Nanoparticle-induced grain growth of carbon-free solution-processed CuIn(S,Se)₂ solar cell with 6% efficiency

Cai, Yongan; Ho, John C. W.; Batabyal, Sudip Kumar; Liu, Wei; Sun, Yun; Mhaisalkar, Subodh Gautam; Wong, Lydia Helena

2013

Cai, Y., Ho, J. C. W., Batabyal, S. K., Liu, W., Sun, Y., Mhaisalkar, S. G., & Wong, L. H. (2013). Nanoparticle-Induced Grain Growth of Carbon-Free Solution-Processed CuIn(S,Se)₂ Solar Cell with 6% Efficiency . ACS Applied Materials & Interfaces, 5(5), 1533-1537.

<https://hdl.handle.net/10356/100341>

<https://doi.org/10.1021/am303057z>

© 2013 American Chemical Society. This is the author created version of a work that has been peer reviewed and accepted for publication by ACS Applied Materials and Interfaces, American Chemical Society. It incorporates referee's comments but changes resulting from the publishing process, such as copyediting, structural formatting, may not be reflected in this document. The published version is available at:
<http://dx.doi.org/10.1021/am303057z>

Downloaded on 26 Apr 2023 18:59:21 SGT

**Nanoparticle-induced grain growth of Carbon-free solution processed
CuIn(S,Se)₂ solar cell with 6% efficiency**

Yongan Cai^{a1}, John C. W. Ho^{a, b1}, Sudip K. Batabyal^{a}, Wei Liu^c, Yun Sun^c, Subodh G.
Mhaisalkar^{a, b} and Lydia H. Wong^{a, b*}*

^a Energy Research Institute @ NTU (ERI@N), Nanyang Technological University, Research Techno Plaza, Singapore 637553.

^b School of Materials Science & Engineering, Nanyang Technological University, Singapore 639798.

^cInstitute of photoelectron, College of Information Technical Science, Nankai University, Tianjin 300071, China

*Corresponding authors.

¹These authors have equal contribution.

Abstract

Chalcopyrite-based solar cell deposited by solution processes is of great research interest due to ease of fabrication and cost effectiveness. Despite the initial promising results, most of the reported methods encounter challenges such as limited grain growth, Carbon-rich interlayer, high thermal budget and the presence of secondary Cu-rich phases, which limit the power conversion efficiency (PCE). In this paper, we develop a new technique to deposit large grain, Carbon-free CISSe absorber layers from aqueous nanoparticle/precursor mixture which resulted in a solar cell with PCE of 6.2%. CuCl_2 , InCl_3 , and thiourea were mixed with CuS and In_2S_3 nanoparticles in water to form the unique nanoparticle/precursor solution. The Carbon layer formation was prevented because organic solvents were not used in the precursor. The copper-rich (CuS) nanoparticles were intentionally introduced as nucleation sites which accelerate grain growth. In the presence of nanoparticles, the grain size of CISSe film increased by a factor of 7 and the power conversion efficiency of the solar cell is 85% higher than the device without nanoparticle. This idea of using nanoparticles as a means to promote grain growth can be further exploited for other types of chalcopyrite thin film deposited by solution methods.

Key words: $\text{CuIn}(\text{S},\text{Se})$, CIGS, Photovoltaics, Solution process, Spray Pyrolysis, Nanoparticle, Grain growth,

Introduction

Cu(In,Ga)Se₂ (CIGS) is a good absorber materials for thin film solar cell and has been reported to yield one of the highest power conversion efficiency for the thin film photovoltaic devices because of its high absorption coefficient and appropriate band gap. Despite the promising efficiency level ¹, the production cost of the conventional vacuum based processes such as co-evaporation or sputtering ²⁻⁴ prevents the wide spread commercialization of CIGS based solar cells. In this regards, CIGS deposited by solution processes ⁵⁻¹³ are promising because of relatively simple and low cost procedures. To date, the reported solution based approaches for CIGS absorber layer deposition include electrochemical ^{6,13}, spray or spin coating of organometallic precursors ⁵, screen printing of CIGS or component metal pastes ⁷⁻⁸, ink jet printing of nanoparticle based ink ^{9,12} and hydrazine based approach¹⁴.

Even though the nano-ink approach allows possibility of controlling the composition uniformity, most of these approaches do not result in significant grain growth and hence limit the power conversion efficiency^{11 9 15}. The formation of Carbon-rich interlayer between Mo substrate and CIS thin film was also frequently reported to limit the power conversion efficiency ¹⁶⁻¹⁸. Jeong et al ¹² reported a method with very little amount of C content but the selenization was carried out at 520°C for 1 hour. The high thermal budget process is not desirable for solar cell fabrication on flexible polymeric substrates. The Hillhouse group recently reported nanoink based device with 12% efficiency by using Na doping to induce grain growth, however a toxic KCN treatment was used to remove unwanted Cu-rich residues.¹⁹ Therefore, it is clear that challenges associated with solution-processed CIGS thin film such as limited grain growth, Carbon-rich interlayer, high thermal budget and the presence of secondary Cu-rich phases, still

need to be addressed in order to realize a low-cost high efficiency CIGS-device from solution processes.

In the vacuum deposited CIGS film, it is well established that Cu-rich phase facilitates grain growth⁴ even though the final CIGS film should be free of Cu-rich phase because they can cause electrical shorts. Inspired by this approach, we used Cu-rich nanoparticles to help grain growth together with Cu-poor precursor to yield a final absorber film which is free from Cu-rich phases. The absorber layer solution contains CuS and In₂S₃ nanoparticles mixed with a clear solution of CuCl₂, InCl₃, and thiourea in water, without any organic solvents. By using excess Sulfur in the precursor, we managed to avoid the molybdenum oxide formation on Mo substrate during spray deposition as well as preventing the formation of C-rich film. CuIn(S,Se)₂ (CISSe) thin film with appropriate grain size and composition was achieved after selenization and solar cell device with 6.2% power conversion efficiency was demonstrated. In a nutshell, the key advantages of our novel approach are 1) all synthesis routes were carried out in aqueous solution without any organic solvents to prevent the formation of Carbon-rich layer, 2) grain growth was assisted by the presence of Cu-rich nanoparticles in the precursor solution and 3) no toxic chemicals (such as hydrazine or KCN etc) were used in the synthesis and device fabrication procedures.

Experimental:

Nanoparticle synthesis: CuS nanoparticles were synthesized by mixing Na₂S and CuCl₂ in the molar ratio of 2:1 in deionised water at room temperature. Similarly, In₂S₃ nanoparticles were synthesized by mixing Na₂S and InCl₃ in the ratio of 5:2 in deionised water at room temperature.

The resultant mixture was centrifuged and washed with deionised water before drying in vacuum. The as synthesized nanoparticles were characterized by FESEM and XRD (the results are shown in ESI). The FESEM analysis shows that the sizes of both the nanoparticles are in the range of 20 nm to 50 nm. From the XRD analysis we found the Indium sulfide nanoparticles are amorphous in nature but the crystallographic phase of copper sulfide nanoparticles is identical with the digenite phase of Cu_9S_5 with the JCPDS number 00-047-1748.

Precursor film preparation: The Cu poor precursor by mixing 8 ml 0.01M CuCl_2 , 10 ml 0.01M InCl_3 , and 0.5 ml 1.0M thiourea in water. This Cu-poor precursor was then sprayed on top of pre-heated Mo-coated glass at 120°C (Fig 1a) to form a thin CIS film. Subsequently, the temperature of the hot plate was increased slowly during spray to reach the final temperature of 350°C . The spray rate was kept at approximately 1-2ml/min. Another precursor was designed by mixing nanoparticle with the aqueous precursor (np-precursor). In a typical procedure, this np-precursor solution was synthesized by adding 0.2 mmol of CuS and 0.3 mmol of In_2S_3 nanoparticles aqueous dispersion with the solution containing 65 ml of 0.01M CuCl_2 , 40 ml of 0.01M InCl_3 , and 5 ml 1.0M thiourea ($\text{SC}(\text{NH}_2)_2$). The precursor solution was sprayed onto Mo-coated glass heated to a temperature of $320\text{-}350^\circ\text{C}$ to form a continuous film. Thereafter, a second precursor solution was prepared by mixing 8 ml 0.01M CuCl_2 , 10 ml 0.01M InCl_3 , and 0.5 ml 1.0M thiourea in water to form a Cu-poor precursor solution. It was then sprayed on top of the film formed previously (Fig 1b). The final Cu/In ratio were obtained as about 0.85 as confirmed by EDX analysis. To prevent the formation of Carbon interlayer after selenization, we judiciously chose water as the solvent in all synthesis steps.

Figure 1. Schematic diagram to illustrate the two precursor film design: (a) Precursor solution approach and (b) Mixed nanoparticles/precursor solution approach containing CuS nanoparticle and In_2S_3 nanoparticles

Device fabrication: The sprayed CIS films were annealed in Se vapor, selenization, at temperature of 480-500°C to form CISSe film. Selenization allows the tuning of bandgap by the substitution of S with Se and induced grain growth in the absorber layer. Thereafter, CdS buffer layer (~50nm) was deposited by chemical bath deposition. Then, i-ZnO and Al:ZnO (TCO layer) were sputtered on top of CdS followed by thermal evaporation of Al electrode on top of the TCO layer. CdS deposition was carried out in the bath containing aqueous solution of cadmium acetate, ammonium acetate and thiourea at 85°C. The pH of the bath was adjusted to 9.0 by ammonium hydroxide. The TCO layer used was aluminum doped zinc oxide and deposited via DC sputtering with an applied power of 200W. After thermal evaporation of Al electrode, the cells were isolated by mechanical scribing with a cell area of 0.08cm².

Characterization: Cross-section images of samples were obtained by Field Emission Scanning Electron Microscope (FESEM), JEOL JSM-7600F, with an energy dispersive X-ray (EDX) spectrometer attachment. The crystal structures of the samples were studied using X-Ray Diffraction (XRD) by Bruker D8 Advance Diffractometer. The current density–voltage (J-V) characteristics of the CuIn(S,Se)₂ devices were measured in ambient conditions under AM 1.5G illumination (100 mW/cm²) using a Keithley SMU 2400 sourcemeter. The light intensity was calibrated by using an NREL calibrated silicon photodiode.

Results and Discussions:

During spray deposition, the proposed chemical reaction of CuInS₂ film formation that occurs when the micron size precursor droplet landed on the heated substrate is described below:

The CuInS₂ film is then transformed to CuIn(S,Se)₂ after selenization. To confirm the above reaction, X-ray diffraction experiments were carried out. The XRD patterns of the np-precursor and precursor-only films before and after selenization are shown in Figures 2a and 2b, respectively. Before selenization, the diffraction peaks match well with the standard data sheet (JCPDS No- 85-1575) of CuInS₂ without any trace of metal oxides. We believe that the excess sulfur in the precursor prevents the unnecessary oxide formation from the precursors and also protect Mo substrate from oxidation at high temperature. The diffraction patterns of the film after selenization matches that of CISSe (JCPDS no. 36-1311) (Figure 2b) with slight variation in peak positions due to the different S/Se ratio that affects the lattice parameters. The S/S+Se ratio for the selenized CISSe films was estimated by Rietveld refinement and found to be approximately 0.29-0.41 (Table 1). The increase in the relative intensity of (112) peaks of both films after selenization (figure 2b) indicate improved crystallinity of these films. This was expected as the spray deposition temperature of 320-350°C might not be sufficient to induce complete

crystallization. The increase in (112) peak intensity also indicates a preferred grain growth along the (112) plane at the expense of (204)/(220) oriented grains which was observed by NREL group²⁰.

Figure 2: a) XRD pattern of the as deposited film from the precursor solution and the nanoparticle incorporated precursor solution. b) XRD pattern of the films after selenization. (peaks are indexed according to the JCPDS No- 85-1575).

Table 1. Rietveld refinement results of CuInS_2 films before and after selenization.

Sample	Lattice parameter		Ratio	
	a (Å)	c (Å)	S (%)	Se (%)
Precursor only	5.518	11.254	100	0
Precursor with nanoparticle	5.495	11.103	100	0
Precursor with nanoparticle –after selenization	5.695	11.501	29	71

Precursor only – after selenization	5.664	11.448	41	59
--	-------	--------	----	----

The grain growth and morphology of the thin film were studied in details by FESEM. Figures 3a and 3c represent the cross-sectional images of the as-deposited film from precursor and np-precursor, respectively. These images clearly show the formation of a single layer CISSe thin film. The difference in grain size is not significant from the FESEM cross-sectional images but the roughness on the top surface of nanoparticle-precursor (np-precursor) thin film is higher than the precursor based film, probably due to the size of nanoparticles.

Figure 3: Cross sectional FESEM image of the as deposited absorber layer from precursor before (a), and after selenization (b), and from nanoparticle incorporated precursor before (c), and after selenization (d).

From the cross-section FESEM images of the absorber layer after selenization considerable grain growth can be observed (Fig 3b and 3d). The np- precursor film (Fig 3d) resulted in much larger grains of 600-700 nm, whereas the grains of the selenized film deposited from precursor only are in the range of 100nm (Fig 3b). The reason for a significant difference in grain size observed between the films can be attributed to the presence of Cu-rich nanoparticles which act as nucleation sites for grain growth. The key idea of incorporating nanoparticles into our precursor spray solution is to promote the formation of Cu-rich regions to mimic the 3 stage co-evaporation technique used in high vacuum CIGS deposition⁴. We postulate that the grain growth starts from the Cu-rich and the In-rich regions, which formed around the CuS nanoparticles and In₂S₃ nanoparticles, respectively. The two regions would subsequently react with each other in the presence of Se at high temperature to form large grain CISSe. The presence of In-rich nanoparticles is important to avoid the formation of CuSe or Cu₂Se phase, which are unfavorable for device performance. Since the formation of CuSe and Cu₂Se phase could be prevented, the toxic KCN etching after selenization, which is commonly used to etch CuSe and Cu₂Se, can be skipped. It should also be noted that the Carbon interlayer between Mo and CISSe, which was reported in many solution processed CIS thin films¹⁶⁻¹⁸, are not observed in Figure 3b and 3d. EDX analysis further confirmed that the absorber layers were free from Carbon.

Figure 4. IV curve of device fabricated from nanoparticle incorporated precursor (blue) film and precursor film without nanoparticle (red). The active area of both devices were 0.08cm^2 .

In order to investigate the photovoltaic performance of the absorber layers deposited from these two precursor designs, we fabricated the solar cells by depositing CdS buffer layer, intrinsic ZnO, AZO and metal grid electrode on the absorber layers. We found the np-precursor film (700nm thick) exhibits higher power conversion efficiency ($\eta=6.15\%$) as compared to the device based on precursor film (800nm thick) ($\eta=3.47\%$) (Fig 4). In general we fabricate 8 devices on the same substrate and we observed the PCE vary for the nanoparticle incorporated system in the range of 5% to 6% where as for the precursor system it varies in the range of 2.5% to 3.5%. The np-precursor film shows a higher efficiency due to increase in V_{oc} (23%) and J_{sc} (35%) as compared to the precursor film. The enhanced J_{sc} of the np-precursor film can be attributed to the larger grain size with less grain boundary and recombination site, while the higher V_{oc} could be attributed to larger and more uniform interface between CdS and the CISSe layer. The relatively low FF (0.53

and 0.50) is attributed to the inefficient charge collection as a result of non-optimized transparent conducting layer (ZnO/AZO) and top electrode. Our best power conversion efficiency here is comparable to the other nanoparticle based approaches⁹⁻¹¹ which does not use any doping to induce grain growth. It should be noted that the highest device efficiency of solution-processed CIGS is 15% and is achieved using toxic hydrazine as a reducing agent¹⁴.

The effect of absorber layer thickness on device performance is shown in Figure 5. The details on device properties (V_{oc} , J_{sc} , FF) are summarized in table 2. We found that J_{sc} increased from 18.1mA/cm² to 26.7mA/cm² for np- precursor film when the absorber layer thickness is increased from 300nm to 700nm. As absorber layer thickens, more light could be absorbed and hence a higher photogenerated carrier density will be generated and collected at the respective contacts (holes are collected by Mo substrate while electrons are collected by Al electrode). The consistent V_{oc} shows a well-controlled CdS deposition process in all films.

Figure 5: The photovoltaic performance of nanoparticle based device with different thickness of absorber layers

Table 2: *The photovoltaic performance of nanoparticle based device with different thickness of absorber layers*

Type	Thickness (nm)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	η (%)
precursor with nanoparticle	300	0.42	18.1	41	3.16
	500	0.42	21.0	43	3.74
	700	0.43	26.7	53	6.15
Precursor only	800	0.35	19.8	50	3.47

Conclusions:

A new deposition technique to deposit *Carbon-free* CISSe absorber layers from aqueous nanoparticle/precursor mixture without the use of any toxic chemicals has been developed. It was found that the nanoparticles incorporated precursor promotes grain growth of CISSe absorber layers as the Cu-rich nanoparticles act as nucleation centers for grain growth. In the presence of nanoparticles, the grain size of CISSe film increased by a factor of 7 and the power conversion efficiency of the solar cell device is 6.2%, 85% higher than the device without nanoparticle. This idea of using nanoparticles as a mean to promote grain growth can be further exploited for other types of chalcopyrite thin film deposited by solution processes.

Acknowledgements:

John Ho thanks Economic Development Board (EDB) of Singapore for the scholarship. Funding for this project is provided by A*STAR SERC Printed Photovoltaic Program (grant no. 1021700143).

Supporting Information:

FESEM and XRD data of the individual nanoparticles are provided in supporting information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Corresponding Author

*E-mail: LydiaWong@ntu.edu.sg (L.H.W.), batabyal@gmail.com (S.K.B.).

Author Contributions

‡Y.C. and J.C.W.H. have contributed equally to this work.

Notes

The authors declare no competing financial interest.

References:

- (1) Jackson, P.; Hariskos, D.; Lotter, E.; Paetel, S.; Wuerz, R.; Menner, R.; Wischmann, W.; Powalla, M. *Prog. Photovoltaics Res. Appl.* **2011**, *19*, 894.
- (2) Chirilă, A.; Buecheler, S.; Pianezzi, F.; Bloesch, P.; Gretener, C.; Uhl, A. R.; Fella, C.; Kranz, L.; Perrenoud, J.; Seyrling, S.; Verma, R.; Nishiwaki, S.; Romanyuk, Y. E.; Bilger, G.; Tiwari, A. N. *Nat. Mater.* **2011**, *10*, 857.
- (3) Kemell, M.; Ritala, M.; Leskelä, M. *Critical Reviews in Solid State Mater. Sc.* **2005**, *30*, 1.
- (4) Repins, I.; Contreras, M. A.; Egaas, B.; DeHart, C.; Scharf, J.; Perkins, C. L.; To, B.; Noufi, R. *Prog. Photovoltaics Res. Appl.* **2008**, *16*, 235.
- (5) Hollingsworth, J. A.; Banger, K. K.; Jin, M. H. C.; Harris, J. D.; Cowen, J. E.; Bohannon, E. W.; Switzer, J. A.; Buhro, W. E.; Hepp, A. F. *Thin Solid Films* **2003**, *431–432*, 63.
- (6) Calixto, M. E.; Dobson, K. D.; McCandless, B. E.; Birkmire, R. W. *J. The Electrochem. Soc.* **2006**, *153*, G521.
- (7) Kaelin, M.; Rudmann, D.; Tiwari, A. N. *Solar Energy* **2004**, *77*, 749.
- (8) Vervaeke, A.; Burgelman, M.; Clemminck, I.; Casteleyn, M. In *10th European Photovoltaic Solar Energy Conference* Lisbon, Portugal, **1991**, p 900.
- (9) Panthani, M. G.; V., A.; Goodfellow, B.; Schmidtke, J. P.; Dunn, L.; Dodabalapur, A.; Barbara, P. F.; Korgel, B. A. *J. Am. Chem. Soc.* **2008**, *130*, 16770.
- (10) Guo, Q.; Ford, G. M.; Hillhouse, H. W.; Agrawal, R. *Nano Lett.* **2009**, *9*, 3060.
- (11) Akhavan, V. A.; Goodfellow, B. W.; Panthani, M. G.; Reid, D. K.; Hellebusch, D. J.; Adachi, T.; Korgel, B. A. *Energy Environ. Sci.* **2010**, *3*, 1600.
- (12) Jeong, S.; Lee, B.-S.; Ahn, S.; Yoon, K.; Seo, Y.-H.; Choi, Y.; Ryu, B.-H. *Energy Environ. Sci.* **2012**, *5*, 7539.

- (13) Bhattacharya, R. N.; Oh, M.-K.; Kim, Y. *Sol. Energy Mater. Sol. Cells* **2012**, 98, 198.
- (14) Mitzi, D. B.; Yuan, M.; Liu, W.; Kellock, A. J.; Chey, S. J.; Gignac, L.; Schrott, A. G. *Thin Solid Films* **2009**, 517, 2158.
- (15) Akhavan, V. A.; Goodfellow, B. W.; Panthani, M. G.; Steinhagen, C.; Harvey, T. B.; Stolle, C. J.; Korgel, B. A. *J. Solid State Chem.* **2012**, 189, 2.
- (16) Ahn, S.; Kim, C.; Yun, J. H.; Gwak, J.; Jeong, S.; Ryu, B.-H.; Yoon, K. *J. Phys. Chem. C* **2010**, 114, 8108.
- (17) Kaelin, M.; Rudmann, D.; Kurdesau, F.; Zogg, H.; Meyer, T.; Tiwari, A. N. *Thin Solid Films* **2005**, 480–481, 486.
- (18) Klugius, I.; Miller, R.; Quintilla, A.; Friedlmeier, T. M.; Blázquez-Sánchez, D.; Ahlswede, E.; Powalla, M. *Phys. Status Solidi RRL* **2012**, 6, 297.
- (19) Guo, Q.; Ford, G. M.; Agrawal, R.; Hillhouse, H. W. *Prog. Photovoltaics Res. Appl.* **2013**, 21, 64.
- (20) Contreras, M. A.; Romero, M. J.; Noufi, R. *Thin Solid Films* **2006**, 511–512, 51.

Electronic supplementary information

**Nanoparticle-induced grain growth of solution processed
CuIn(S,Se)₂ solar cell with 6% efficiency**

Yongan Cai^{a1}, John C. W. Ho^{a,b1}, Sudip K. Batabyal^{a}, Wei Liu^c, Yun Sun^c, Subodh G.*

Mhaisalkar^{a, b} and Lydia H. Wong^{a, b}*

^a Energy Research Institute @ NTU (ERI@N), Nanyang Technological University, Research Techno Plaza, Singapore 637553.

^b School of Materials Science & Engineering, Nanyang Technological University, Singapore 639798.

^c Institute of photoelectron, College of Information Technical Science, Nankai University, Tianjin 300071, China

ESI1: FESEM image of the Indium sulfide (a) and copper sulfide (b) nanoparticles.

(a)

(b)

ESI2: XRD patterns of as synthesized indium sulfide and copper sulfide nanoparticles. Vertical line on X-axis represents the standard data of CuS (black) and In₂S₃ (red) of JCPDS number 00-026-0476 and 00-033-0624 respectively.