be used to solve them. There is no clear superiority of two-step processes over one-step processes, even if until now the best results were obtained with one-step processes. For both types of processes, a focus on binary control formation by atmosphere control and adaptation of interfaces to kesterites materials are the key points for increasing photovoltaic efficiencies for both types of processes.

The author is thankful for financial support of the French Agence Nationale de la Recherche (ANR) under grant No-vACEZ (ANR-10-HABISOL-008).

References

1. International Energy Agency, *World Energy Outlook 2011* (2011)
2. Greenpeace and the European Photovoltaic Industry Association, *Solar Generation VI* (2011)
3. European Climate Foundation, *Roadmap 2050, a practical guide to a prosperous, low-carbon Europe* (2010)
4. International Energy Agency, *Technology Roadmap, Solar photovoltaic energy* (IEA, 2009)
5. A. Zaman, S. Lockman, *Solar industry growth: you ain't seen nothing yet. The grid parity decade* (Piper Jaffray Investment Research, 2011)
6. C. Breyer, M. Görig, J. Schmid, Fuel-parity: impact of photovoltaics on global fossil fuel fired power plant business, presented at the 26, *Symposium Photovoltaische Solarenergie, Bad Staffelstein* (2011)
7. C.S. Tao, J. Jiang, M. Tao, *Solar Energy Mater. Solar Cells* **95**, 3176 (2011)
8. A. Feltrin, A. Freundlich, *Renew. Energy* **33**, 180 (2008)
9. U.S. Department of Energy, *Critical Materials Strategy* (2010)
10. European Commission, *Critical Raw Materials for the EU* (2010)
11. A. Zuser, H. Rechberger, *Resour. Conserv. Recycl.* **56**, 56 (2011)
12. V. Fthenakis, *Renew. Sust. Energy Rev.* **13**, 2746 (2009)
13. H. Katagiri, K. Jimbo, W.S. Maw, K. Oishi, M. Yamazaki, H. Araki, A. Takeuchi, *Thin Solid Films* **517**, 2455 (2009)
14. D.A.R. Barkhouse, O. Gunawan, T. Gokmen, T.K. Todorov, D.B. Mitzi, *Prog. Photovol. Res. Appl.* **20**, 6 (2012)
15. K. Ito, T. Nakazawa, *Jpn J Appl. Phys.* **27**, 2094 (1988)
16. C.P. Chan, H. Lam, C. Surya, *Solar Energy Mater. Solar Cells* **94**, 207 (2010)
17. W. Xinkun, L. Wei, C. Shuying, L. Yunfeng, J. Hongjie, *J. Semiconductors* **33**, 022002 (2012)
18. S. Chen, X.G. Gong, A. Walsh, S.H. Wei, *Appl. Phys. Lett.* **94**, 041903 (2009)
19. K. Timmo, M. Altosaar, J. Raudoja, K. Muska, M. Pilvet, M. Kauk, T. Varema, M. Danilson, O. Volobujeva, E. Mellikov, *Solar Energy Mater. Solar Cells* **94**, 1889 (2010)
20. J. He, L. Sun, S. Chen, Y. Chen, P. Yang, J. Chu, *J. Alloys Compd.* **511**, 129 (2012)
21. M. Moynihan, G. Zoppi, R. Miles, I. Forbes, Investigating synthesis of $\text{Cu}_2\text{ZnSn}(\text{Se}_{1-x}\text{S}_x)_4$ for values of $0 \leq x \leq 1$ by S for Se substitution and direct sulphidisation of metallic precursors, *presented at the 26th European Photovoltaic Solar Energy Conference and Exhibition, Hamburg* (2011)
22. J. He, L. Sun, N. Ding, H. Kong, S. Zuo, S. Chen, Y. Chen, P. Yang, J. Chu, *J. Alloys Compd.* **529**, 34 (2012)
23. E. Mellikov, D. Meissner, M. Altosaar, M. Kauk, J. Krustok, A. Öpik, O. Volobujeva, J. Iljina, K. Timmo, I. Klavina, J. Raudoja, M. Grossberg, T. Varema, K. Muska, M. Ganchev, S. Bereznev, M. Danilson, *AMR* **222**, 8 (2011)
24. S. Levencenco, D. Dumcenco, Y.P. Wang, Y.S. Huang, C.H. Ho, E. Arushanov, V. Tezlevan, K.K. Tiong, *Opt. Mater.* **34**, 1362 (2012)
25. G.M. Ford, Q. Guo, R. Agrawal, H.W. Hillhouse, *Chem. Mater.* **23**, 2626 (2011)
26. W. Shockley, H.J. Queisser, *J. Appl. Phys.* **32**, 510 (1961)
27. L. Choubac, A. Lafond, C. Guillot-Deudon, Y. Moëlo, S. Jobic, *Inorg. Chem.* **51**, 3346 (2012)
28. USGS, *Commodity Statistics and Information, USGS Minerals Information* (2010), <http://minerals.usgs.gov/minerals/pubs/commodity/>
29. S. Bag, O. Gunawan, T. Gokmen, Y. Zhu, T.K. Todorov, D.B. Mitzi, *Energy Environ. Sci.* **5**, 7060 (2012)
30. J.B. Li, V. Chawla, B.M. Clemens, *Adv. Mat.* **24**, 720 (2012)
31. S. Siebentritt, S. Schorr, *Prog. Photovolt. Res. Appl.* in press
32. S. Chen, X.G. Gong, A. Walsh, S.H. Wei, *Phys. Rev. B* **79**, 165211 (2009)
33. S.R. Hall, J.T. Szymanski, J.M. Stewart, *Can. Mineral.* **16**, 131 (1978)
34. L.O. Brockway, *Z. Kristallogr.* **89**, 434 (1934)
35. P. Bonazzi, L. Bindi, G.P. Bernardini, S. Menchetti, *Can. Mineral.* **41**, 639 (2003)
36. S. Schorr, H.J. Hoebler, M. Tovar, *Eur. J. Min.* **19**, 65 (2007)
37. S. Schorr, *Sol. Energy Mater. Solar Cells* **95**, 1482 (2011)
38. J. Paier, R. Asahi, A. Nagoya, G. Kresse, *Phys. Rev. B* **79**, 115126 (2009)
39. A. Walsh, S. Chen, X.G. Gong, S.H. Wei (CZTS): Theoretical insights, http://web.mac.com/aronwalsh/publications/10/icps_czts_10.pdf
40. A. Walsh, S.H. Wei, S. Chen, X.G. Gong, Design of quaternary chalcogenide photovoltaic absorbers through cation mutation, in *34th IEEE Photovoltaic Specialists Conference* (2009)
41. A. Walsh, S. Chen, S. Wei, X. Gong, Kesterite Thin-Film Solar Cells: Advances in Materials Modelling of $\text{Cu}_2\text{ZnSnS}_4$, *Adv. Energy Mater.* **2**, 400 (2012)
42. Y. Zhang, X. Sun, P. Zhang, X. Yuan, F. Huang, W. Zhang, *J. Appl. Phys.* **111**, 063709 (2012)
43. H. Nozaki, T. Fukano, S. Ohta, Y. Seno, H. Katagiri, K. Jimbo, *J. Alloys Compd.* **524**, 22 (2012)
44. X. He, H. Shen, *Physica B: Condensed Matter* **406**, 4604 (2011)
45. X. He, H. Shen, *Phys. Scr.* **85**, 035302 (2012)

46. P.A. Fernandes, P.M.P. Salom, A.F. da Cunha, *Thin Solid Films*, **517**, 2519 (2009)
47. J. Just, D. Ltzenkirchen-Hecht, R. Frahm, S. Schorr, T. Unold, *Appl. Phys. Lett.* **99**, 262105 (2011)
48. A. Nagoya, R. Asahi, R. Wahl, G. Kresse, *Phys. Rev. B* **81**, 113202 (2010)
49. S. Chen, X.G. Gong, A. Walsh, S.H. Wei, *Appl. Phys. Lett.* **96**, 021902 (2010)
50. P.J. Dale, K. Hoenes, J. Scragg, S. Siebentritt, A review of the challenges facing kesterite based thin film solar cells, in *Photovoltaic Specialists Conference (PVSC), 2009 34th IEEE* (2010), pp. 002080–002085
51. T. Maeda, S. Nakamura, T. Wada, *Thin Solid Films* **519**, 7513 (2011)
52. M.J. Romero, H. Du, G. Teeter, Y. Yan, M.M. Al-Jassim, *Phys. Rev. B* **84**, 165324 (2011)
53. E. Kask, T. Raadik, M. Grossberg, R. Josepson, J. Krustok, *Energy Procedia* **10**, 261 (2011)
54. S. Chen, J.H. Yang, X.G. Gong, A. Walsh, S.H. Wei, *Phys. Rev. B* **81**, 245204 (2010)
55. T. Maeda, S. Nakamura, T. Wada, *Jpn J. Appl. Phys.* **50**, 04DP07 (2011)
56. A. Jeong, W. Jo, S. Jung, J. Gwak, J. Yun, *Appl. Phys. Lett.* **99**, 082103 (2011)
57. A. Nagaoka, K. Yoshino, H. Taniguchi, T. Taniyama, H. Miyake, *J. Cryst. Growth* **341**, 38 (2012)
58. T. Washio, H. Nozaki, T. Fukano, T. Motohiro, K. Jimbo, H. Katagiri, *J. Appl. Phys.* **110**, 074511 (2011)
59. I. Repins et al., Kesterites and Chalcopyrites: A Comparison of Close Cousins, in *MRS Proceedings* (2011), Vol. 1324
60. K. Muska, M. Kauk, M. Altosaar, M. Pilvet, M. Grossberg, O. Volobujeva, *Energy Procedia* **10**, 203 (2011)
61. H. Katagiri, K. Jimbo, M. Tahara, H. Araki, K. Oishi, The influence of the composition ratio on CZTS-based thin film solar cells, in *Materials Research Society Symposium Proceedings* (2009), p. 1165
62. A. Ennaoui, M. Lux-Steiner, A. Weber, D. Abou-Ras, I. Ktschau, H.-W. Schock, R. Schurr, A. Hlzing, S. Jost, R. Hock, T. Vo, J. Schulze, A. Kirbs, *Thin Solid Films* **517**, 2511 (2009)
63. P.A. Fernandes, P.M.P. Salom, A.F. da Cunha, *Semicond. Sci. Technol.* **24**, 105013 (2009)
64. T.K. Todorov, K.B. Reuter, D.B. Mitzi, *Adv. Mat.* **22**, (2010)
65. K. Jimbo, R. Kimura, T. Kamimura, S. Yamada, W.S. Maw, H. Araki, K. Oishi, H. Katagiri, *Thin Solid Films* **515**, 5997 (2007)
66. M. Valentini, C. Malerba, F. Biccari, R. Chierchia, P. Mangiapane, E. Salza, A. Mittiga, Growth and characterization of Cu₂ZnSnS₄ thin films prepared by sulfurization of evaporated precursors, in *26th EUPVSEC* (Hamburg, 2011)
67. S.J. Ahn, S. Jung, J. Gwak, A. Cho, K. Shin, K. Yoon, D. Park, H. Cheong, J.H. Yun, *Appl. Phys. Lett.* 021905 (2010)
68. D. Park, D. Nam, S. Jung, S.J. An, J. Gwak, K. Yoon, J.H. Yun, H. Cheong, *Thin Solid Films* **519**, 7386 (2011)
69. H. Wang, *Int. J. Photoenergy* **2011** (2011)
70. M. Edoff, S. Schleussner, E. Wallin, O. Lundberg, *Thin Solid Films* **519**, 7530 (2011)
71. S. Ahmed, K.B. Reuter, O. Gunawan, L. Guo, L.T. Romankiw, H. Deligianni, *Adv. Energy Mater.* in press
72. B. Shin, O. Gunawan, Y. Zhu, N.A. Bojarczuk, S.J. Chey, S. Guha, *Prog. Photovolt. Res. Appl.* in press
73. I. Repins, C. Beall, N. Vora, C. DeHart, D. Kuciauskas, P. Dippo, B. To, J. Mann, W.-C. Hsu, A. Goodrich, R. Noufi, *Solar Energy Mater. Solar Cells*, in press
74. M. Kauk, K. Muska, M. Altosaar, J. Raudoja, M. Pilvet, T. Varema, K. Timmo, O. Volobujeva, *Energy Procedia* **10**, 197 (2011)
75. B.-A. Schubert, B. Marsen, S. Cinque, T. Unold, R. Klenk, S. Schorr, H.-W. Schock, *Prog. Photovolt. Res. Appl.* **19**, 93 (2011)
76. E. Mellikov, D. Meissner, T. Varema, M. Altosaar, M. Kauk, O. Volobujeva, J. Raudoja, K. Timmo, M. Danilson, *Energy Mater. Solar Cells* **93**, 65 (2009)
77. X.Y. Li, D.C. Wang, Q.Y. Du, W.F. Liu, G.S. Jiang, C.F. Zhu, *Adv. Mater. Res.* **418–420**, 67 (2011)
78. T.K. Chaudhuri, D. Tiwari, *Solar Energy Mater. Solar Cells* **101**, 46 (2012)
79. T. Rath, W. Haas, A. Pein, R. Saf, E. Maier, B. Kunert, F. Hofer, R. Resel, G. Trimmel, *Solar Energy Mater. Solar Cells* **101**, 87 (2012)
80. N.M. Shinde, C.D. Lokhande, J.H. Kim, J.H. Moon, J. Photochem. Photobiol. A: Chem., in press
81. R.A. Wibowo, W.S. Kim, E.S. Lee, B. Munir, K.H. Kim, *J. Phys. Chem. Solids* **68**, 1908 (2007)
82. F. Hergert, R. Hock, *Thin solid films* **515**, 5953 (2007)
83. A.J. Cheng, M. Manno, A. Khare, C. Leighton, S. Campbell, E. Aydil, J. Vac. Sci. Technol. A Vac. Surf. Films **29**, 051203 (2011)
84. O. Volobujeva, J. Raudoja, E. Mellikov, M. Grossberg, S. Bereznev, R. Traksmaa, *J. Phys. Chem. Solids* **70**, 567 (2009)
85. R. Schurr et al., *Thin Solid Films* **517**, 2465 (2009)
86. M. Ganchev, J. Iljina, L. Kaupmees, T. Raadik, O. Volobujeva, A. Mere, M. Altosaar, J. Raudoja, E. Mellikov, *Thin Solid Films* **519**, 7394 (2011)
87. K. Maeda, K. Tanaka, Y. Nakano, H. Uchiki, *Jpn J. Appl. Phys.* **50**, 05FB08 (2011)
88. A. Redinger, S. Siebentritt, *Appl. Phys. Lett.* **97**, 092111 (2010)
89. H. Yoo, J. Kim, *Thin Solid Films* **518**, 6567 (2010)
90. J. Ge, Y. Wu, C. Zhang, S. Zuo, J. Jiang, J. Ma, P. Yang, J. Chu, *Appl. Surf. Sci.* **258**, 7250 (2012)
91. K. Maeda, K. Tanaka, Y. Fukui, H. Uchiki, *Solar Energy Mater. Solar Cells* **95**, 2855 (2011)
92. K. Maeda, K. Tanaka, Y. Nakano, Y. Fukui, H. Uchiki, *Jpn J. Appl. Phys.* **50**, 05FB09 (2011)
93. J.J. Scragg, *Studies of Cu₂ZnSnS₄ Films Prepared by Sulfurisation of Electrodeposited Precursors*, Ph.D. thesis, University of Bath, Department of Chemistry, Bath, 2010
94. G. Teeter, H. Du, J.E. Leisch, M. Young, F. Yan, S. Johnston, P. Dippo, D. Kuciauskas, M. Romero, P. Newhouse, S. Asher, D. Ginley, Combinatorial study of thin-film Cu₂ZnSnS₄ synthesis via metal precursor sulfurization, in *35th IEEE-PVSEC* (2010)
95. A. Weber, R. Mainz, H.W. Schock, *J. Appl. Phys.* **107**, 013516 (2010)
96. H. Yoo, J. Kim, L. Zhang, *Curr. Appl. Phys.* in press
97. A. Redinger, D.M. Berg, P.J. Dale, R. Djemour, L. Gutay, T. Eisenbarth, N. Valle, S. Siebentritt, *IEEE J. Photovoltaics* **1**, 200 (2011)

98. A. Redinger, D.M. Berg, P.J. Dale, S. Siebentritt, J. Am. Chem. Soc. **156** (2011)
99. C.M. Fella, G. Ilari, A.R. Uhl, A. Chirilă, Y.E. Romanyuk, A.N. Tiwari, Non-vacuum deposition of Cu₂ZnSnSe₄ absorber layers for thin film solar cells, in *26 EUPVSEC* (Hamburg, 2011)
100. F. Biccari, R. Chierchia, M. Valentini, P. Mangiapane, E. Salza, C. Malerba, C.L.A. Ricardo, L. Mannarino, P. Scardi, A. Mittiga, Energy Procedia **10**, 187 (2011)
101. S. Guha, D.B. Mitzi, T.K. Todorov, K. Wang, *Annealing Thin Films*, US Patent United States Patent Application 2012007093622, 2012
102. P. Salomé, J. Malaquias, P. Fernandes, M. Ferreira, J. Leitão, A. da Cunha, J. González, F. Matinaga, G. Ribeiro, E. Viana, Solar Energy Mater. Solar Cells **95**, 3482 (2011)
103. K. Wang, B. Shin, K.B. Reuter, T. Todorov, D.B. Mitzi, S. Guha, Appl. Phys. Lett. **98**, 051912 (2011)
104. R. Juškėnas, S. Kanapeckaitė, V. Karpavičienė, Z. Mockus, V. Pakštas, A. Selskienė, R. Giraitis, G. Niaura, Solar Energy Mater. Solar Cells **101**, 277 (2012)
105. S.W. Shin, S. Pawar, C.Y. Park, J.H. Yun, J.H. Moon, J.H. Kim, J.Y. Lee, Solar Energy Mater. Solar Cells **95**, 3202 (2011)
106. L. Grenet, S. Bernardi, D. Kohen, C. Lepoittevin, S. Noël, N. Karst, A. Brioude, S. Perraud, H. Mariette, Solar Energy Mater. Solar Cells **101**, 11 (2012)
107. H. Yoo, J. Kim, Solar Energy Mater. Solar Cells **95**, 239 (2011)
108. R. Chalapathy, G.S. Jung, B.T. Ahn, Solar Energy Mater. Solar Cells **95**, 3216 (2011)
109. W. Hlaing Oo, J. Johnson, A. Bhatia, E. Lund, M. Nowell, M. Scarpulla, Journal of Electronic Materials **40**, 2214
110. T. Prabhakar, N. Jampana, Solar Energy Mater. Solar Cells **95**, 1001 (2011)
111. M. Bär, B.A. Schubert, B. Marsen, S. Krause, S. Pookpanratana, T. Unold, L. Weinhardt, C. Heske, H.W. Schock, Appl. Phys. Lett. **99**, 112103 (2011)
112. A. Nagoya, R. Asahi, G. Kresse, J. Phys. Condens. Matter **23**, 404203 (2011)
113. N. Sakai, H. Hiroi, H. Sugimoto, Development of cd-free buffer layer for Cu₂ZnSnS₄ thin-film solar cells, in *37th IEEE PVSC Conference* (2011)
114. F. Jiang, H. Shen, W. Wang, L. Zhang, Appl. Phys. Expr. **4**, 074101 (2011)
115. P.K. Sarswat, M.L. Free, Phys. Status Solidi **208**, 2861 (2011)
116. P.K. Sarswat, M. Snure, M.L. Free, A. Tiwari, Thin Solid Films **520**, 1694 (2012)
117. Q.-M. Chen, Z.-Q. Li, Y. Ni, S.-Y. Cheng, X.-M. Dou, Chin. Phys. B **21**, 038401 (2012)
118. Q. Tian, X. Xu, L. Han, M. Tang, R. Zou, Z. Chen, M. Yu, J. Yang, J. Hu, Cryst. Eng. Commun., **14**, 3847 (2012)
119. O. Gunawan, T.K. Todorov, D.B. Mitzi, Appl. Phys. Lett. **97**, 233506 (2010)
120. K. Wang, O. Gunawan, T. Todorov, B. Shin, S.J. Chiy, N.A. Bojarczuk, D. Mitzi, S. Guha, Appl. Phys. Lett. **97**, 143508 (2010)
121. B. Shin, K. Wang, O. Gunawan, K.B. Reuter, S.J. Chey, N.A. Bojarczuk, T. Todorov, B. Mitzi, S. Guha, in *37th IEEE PVSC Conference* (Seattle, 2011), Vol. 1
122. M. Bär, B.-A. Schubert, B. Marsen, R.G. Wilks, M. Blum, S. Krause, S. Pookpanratana, Y. Zhang, T. Unold, W. Yang, L. Weinhardt, C. Heske, H.-W. Schock, J. Mater. Res. FirstView, 1
123. T. Tanaka, T. Sueishi, K. Saito, Q. Guo, M. Nishio, K.M. Yu, W. Walukiewicz, J. Appl. Phys. **111**, 053522 (2012)
124. M. Bär, B.-A. Schubert, B. Marsen, S. Krause, S. Pookpanratana, T. Unold, L. Weinhardt, C. Heske, H.-W. Schock, Appl. Phys. Lett. **99**, 152111 (2011)
125. M. Bär, B.-A. Schubert, B. Marsen, R.G. Wilks, S. Pookpanratana, M. Blum, S. Krause, T. Unold, W. Yang, L. Weinhardt, C. Heske, H.-W. Schock, Appl. Phys. Lett. **99**, 222105 (2011)
126. R. Haight, A. Barkhouse, O. Gunawan, B. Shin, M. Copel, M. Hopstaken, D.B. Mitzi, Appl. Phys. Lett. **98**, 253502 (2011)
127. J.M. Raulot, C. Domain, J.F. Guillemoles, J. Phys. Chem. Solids **66**, 2019 (2005)
128. A. Opanasyuk, D. Kurbatov, M. Ivashchenko, I.Y. Protsenko, H. Cheong, Journal of Nano- and Electronic Physics **4**, 01024 (2012)
129. C. Tao, J. Jiang, M. Tao, ECS Transactions **33**, 3 (2011)
130. D.B. Mitzi, T.K. Todorov, *Method of Forming Semiconductor Film and Photovoltaic Device Including the Film*, US Patent US2011094557 (A1)Apr-2011
131. D.B. Mitzi, T.K. Todorov, Aqueous-based method of forming semiconductor film and photovoltaic device including the film, US Patent US 2011097496 (A1), 2011
132. E. Melikov, M. Altosaar, J. Raudoja, K. Timmo, O. Volobujeva, M. Kauk, J. Krustok, T. Varema, M. Grossberg, M. Danilson, K. Muska, K. Ernits, F. Lehner, D. Meissner, Materials Challenges in Alternative and Renewable Energy: Ceramic Transactions **224**, 137
133. J.J. Scragg, P.J. Dale, L.M. Peter, Electrochem. Commun. **10**, 639 (2008)
134. J.J. Scragg, D.M. Berg, P.J. Dale, J. Electroanal. Chem. **646**, 52 (2010)
135. H. Araki, Y. Kubo, A. Mikaduki, K. Jimbo, W.S. Maw, H. Katagiri, M. Yamazaki, K. Oishi, A. Takeuchi, Solar Energy Mater. Solar Cells **93**, 996 (2009)
136. J.J. Scragg, P.J. Dale, L.M. Peter, Thin Solid Films **517**, 2481 (2009)
137. J.J. Scragg, P.J. Dale, L.M. Peter, G. Zoppi, I. Forbes, Phys. Stat. Sol. B **245**, 1772 (2008)
138. M. Kurihara, D. Berg, J. Fischer, S. Siebentritt, P.J. Dale, Physica Status Solidi **6**, 1241 (2009)
139. X. Zhang, X. Shi, W. Ye, C. Ma, C. Wang, Appl. Phys. A **94**, 381 (2009)
140. H. Deligianni, L. Guo, R. Vaidyanathan, *Electrodeposition of Thin-Film Cells Containing Non-Toxic Elements*, US Patent United States Patent Application 2012004837803, 2012
141. S. Ahmed, H. Deligianni, L.T. Romankiw, K. Wang, *Structure and Method of Fabricating a CZTS Photovoltaic Device by Electrodeposition*, US Patent United States Patent Application 2012006179015, 2012
142. Q. Guo, G.M. Ford, W.C. Yang, B.C. Walker, E.A. Stach, H.W. Hillhouse, R. Agrawal, J. Am. Chem. Soc. **132**, 2844 (2010)
143. T. Washio, T. Shinji, S. Tajima, T. Fukano, T. Motohiro, K. Jimbo, H. Katagiri, J. Mater. Chem., **22**, 4021 (2012)
144. K. Woo, Y. Kim, J. Moon, Energy Environ. Sci. **5**, 5340 (2012)

145. W. Ki, H.W. Hillhouse, *Adv. Energy Mater.* **1**, 732 (2011)
146. N. Momose, M.T. Htay, T. Yudasaka, S. Igarashi, T. Seki, S. Iwano, Y. Hashimoto, K. Ito, *Jpn. J. Appl. Phys.* **50**, 01BG09 (2011)
147. H. Flammersberger, *Experimental study of Cu₂ZnSnS₄ thin films for solar cells*, Master thesis, Uppsala University, 2010
148. C. Platzer-Bjrkman, J. Scragg, H. Flammersberger, T. Kubart, M. Edoff, *Solar Energy Mater. Solar Cells* **98**, 110 (2012)
149. K.H. Kim, I. Amal, *Electronic Materials Letters* **7**, 225 (2011)
150. H. Araki, Y. Kubo, K. Jimbo, W.S. Maw, H. Katagiri, M. Yamazaki, K. Oishi, A. Takeuchi, *Phys. Status Solidi* **6**, 1266 (2009)
151. H. Khnlein, J. Schulze, T. Voss, *Metal Plating Composition And Method For The Deposition Of Copper-zinc-tin Suitable For Manufacturing Thin Film Solar Cell*, US Patent US2009/0205714 (A1)20, 2009
152. H.H. Khnlein, *Elektrochemische Legierungsabscheidung zur Herstellung von Cu₂ZnSnS₄ Dnnschichtsolarzellen*, Ph.D. thesis, Dresden, 2007
153. M.L. Free, P.K. Sarswat, A. Tiwari, M. Snure, *Modified copper-zinc-tin semiconductor films, uses thereof and related methods*, US Patent United States Patent Application 20110132462A106, 2011
154. B.S. Pawar, S.M. Pawar, S.W. Shin, D.S. Choi, C.J. Park, S.S. Kolekar, J.H. Kim, *Appl. Surf. Sci.* **257**, 1786 (2010)
155. S.M. Pawar, B.S. Pawar, A.V. Moholkar, D.S. Choi, J.H. Yun, J.H. Moon, S.S. Kolekar, J.H. Kim, *Electrochimica Acta* **55**, 4057 (2010)
156. M. Jeon, Y. Tanaka, T. Shimizu, S. Shingubara, *Energy Procedia* **10**, 255 (2011)
157. M. Jeon, T. Shimizu, S. Shingubara, *Mater. Lett.* **65**, 2364 (2011)
158. G. Zoppi, I. Forbes, R.W. Miles, P.J. Dale, J.J. Scragg, L.M. Peter, *Progress in Photovoltaics: Research and Applications* **17**, 315 (2009)
159. K. Moriya, K. Tanaka, H. Uchiki, *Jpn J. Appl. Phys.* **46**, 5780 (2007)
160. A.V. Moholkar, S.S. Shinde, A.R. Babar, K.-U. Sim, Y. Kwon, K.Y. Rajpure, P.S. Patil, C.H. Bhosale, J.H. Kim, *Solar Energy* **85**, 1354 (2011)
161. L. Sun, J. He, H. Kong, F. Yue, P. Yang, J. Chu, *Solar Energy Mater. Solar Cells* **95**, 2907 (2011)
162. A. Moholkar, S. Shinde, A. Babar, K. Sim, K. Hyun, K. Rajpure, P. Patil, C. Bhosale, J. Kim, *J. Alloys Compd.* **509**, 7439 (2011)
163. K. Tanaka, Y. Fukui, N. Moritake, H. Uchiki, *Solar Energy Mater. Solar Cells* **95**, 838 (2011)
164. C. Lokhande, N. Shinde, J. Kim, J. Moon, *Invertis Journal of Renew. Energy* **1**, 142 (2011)
165. S.S. Mali, B.M. Patil, C.A. Betty, P.N. Bhosale, Y.W. Oh, S.R. Jadkar, R.S. Devan, Y.-R. Ma, P.S. Patil, *Electrochimica Acta* **66**, 216 (2012)
166. H. Araki, A. Mikaduki, Y. Kubo, T. Sato, K. Jimbo, W.S. Maw, H. Katagiri, M. Yamazaki, K. Oishi, A. Takeuchi, *Thin Solid Films* **517**, 1457 (2008)
167. F. Liu, Y. Li, K. Zhang, B. Wang, C. Yan, Y. Lai, Z. Zhang, J. Li, Y. Liu, *Solar Energy Mater. Solar Cells* **94**, 2431 (2010)
168. V. Chawla, B. Clemens, Inexpensive, abundant, non-toxic thin films for solar cell applications grown by reactive sputtering, in *Photovoltaic Specialists Conference (PVSC), 2010 35th IEEE* (2010), pp. 001902–001905
169. A. Wangperawong, J.S. King, S.M. Herron, B.P. Tran, K. Pangan-Okimoto, S.F. Bent, A chemical bath process for depositing Cu₂ZnSnS₄ photovoltaic absorbers, in *35th IEEE-PVSEC* (Hawaii, 2010)
170. C. Shi, G. Shi, Z. Chen, P. Yang, M. Yao, *Mater. Lett.* **73**, 89 (2012)