Accepted Manuscript

Formation of Cu₂SnSe₃ from stacked elemental layers investigated by combined in-situ X-ray diffraction and differential scanning calorimetry techniques

Rachmat Adhi Wibowo, Stefan Moeckel, Hyesun Yoo, Astrid Hoelzing, Rainer Hock, Peter J. Wellmann

 PII:
 S0925-8388(13)02709-6

 DOI:
 http://dx.doi.org/10.1016/j.jallcom.2013.10.248

 Reference:
 JALCOM 29819

To appear in:

Received Date:	11 June 2013
Revised Date:	31 October 2013
Accepted Date:	31 October 2013



Please cite this article as: R.A. Wibowo, S. Moeckel, H. Yoo, A. Hoelzing, R. Hock, P.J. Wellmann, Formation of Cu₂SnSe₃ from stacked elemental layers investigated by combined in-situ X-ray diffraction and differential scanning calorimetry techniques, (2013), doi: http://dx.doi.org/10.1016/j.jallcom.2013.10.248

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Formation of Cu₂SnSe₃ from stacked elemental layers investigated by combined in-situ

X-ray diffraction and differential scanning calorimetry techniques

Rachmat Adhi Wibowo^{*1}, Stefan Moeckel², Hyesun Yoo¹, Astrid Hoelzing¹, Rainer Hock¹, Peter J. Wellmann²

- ¹ Chair for Crystallography and Structure Physics, University of Erlangen-Nürnberg, Staudtstr. 3, 91058 Erlangen, Germany.
- ² Department of Materials Science, University of Erlangen-Nürnberg, Martenstr. 9, 91058 Erlangen, Germany.

Abstract

Stacked elemental layers of Mo/Cu/Sn and Mo/Cu/Sn/Se were employed as samples for investigating the formation reaction of Cu-Sn intermetallic compounds as well as Cu₂SnSe₃ phases by in-situ technique of X-ray diffraction and differential scanning calorimetry. The use of a combined in-situ technique allows a real-time observation on solid-state reactions as well as any crystalline phase changes during annealing towards the crystallization of Cu₂SnSe₃. It is found that Cu and Sn form intermetallic compounds of Cu₆Sn₅, Cu₃Sn and Cu₄₁Sn₁₁ as the annealing temperature rises from 30 to 550°C. The reaction of Se with Cu to form a CuSe phase dominates the binary phase formation at a low annealing temperature. The annealing of a stacked Mo/Cu/Sn/Se layer suggests that only Cu₆Sn₅ intermetallic compound directly acts as a reactant for the Cu-selenide phase formation. A SnSe phase mostly forms from a liquidstate reaction of Sn and Se above the Sn melting point. The in-situ investigation also reveals a complete set of Cu-selenide peritectic decompositions of CuSe₂→ CuSe → Cu_{1.8}Se at 360 and 412 °C. The formation of Cu₂SnSe₃ phase starts at 450°C as a product from a reaction between Cu_{1.8}Se and SnSe in a presence of liquid Se. Comparisons on the initial formation

temperatures of all involved phases and on the formation pathways between Cu_2SnSe_3 and Cu_2SnS_3 are discussed as well.

Keywords : Intermetallics; thermoelectic materials; solid state reactions; phase transitions

* Corresponding author

Tel	: +4991318525195
Fax	: +4991318525182
E-mail	: wibowo@krist.uni-erlangen.de (R.A. Wibowo)
Present address	: Austrian Institute of Technology, Giefinggasse 2, 1210 Vienna,
	Austria

1. Introduction

The research and development of the earth abundant semiconducting compound materials for photonics application have recently been attracting a great interest. The application of this sort of materials may not only reduce the photovoltaic cost but also take an advantage on the sustainable raw materials supply for large-scale and long term photovoltaic production. This emerging research field has been promoting the utilization of the earth abundant kesterite $Cu_2ZnSn(S,Se)_4$ as a promising photovoltaic materials that may replace silicon and $Cu(In,Ga)(S,Se)_2$ [1]. To improve the kesterite solar cell performance comparable to its counterparts, a fabrication of device-quality kesterite materials free of any detrimental secondary phases has been a particular challenge to overcome [2]. Some of the secondary phases are well-recognized as Cu_2SnX_3 (X = S, Se) compounds which deteriorate the kesterite solar cell performance due to their lower band gaps compared with the kesterite [3]. In conjunction with this particular challenge, studies of Cu_2SnX_3 have mostly been dedicated to support the kesterite researches, for instances the detection of a Cu_2SnX_3 secondary phase in

kesterite films [4], the study of its corresponding Raman spectra for distinguishing it from kesterite spectra [5-6], the investigation of Cu_2SnS_3 formation during annealing [7] and the synthesis of Cu_2SnX_3 as a precursor for kesterite crystallization [8]. On a basis of these studies, Cu_2SnX_3 has been regarded as an essential intermediate phase in the kesterite fabrication since the kesterite formation is normally completed by the solid state reaction of Cu_2SnX_3 with ZnX. Nevertheless an in-depth experimental study of the formation of Cu_2SnSe_3 has not been reported yet.

This contribution presents the formation of Cu₂SnSe₃ films from stacked elemental layers of Mo/Cu/Sn/Se by combined in-situ X-ray diffraction (XRD) and Differential Scanning Calorimetry (DSC). This study is performed not only to comprehend the formation reactions during the selenization of metallic precursors towards the optimization of kesterite absorber and photovoltaic device fabrication, but also to give a chemical reaction insights on the synthesis of a Cu₂SnSe₃ compound for other completely different applications. Although Cu₂SnX₃ compounds as secondary phases in the kesterite deteriorates cell performance, it has been explored that their low band gap characteristic offers a technological advantage for the acousto-optic application in the IR region [9]. Moreover, their outstanding thermal and mechanical properties make them a suitable material for solid lubricant [10]. Most recent investigation also suggests that Cu₂SnX₃ could also be used as a high efficient thermoelectric materials especially when it is doped by foreign elements [11,12]. Important consequences of the Cu₂SnSe₃ formation for kesterite fabrication optimization and synthesis of Cu₂SnSe₃ are discussed herein.

2. Experimental details

The Mo/Cu/Sn metallic stacked layers were prepared by DC magnetron sputtering from high purity (4N) elemental targets on two different substrates; polymide flexible foils for in-situ XRD and Al pans (6 mm in diameter and 1 mm in height, Perkin-Elmer) for DSC

measurement. A Mo layer (0.4 microns thick) was deposited followed by the deposition of Cu and Sn layers at a working pressure about 7.5 x 10^{-2} Pa. The composition of Mo/Cu/Sn stacked layers was targeted to possess a Cu-poor kesterite-like [Cu]:[Sn] compositional ratio of ~1.76 by depositing the Cu layer at a thickness of 255 nm and the Sn layer at a thickness of 330 nm. The as-deposited metallic stacked layer surfaces were investigated by a scanning electron microscope (Jeol JSM 6400). Se capping layers with the thickness of 2 micrometers were thermally evaporated on the metallic layers, yielded Mo/Cu/Sn/Se stacked layers. After the Se thermal evaporation, the pans with the Mo/Cu/Sn/Se layers were hermetically encapsulated with another Al pans under 2000 Pa nitrogen gas in order to prepare DSC samples. The DSC measurements were performed using the differential scanning calorimeter Q1000 with a Q2000 cell (TA Instruments) under nitrogen gas in the range of room temperature to about 550 °C with a heating rate of 0.5 °C/sec. Due to the DSC sensitivity limitation on detecting reactions between pure metals, only metals/Se samples were investigated. The in-situ XRD measurements on Mo/Cu/Sn, and Mo/Cu/Sn/Se stacked layers samples were performed using an angle-dispersive XRD using a rotating Cu anode driven at 44 kV and 75 mA (Cu Ka radiation = 1.5418 nm). The resulting powder Debye-Scherrer diffraction rings were recorded in transmission geometry by a CCD area detector. The in-situ XRD sample preparation and setup has frequently been described elsewhere [7,13]. The samples were annealed under vacuum (10^{-3} Pa) from 30-550°C with a similar heating rate with DSC measurement and held at 550°C for about 5 minutes. The sample preparation for both in-situ XRD and DSC measurements anticipated the possible loss of Se during annealing due to its evaporation and ensured the Se partial pressure or Se amounts involved in the reactions did not decrease abruptly regardless the different reaction chamber environment, i.e. vacuum as used in in-situ XRD or nitrogen atmosphere as used in DSC. The obtained diffraction patterns were qualitatively analyzed by JADE 9 software bundled with

International Committee of Diffraction Data (ICDD) database to identify the recorded crystalline phases [14].

3. **Results and discussion**

The plane sectional image of the Mo/Cu/Sn layer shows a typical island-like morphology with an average island size of about one micrometer as seen in Figure 1. Visual and phase analysis allow us to deduce that this morphology originates from the deposited Sn layer on Cu layer. Sn is naturally found to form a discontinuous layer of spherical island-like grains. The Sn layer on Cu also demonstrates a relatively poor wetting due mostly to a Cu/Sn high interfacial energy. This identical surface morphology can also be found in the electron beam evaporated Mo/Cu/Sn [15]. Another identical result but having much less dense layer can be seen in the electrochemically deposited Mo/Cu/Sn surface [16]. This island-like morphology consequently produces an exposed narrow space of Cu layer due to incomplete Cu layer coverage by Sn.

The in-situ XRD patterns of the Mo/Cu/Sn stacked layer during annealing demonstrate a set of Cu-Sn alloy phase evolution as presented in Figure 2. The polymide foil background at $2\theta = 19-25^{\circ}$ along with a Mo reflection at $2\theta = 40.5^{\circ}$ are clearly detected throughout all measuring temperatures. The as-deposited Mo/Cu/Sn layer exhibits tetragonal Sn (ICDD # 03-065-2631), monoclinic Cu₆Sn₅ (ICDD # 00-045-1488) and cubic Cu (ICDD # 00-004-0836) phases as represented by a diffractogram at room temperature (30 °C). Principal Sn 200 and 101 reflections are clearly visible at $2\theta = 30.63^{\circ}$ and 32° along with a weak 211 reflection at $2\theta = 44.95$, whereas a Cu₆Sn₅ phase is recognized at $2\theta = 30.07^{\circ}$ (in the left shoulder of a Sn 200 reflection), 36.11° and 43.09° . Qualitative phase identification on a reflection at $2\theta =$ 43.3° deduces that this broad reflection composes of overlapped Cu 111 reflection ($2\theta =$ 43.38°) as well as a Cu₆Sn₅ -514 reflections at $2\theta = 43.09^{\circ}$.

A melting of Sn represents the first observed phase change in the Mo/Cu/Sn stacked layer during annealing. It is recognized by a complete disappearance of Sn reflections at an annealing temperature of 230 °C. Almost immediately after the Sn melts, intermetallic compound (IMC) of cubic $Cu_{41}Sn_{11}$ 642 reflection at $20 = 37.38^{\circ}$ (ICDD # 00-030-0510) and orthorhombic Cu_3Sn 101 and 002 reflections at $2\theta = 27.8^{\circ}$ and 41.63° (ICDD # 01-074-6752) simultaneously appear. During annealing from 230 to 450 °C, in-situ diffractograms reveal a continuous shift of the $2\theta = 43.3^{\circ}$ overlapped reflection from its original position to a smaller diffraction angle. This shift is interpreted as an enhancement of a Cu_6Sn_5 phase in the expense of Cu elemental phase. At about 450 °C, the reflections of Cu_6Sn_5 phase are no longer visible, whereas the reflection of Cu_3Sn gets more pronounce. Holding the annealing process at 550 °C for about 5 minutes eliminates Cu_3Sn phase while the $Cu_{41}Sn_{11}$ reflection becomes more pronounce. Taking a consideration the [Cu]:[Sn] ratio is more than 1, the reflection at $2\theta \sim 43.3^{\circ}$ strongly indicates that the remaining elemental Cu phase still exists in the stacked layer sample.

A monoclinic Cu_6Sn_5 is an IMC phase that naturally forms right after the Sn is in contact with Cu. It is also well-known to be the first phases which form as a thin layer at a Cu/Sn interface in accordance with the effective heat formation theory as well as experimental works [17, 18]. The highly energetic Sn adatoms during sputtering deposition on a Cu layer seem to provide a sufficient energy for a Cu_6Sn_5 formation, thus produces as-deposited layers having an actual Mo/Cu/Cu₆Sn₅/Sn stacked phase. The other detected Cu-Sn IMC phases form upon annealing could be a result from a continuous Cu outward diffusion into the Cu_6Sn_5 thin layer. Cu_3Sn and $Cu_{41}Sn_{11}$ which forms above 230 °C, are products of a reaction between Cu and Cu_6Sn_5 as indicated by the shift of the original 43.3° reflection (closer to Cu reflection) to a smaller angle (closer to a Cu_6Sn_5 reflection) while the Cu_3Sn and $Cu_{41}Sn_{11}$ reflections simultaneously appear. In accordance to the studies on the Cu/Sn_5 at elevating

temperature [19, 20]. Nevertheless, in-situ diffractograms show that the Cu_6Sn_5 phase does not completely disappear although it reacts with Cu to form Cu_3Sn and $Cu_{41}Sn_{11}$ at elevating temperature up to 450 °C. It is suggested that the rate of Cu_6Sn_5 consumed by Cu to form Cu_3Sn and $Cu_{41}Sn_{11}$ at the Cu/Cu_6Sn_5 interface must be compensated by the rate of new Cu_6Sn_5 growth from a reaction between Cu and liquid Sn at the Cu_6Sn_5 /liquid Sn interface. The new Cu_6Sn_5 formation is enabled through the Cu diffusion into liquid Sn along Cu_6Sn_5 grain boundaries at this range of temperature [19, 21]. The complete disappearance of Cu_6Sn_5 phase reflections at 450 °C reflects its peritectic decomposition into Cu_3Sn and liquid Sn which is in an agreement with Cu-Sn binary phase diagram [22]. All phase changes could be summarized in the following reaction chemistry:

$$Sn (s) \rightarrow Sn (l) (230^{\circ}C)$$
(1)

$$Cu(s) + Cu_6Sn_5(s) \rightarrow Cu_3Sn(s) + Cu(s) \rightarrow Cu_{41}Sn_{11}(s) (> 230°C)$$
 (2)

$$Cu_6Sn_5(s) \rightarrow Cu_3Sn(s) + Sn(l)(450^{\circ}C)$$
(3)

The reaction of the metallic stacked layer with Se is represented in the in-situ XRD patterns of Figure 3. Although an evaporated Se layer was deposited on top of the metals stacked layer, the as-deposited diffractogram contains identical information with the Mo/Cu/Sn stacked layer phase composition in Figure 2. It also possesses the existence of Sn, Cu and Cu₆Sn₅ metallic phases. In contrary with the Figure 2, the first detectable phase formation upon annealing is the appearance of the new two reflections at $2\theta = 23.28^{\circ}$ and 29.56° at about 142 °C. Phase analysis identified that these two reflections belong to a hexagonal crystalline Se 100 and 101 reflections (ICDD # 00-006-0362). This result also implies that the evaporated Se layer on Mo/Cu/Sn at room temperature was in an amorphous state. Following the Se crystallization, a set of reflections at $2\theta = 26.64^{\circ}$ is detected at approximately 187 °C which is a signature of a low temperature (LT) orthorhombic CuSe phase (ICDD # 00-089-1239) formation which has a 112 corresponding crystalline reflection. This orthorhombic structure of Cu-selenide forms through a solid-state reaction between Cu

and Se which may take place at the narrow exposed Cu surface in between Sn islands. The complete vanishing of Se reflections at 220 °C and a subsequent disappearance of Sn reflections at approximately 240 °C obviously correspond to their melting temperatures. In summary, the reaction chemistries of phase changes are:

Se (amorph.)	→ Se (cryst.) (142 °C)	(4)
Cu(s) + Se(s)	→ LT CuSe (s) (187 °C)	(5)
Se (cryst.)	→ Se (l) (220 °C)	(6)
Sn (s)	→ Sn (l) (240 °C)	(7)

Immediately after Sn melts, four simultaneous phase changes occur. An orthorombic SnSe phase (ICDD # 97-005-0547) is well resolved which can be seen from its 001, 111 and 311 reflections at $2\theta = 29.33$, 30.37 and 37.60° . On the other side, both Cu₆Sn₅ and Cu metallic phases completely disappear after noticing the absence of the $2\theta = 43.3^{\circ}$ overlapped reflection at 240 °C. All of these phase changes are accompanied by a formation of an orthorhombic CuSe₂ phase (ICDD # 19-0400) which can be recognized by its 111 and 120 reflections at $2\theta = 33.14^{\circ}$ and 33.94° . The last observable phase change is a gradual weakening of LT CuSe reflections during the formation of SnSe and CuSe₂ at this particular annealing temperature. Overall, annealing the stacked layer at 240 °C successfully converts all metallic phases into selenide phases.

A SnSe phase forms from a liquid-state reaction of Sn and Se right after the melting point of Sn following a similar behaviour of the formation of SnSe from a Mo/Sn/Se stacked layer [23]. Additionally, a SnSe phase could be formed from a complete reaction of Cu_6Sn_5 with liquid Se which also produces a LT CuSe phase, as indicated by a vanishing of the overlapped Cu_6Sn_5 and $Cu \ 2\theta = 43.3^\circ$ reflection at 240 °C. The Cu_6Sn_5 that forms as a thin layer between Cu and Sn layers seems to be selenized more rapidly during annealing, yielding a complete consumption of Cu_6Sn_5 phase far below its peritectic decomposition temperature at 420 °C. The annealing of a stacked Mo/Cu/Sn/Se layer also suggests that only Cu_6Sn_5

directly acts as a reactant for the Cu-selenide phase formation. Moreover, annealing the layer at 240 °C seems to provide sufficient temperature for the further formation of CuSe₂ which certainly originates from a reaction of LT CuSe with liquid Se, causing the LT CuSe reflections weaker in the in-situ diffractogram. SnSe and CuSe₂ phases sustain their reflection up to annealing temperature of 360 °C. The possible reaction chemistries at this particular range of temperature are therefore:

$$Cu_{6}Sn_{5}(s) + Se(l) \rightarrow LT CuSe(s) + SnSe(s)(240 °C)$$

$$LT CuSe(s) + Se(l) \rightarrow CuSe_{2}(s)(240 °C)$$
(8)
(9)

The phases continuously evolve upon annealing above 240 °C. The CuSe₂ phase reflections intensity exerts a gradual decrease from 360 °C until their complete disappearance at about 412 °C. At the same time, reflections at $2\theta = 27.95^{\circ}$ and 45.38° which are attributed to the hexagonal high temperature (HT) CuSe 102 and 107 reflections (ICDD # 00-034-0171), gradually appear and finally show their maximum intensity at approximately 412 °C. The HT CuSe phase does not, however, sustain its crystalline form since its existence rapidly vanishes after reaches the maximum intensity. A detectable cubic $Cu_{1,8}Se$ (ICDD # 97-004-1143) phase identified by its principal 111 and 220 reflections at $2\theta = 27.66^{\circ}$ and 44.41° replaces the HT CuSe phase reflections. These Cu-selenides phase changes at 360-412 °C resemble two peritectic decompositions [24, 25]. The first decomposition at 360°C is assigned to a decomposition of CuSe₂ into CuSe and liquid Se. The gradual decrease of CuSe₂ phase reflection intensity and the simultaneous appearance of a HT CuSe reflection started at 360 $^{\circ}$ C obviously illustrate this decomposition. The decomposition of HT CuSe to Cu_{1.8}Se at 412 °C represents the second peritectic decomposition as represented by the appearance of $Cu_{1,8}Se$ at the expense of HT CuSe phase in the diffractograms. The peritectic decompositions could be expressed as follows:

$$CuSe_2 (s) \rightarrow HT CuSe (s) + Se (l) (360 °C)$$
(10)

$$HT CuSe (s) \rightarrow Cu_{1.8}Se (s) + Se (l) (412 °C)$$
(11)

The SnSe and Cu_{1.8}Se phase reflections are no longer observable at 450 °C. These reflections are replaced by new peaks at $2\theta = 27.14$ and 45.07° that can be assigned with reasonable confidence to monoclinic Cu₂SnSe₃ 200/-112 and -331 reflections (ICDD #00-056-1111). At annealing temperature of 550 °C, a broad reflection at $2\theta = 31,43^{\circ}$ suggests that a formation of a MoSe₂ phase also takes place (ICDD# 01-029-0914). The degree of crystallinity of Cu₂SnSe₃ phase enhances during 5 minutes holding time at 550 °C as revealed by an increase of their reflection intensities. On a basis of in-situ diffractograms observation, a Cu₂SnSe₃ phase crystallizes from a reaction of Cu_{1.8}Se and SnSe which is different from its theoretical reaction path [26]. In order to satisfy the reaction scheme, it is reasonable that a contribution of liquid Se for the complete formation of Cu₂SnSe₃ must also be taken into account;

$$Cu_{1.8}Se (s) + SnSe (s) + Se (l) → Cu_2SnSe_3(s) (450-550 °C)$$
(12)
Mo (s) + Se (l) → MoSe₂ (s) (550 °C) (13)

A complementary DSC analysis during annealing is presented in Figure 4 on a Mo/Cu/Sn/Se stacked layer. By comparing temperatures of all DSC signals with the temperatures of corresponding phase change from Figure 3, all recorded DSC signals are therefore attributed solely to the crystallization and melting events of elemental phases as well as formation or decomposition of selenide phases. The first DSC signal at 140 °C (signal A) corresponds to the exothermic reaction of Se phase change from amorphous state to crystallization on, in a perfect agreement with in-situ XRD results of reaction (4). Following after the crystallization of Se, the signal B must reflect a formation of LT CuSe at about 185-189 °C in according to reaction (5) which is also defined as an exothermic reaction. Two consecutive melting events of Se at 220 °C and Sn at 230 °C (reactions (1) and (6)) are recognized from their strong endothermic signals C and D, confirming the results of in-situ XRD are accurate. The formation of SnSe from liquid state reaction (8) and from Cu₆Sn₅ (reaction (8)) accompanied by the CuSe₂ formation of reaction (9) must be related to a broad

exothermic signal E just above the Sn melting temperature. It is likely that the formation of $CuSe_2$ may also occur at the signal E since its formation temperature is so close with other three simultaneous reactions (7) – (8) resulting a complete overlapped DSC signal composed of individual exothermic reactions (7) – (9) at signal E. An apparent endothermic signal F at 360 °C definitely resembles a peritectic decomposition of $CuSe_2$ into HT CuSe as described in reaction (10). The weak signal G at 412 °C represents the reaction (11) where HT CuSe is subjected to further peritectic decomposition into $Cu_{1.8}Se$. Approaching the DSC final measuring temperature of 540-550 °C, the DSC profile shows a gradual exothermic slope which starts from 450 °C up to minima at about 530 °C (signal H) where the crystallization of Cu_2SnSe_3 takes place according to the reaction (13). These results also demonstrate the ability of combined in-situ XRD and DSC techniques to perform a real-time observation on crystalline phase formation at elevating temperature.

After comparing these results with the formation reactions of Cu₂SnS₃ in Ref. [7], it is interesting to find that the formation temperatures of binary Cu-chalcogenides and Snchalcogenide phases are roughly identical despite the use of different chalcogens as summarized in Table 1. The LT Cu-chalcogenides forms at about 185-187 °C whereas Snchalcogenides are always formed after the melting event of Sn, ensuring that both SnS and SnSe phases form through a liquid-state reaction. In contrast with the Cu-selenides, typical phase transformations of Cu-sulphides (e.g. peritectic decompositions CuS₂ into CuS and Cu₂S) were not observed during the formation of Cu₂SnS₃. The Cu₂SnS₃ initial formation temperature is, however, much lower than that of Cu₂SnSe₃ one. A possible explanation can be subjected to the different formation pathways of these ternary Cu-Sn-chalcogenides. The Cu₂SnS₃ formation can be completed solely by a direct reaction of CuS and SnS at lower temperature without any necessity to exhibit a CuS peritectic decomposition. On a contrary, a higher temperature is obviously needed in order to perform a complete peritectic decomposition of HT CuSe into Cu_{1.8}Se phase prior to the formation of Cu₂SnSe₃. It is

noteworthy that the Ref. [7] employed different [Cu]/[Sn] and [S]/[Metals] ratios. Nevertheless the difference in ratio is thought only to lead to the formation of secondary phases at the final stage of annealing and would not affect the initial formation temperature. In the end, an arrow diagram for the formation reaction of Cu₂SnSe₃ from Mo/Cu/Sn/Se stacked layers is constructed as seen in Figure 5.

Conclusions

The formation of Cu_2SnSe_3 from stacked Mo/Cu/Sn/Se layers investigated by combined in-situ XRD and DSC was presented and discussed. The crystallization of Se and formation of LT CuSe dominates the phase evolution during annealing at low temperature. The SnSe phase is suggested to form as a result of both a liquid-state reaction of Sn and Se as well as a reaction of Cu_6Sn_5 with liquid Se at 230 °C. It is obvious that Cu-selenide phases exert peritectic decompositions during annealing. All phase changes are apparently recorded and clarified by the DSC as well, demonstrating a capability of both techniques as in-situ analytical tools for investigating the phase changes. The formation of Cu_2SnSe_3 phase starts at 450°C as a product from a reaction between $Cu_{1.8}Se$ and SnSe in a presence of liquid Se which occurs at a higher temperature than that of its counterpart Cu_2SnS_3 .

Acknowledgement

R.A. Wibowo would like to thank the Alexander von Humboldt Foundation for the financial support.

References

[1] D. B. Mitzi, O. Gunawan, T. K. Todorov, K. Wang, S. Guha, The path towards a high-performance solution-processed kesterite solar cell, Sol. Energy Mater. Sol. Cells 95 (2011) 1421–1436.

- [2] A. Redinger, D. M. Berg, P. J. Dale, R. Djemour, L. Gütay, T. Eisenbarth, N. Valle, S. Siebentritt, Route Toward High-Efficiency Single-Phase Cu₂ZnSn(S,Se)₄ Thin-Film Solar Cells: Model Experiments and Literature Review IEEE J. Photovolt. 1 (2011) 200-206.
- [3] S. Siebentritt, Why are kesterite solar cells not 20% efficient? Thin Solid Films (2013), http://dx.doi.org/10.1016/j.tsf.2012.12.089
- [4] M. Altosaar, J. Raudoja, K. Timmo, M. Danilson, M. Grossberg, J. Krustok, E. Mellikov, $Cu_2Zn_{1-x}Cd_xSn(Se_{1-y}S_y)4$ solid solutions as absorber materials for solar cells Phys. Stat. Sol. (a) 205 (2008) 167–170.
- [5] D. M. Berg, R. Djemour, L. Gutay, S. Siebentritt, P.J. Dale, X. Fontane, V.Izquierdo-Roca, A. Perez-Rodriguez, Raman analysis of monoclinic Cu₂SnS₃ thin films Appl. Phys. Lett. 100 (2012) 1921031-1921034.
- [6] G. Marcano, C. Rincón, S.A. López, G. Sánchez Pérez, J.L. Herrera-Pérez, J.G.
 Mendoza-Alvarez, P. Rodríguez, Raman spectrum of monoclinic semiconductor
 Cu₂SnSe₃, Sol. State Commun. 151 (2011) 84–86.
- [7] R. Schurr, A. Hölzing, R. Hock, Real-time investigations on the formation reactions during annealing of sulfurized Cu–Sn precursors, Thin Solid Films 519 (2011) 7412– 7415.
- [8] P. Uday Bhaskar, G. Suresh Babu, Y.B. Kishore Kumar, V. Sundara Raja, Investigations on co-evaporated Cu₂SnSe₃ and Cu₂SnSe₃–ZnSe thin films, Appl. Surf. Sci. 257 (2011) 8529–8534.
- [9] G. Marcano, C. Rincon, L. M. de Chalbaud, D. B. Bracho, G. Sanchez Perez, Crystal growth and structure, electrical, and optical characterization of the semiconductor Cu₂SnSe₃, J Appl Phys 90 (2001) 1847-1853.

- [10] G. Hema Chandra, O. Lakshmana Kumar, R. Prasada Rao, S. Uthanna, Influence of substrate and selenization temperatures on the growth of Cu₂SnSe₃ films, J Mater Sci 46 (2011) 6952–6959.
- [11] E. J. Skoug, J. D. Cain, D. T. Morelli, Thermoelectric properties of the Cu₂SnSe₃ Cu₂GeSe₃ solid solution, J. Alloys Compd. 506 (2010) 18–21.
- [12] X. Lu, D. T. Morelli, Thermoelectric Properties of Mn-Doped Cu₂SnSe₃ J. Elec. Mater. 41 (2012) 1554-1558.
- [13] R. Schurr, A. Hölzing, S. Jost, R. Hock, T. Voβ, J. Schulze, A. Kirbs, A. Ennaoui, M. Lux-Steiner, A. Weber, I. Kötschau, H.-W. Schock, The crystallisation of Cu₂ZnSnS₄ thin film solar cell absorbers from co-electroplated Cu–Zn–Sn precursors, Thin Solid Films 517 (2009) 2465–2468.
- [14] International Centre for Diffraction Data (ICDD), 12 Campus Blvd., Newtown Square, PA 19073-3273 U.S.A. 2011.
- [15] H. Araki, A. Mikaduki, Y. Kuno, T. Sato, K. Jimbo, W.S. Maw, H. Katagiri, M. Yamazaki, K. Oishi, A. Takeuchi, reparation of Cu₂ZnSnS₄ thin films by sulphurization of stacked metallic layers, Thin Solid Films 517 (2008) 1457-1460.
- [16] J.J. Scragg, P.J. Dale, L. M. Peter, Towards sustainable materials for solar energy conversion: Preparation and photoelectrochemical characterization of Cu₂ZnSnS₄, Electrochem. Commun. 10 (2008) 639-642.
- [17] R. Pretorius, T.K. Marais and C.C. Theron, Thin film compound phase formation sequence: An effective heat of formation model, Mater. Sci. Eng. R 10 (1993) 1-83.
- [18] Yu.S. Kaganovskii, L.N. Paritskaya, W. Lojkowski, Kinetics of chemical compound growth by surface interdiffusion, Surf. Sci. 454-456 (2000) 591-597.
- [19] P.J. Shang, Z.Q. Liu,, X.Y. Pang, D.X. Li, J.K. Shang, Growth mechanisms of Cu3Sn on polycrystalline and single crystalline Cu substrates, Acta Mater. 57 (2009) 4697–4706

- [20] Y. M. Kim, H. R. Roh, S.T. Kim, Y. H. Kim, Kinetics of Intermetallic Compound Formation at the Interface Between Sn-3.0Ag-0.5Cu Solder and Cu-Zn Alloy Substrates, J. Elec. Mater. 39 (2010) 2504-2512.
- [21] R. A. Gagliano, M. E. Fine, Thickening Kinetics of Interfacial Cu6Sn5 and Cu3Sn Layers during Reaction of Liquid Tin with Solid Copper, J. Elec. Mater. 32 (2003) 1441-1447.
- [22] N. Ssunders, A.P. Miodownik, The Cu-Sn (Copper-Tin) System, Bulletin of Alloy Phase Diagrams 11 (1990) 278-287.
- [23] H. Yoo, R.A. Wibowo, A. Hölzing, R. Lechner, J. Palm, S. Jost, M. Gowtham, B. Louis, R. Hock, Investigation of the solid state reactions by time-resolved X-ray diffraction while crystallising kesterite Cu₂ZnSnSe₄ (CZTSe) thin films, Thin Solid Films (2012) doi: 10.1016/j.tsf.2013.01.054.
- [24] D. J. Chakrabarti, D. E Laughlin, The Cu-Se (Copper-Selenium) System, Bulletin of Alloy Phase Diagram 2 (1981) 305-315.
- [25] G. P. Bernardini, A. Catani, The Cu-Se System, Mineral. Deposita (Bed.) 3 (1968)375—380.
- [26] F. Hergert, R. Hock, Predicted formation reactions for the solid-state syntheses of the semiconductor materials Cu₂SnX₃ and Cu₂ZnSnX₄ (X = S, Se) starting from binary chalcogenides, Thin Solid Films, 515 (2007) 5953-5956.

List of Tables

Initial formation temperature of detected phases in the formation of Cu₂SnSe₃ Table 1. (this contribution) and Cu_2SnS_3 (Ref. [7]). The Cu-sulphides peritectic cush decomposition was not observed during the formation of Cu₂SnS₃.

List of Figures

- Figure 1. Electron microscope plane sectional images of Sn layer on Cu layer. The sputtered Sn layer forms island-like surface morphology.
- Figure 2. The in-situ X-ray diffractograms of Mo/Cu/Sn at elevated temperature to 550 °C shows IMC phase changes. The detected phases are; (1) Sn, (2) Cu₆Sn₅, (3) Cu₃Sn and (4) Cu₄₁Sn₁₁ respectively. A red vertical line marks the overlapped Cu (111) and Cu₆Sn₅ (-514) reflections originated at $2\theta = 43.3^{\circ}$ at $30 ^{\circ}$ C.
- Figure 3. The phase evolution during annealing of Mo/Cu/Sn/Se stacked layer as recorded by in-situ XRD. The recorded crystalline phases are; (1) Sn, (2) Cu_6Sn_5 , (3) Se, (4) LT CuSe, (5) SnSe, (6) CuSe_2, (7) HT CuSe, (8) $Cu_{1.8}Se$, (9) Cu_2SnSe_3 . A red vertical line marks the overlapped Cu (111) and Cu_6Sn_5 (-514) reflections originated at $2\theta = 43.3^{\circ}$ at 30 °C.
- Figure 4. A DSC profile of the Mo/Cu/Sn/Se sample upon heating to about 550 °C.
- Figure 5. An arrow diagram of the formation of Cu_2SnSe_3 during annealing the Mo/Cu/Sn/Se stacked layers which shows the reaction of metal phases with Se.

Table 1.Initial formation temperature of detected phases in the formation of Cu_2SnSe_3
(this contribution) and Cu_2SnS_3 (Ref. [7]). The Cu-sulphides peritectic
decomposition was not observed during the formation of Cu_2SnS_3 .

No.	Phase	Formation temperature (°C)
	Selenide	
1.	LT CuSe,	187
2.	SnSe	230
3.	CuSe ₂	240
4.	HT CuSe	360
5.	Cu _{1.8} Se	412
6.	Cu ₂ SnSe ₃	450
	Sulphide	
1.	LT CuS	185
2.	SnS	235
2	Cu ₂ SnS ₃	320





Intensity (arb. units)



Intensity (arb. units)













Highlights

- In-situ investigation revealed intermetallic compounds and Cu₂SnSe₃ formations. •
- CuSe phase dominates binary phase formations at a low annealing temperature. •
- SnSe forms from luquid phase reaction of Sn and Se. ٠
- Binary Cu-selenide phase exerts sequential phase decompositions. •
- Crystalline Cu₂SnSe₃ forms above 450 °C. •