

Formation and characterization of CuInSe₂ thin films from binary CuSe and In₂Se₃ nanocrystal-ink spray

Hyungmin Lee*, Dong-seob Jeong*, Taehong Mun*, Babu Pejjaï*, Vasudeva Reddy Minnam Reddy*, Timothy James Anderson**, and Chinho Park*,†

*School of Chemical Engineering, Yeungnam University, 280 Daehak-ro, Gyeongsan 38541, Korea

**Department of Chemical Engineering, University of Florida, Gainesville, FL 32611, U.S.A.

(Received 12 February 2016 • accepted 7 April 2016)

Abstract—CuInSe₂ (CISE) thin films were grown on Mo-coated glass substrates by spray coating technique using nanocrystalline ink. The ink was prepared by dissolving binary CuSe and In₂Se₃ nanoparticles in iso-butanol. The grown films were subsequently annealed in vacuum and selenium atmosphere, and examined by various characterization techniques. The vacuum-annealed films showed the CuSe binary phase along with the CuInSe₂ phase, whereas the selenized films showed a single phase CuInSe₂. The elemental analysis of the selenized film exhibited near stoichiometry, and the photoluminescence peak was observed in the region of band-to-band transitions (0.97 eV), which indicated the good structural quality of the selenized films. The developed method opens a new prospect for the fine-tuning of CISE composition by pre-adjusting the composition of each element in the binary to best fit of CISE in the photovoltaic devices.

Keywords: CuSe, In₂Se₃, CuInSe₂ Thin Films, Non-vacuum Process, Spray Coating

INTRODUCTION

CuInSe₂ (CISE)/CuIn_xGa_{1-x}Se₂ (CIGSe) is considered a promising absorber material in photovoltaic devices due to numerous advantages such as high optical absorption coefficient ($>10^5 \text{ cm}^{-1}$), optimal direct band gap for efficient absorption of solar radiation, fitted work function with metal partners, high thermal and chemical stability. Moreover, it consists of eco-friendly elements and shows a theoretical maximum conversion efficiency of ~32%. Even though the highest efficiency was obtained in vacuum-processed CISE/CIGSe-based thin film solar cells, the massive production of these photovoltaic modules from vacuum-based techniques faces a number of challenges that include cost reduction, precise composition control and inadequacy of large area deposition. Alternatively, liquid-based processing of CISE absorbers has attained an accelerated interest due to its simplicity and high-throughput. This route is comprised of two different paths, namely, solution-based and nanoparticle-based process depending on the nature of the precursors selected for the absorber synthesis [1-3]. Usually, in the solution-based approach, the metal salts are dissolved in an organic solvent followed by the addition of polymer binders and then coated on the substrate with a subsequent annealing under inert atmosphere [1-3]. Whereas, in nanoparticle-based approach the binary compound precursors such as Cu₂S, In₂Se₃ and Ga₂Se₃ are dissolved in mostly hydrazine solution to form ink and then coated on the substrate with a subsequent annealing under inert atmosphere [4-10]. How-

ever, in both the aforementioned approaches, the usage of hydrazine or polymer binders residues toxicity or carbon contamination in the absorber layers, which ultimately degrades the efficient utilization of these thin films in solar cells [11]. Moreover, the reported lower efficiency of nanoparticle based CISE/CIGSe solar cells [12] was addressed in terms of carbon contamination (between the absorber and metal back contact) and incomplete selenization. These two problems mainly arise due to the application of binders during the deposition, which prevents the complete crystallization of the absorber material and restricts the larger grain growth during the absorber layer formation.

The aforesaid aspects strongly insist the preparation of CISE absorber layer by the new routes that should be free from the usage of toxic solvents, surfactants and/or binders to reduce the carbon contamination. In this scenario, we deposited the CISE absorber layer using a facile and short-route method, which is free from consumption of toxic solvents, surfactants and binders. Moreover, the films were processed at relatively lower temperatures with less carbon contamination, and hence we believe that this method is suitable for large scale production.

In this work, we demonstrate for the first time the synthesis of CuSe and In₂Se₃ binary nanoparticles by solution processing without using surfactants and the preparation of precursor ink using the nanoparticles dispersed in iso-butanol solvent without using binders as well as the formation of CuInSe₂ thin film precursor layer by air-spraying technique using the ink. The air-spray deposited CISE precursor layer was further crystallized into single phase CISE layer by a subsequent heat treatment process, and used for characterization to estimate its potential as an absorption layer in the solar cell.

†To whom correspondence should be addressed.

E-mail: chpark@ynu.ac.kr

Copyright by The Korean Institute of Chemical Engineers.

EXPERIMENTAL DETAILS

1. Preparation of CuSe and In₂Se₃ Nanoparticles

CuSe and In₂Se₃ nanoparticles were synthesized by using a vacuum-gas manifold. All the reactions progressed in a rounded two-neck flask. The flask was placed in an oil bath and heated to the desired temperature with a hot plate. The center neck of the flask was connected to a condenser, and the other was connected to a thermocouple for temperature monitoring and control. Long carbon-chain surfactants of any kind were not involved in the synthesis.

1-1. Synthesis of CuSe Nanocrystals

7.5 mmol of CuCl (99%, Sigma-Aldrich) was dissolved in 60 ml of ethanol and stirred for one hour at 25 °C. Next, 10 mmol of Se powder (Sigma-Aldrich) was added to the above solution. Then, the mixture was allowed to react in the two-neck round bottom flask for 20 hours at 110 °C. After completion of the reaction, the mixture was cooled slowly with the addition of ethanol, and isolated as precipitation by centrifugation. The precipitation was washed several times with deionized water and dried for 5 hours at 80 °C in N₂ atmosphere using a vacuum oven to produce the pure CuSe nanocrystals.

1-2. Synthesis of In₂Se₃ Nanocrystals

30 mmol of InCl₃ (98%, Sigma-Aldrich) was dissolved in 30 ml of n-propanol and stirred for 2 hours at 25 °C. Separately, 18 mmol of Se powder was dissolved in 40 ml of ethylenediamine and stirred for 2 hours at 50 °C. Then, the above two solutions were mixed together and allowed to react under stirring for 24 hours at 110 °C. After completion of the reaction, the mixture was cooled slowly by adding methanol and isolated as precipitation by centrifugation. After the washing process, the obtained nanocrystals were dried in the same manner that followed for CuSe nanocrystals.

2. Deposition of CISE Thin Film Precursor Layer and Heat Treatment

The binary CuSe and In₂Se₃ nanoparticles were dispersed in iso-butanol in the ratio of 1 : 1 to form nanocrystalline ink. Organic binders of any kind were not involved in preparing the ink. This ink was used as precursor in the deposition of CISE thin film. CISE precursor films were deposited on Mo-coated soda-lime glass (SLG) substrates via an air-spraying technique, and the subsequent heat treatment process was organized in two steps. A schematic of the two-step annealing process is shown in Fig. 1. In the first step, the as-deposited CISE precursor films were annealed at 200 °C for 20 min. In the second step, the temperature was quickly raised to 500 °C, and the second annealing was carried out at this tempera-

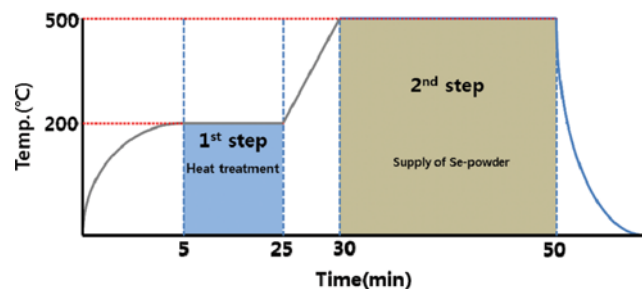


Fig. 1. Schematic of two-step annealing process profile.

ture for 20 min with or without supply of excess elemental selenium. Presumably, the process of selenization was included to compensate the selenium deficiency in the deposited film while annealing.

3. Characterizations

The morphology and composition of samples were investigated by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX) (Hitachi S-4800). The crystalline structure was identified by the X-ray diffraction (PANalyticalX'Pert-PRO MPD) using CuK α line ($\lambda=1.056$ nm). The photoluminescence was measured at 10 K by low-temperature photoluminescence spectrometer (SPEX 750M) using 514.5 nm laser source and InGaAs solid detector. XPS spectra were recorded by Thermo ESCALAB 250 Instrument with Al K α X-ray as the excitation source. Micro-Raman analysis was performed at room temperature by Raman spectrometer (using 532 nm crystal laser as the excitation light source and CCD camera as a detector).

RESULTS AND DISCUSSION

1. Properties of Binary CuSe and In₂Se₃ Nanoparticles

A number of trials were made to optimize the synthesis protocols of both nanoparticles. The XRD patterns of as-prepared CuSe and In₂Se₃ nanoparticles are shown in Fig. 2. The pattern of CuSe nanoparticles showed hexagonal structure of CuSe with (102) as the preferred orientation (JCPDS No. 27-0184), whereas In₂Se₃ nanoparticles showed polycrystalline nature with hexagonal structure of In₂Se₃ along (110) orientation (JCPDS No. 23-0294). The corresponding SEM images of CuSe and In₂Se₃ nanoparticles are shown in Fig. 2. The SEM images indicate that CuSe had plank-like shape nanoparticles, which seems to result from the growth of hexagonal shaped particles on one another. Whereas, In₂Se₃ showed agglomerated and infused spherical nanoparticles. From the EDAX analysis, the ratio of Cu/Se was determined as 1.03 in CuSe nanoparticles, while for In₂Se₃ nanoparticles the ratio of In/Se was estimated as 0.62. The structural and compositional analysis revealed a high phase purity and good stoichiometry of the synthesized nanoparticles.

2. Properties of CISE Films

The phase identification of CISE films was by XRD pattern. Fig. 3(top) depicts the XRD pattern of CISE films that were annealed at two different annealing environments. The vacuum-annealed film showed co-existence of CISE, Cu₂Se and CuSe phases, whereas the selenized film showed a single phase CISE. The XRD spectra of selenized film showed three major peaks that related to (112), (220)/(204), and (312)/(116) planes of tetragonal structure of chalcopyrite CISE phase [11,13]. Since no other secondary phases were evident from the XRD pattern of selenized film, it is clear that the selenized film had a better phase purity as compared to vacuum-annealed film. Moreover, the selenized film showed strong orientation along the (112) direction. It was reported that this particular orientation is favorable for the effective solar energy conversion [11,13]. As our selenized film exhibited high phase purity with (112) orientation, we believe that this film has better aligned absorber layer properties.

Fig. 3(bottom) shows the SEM images of (a) vacuum-annealed and (b) selenized CISE films. The surface morphology of vacuum-annealed and selenized films was quite different. The SEM image of vacuum-annealed film exhibited many pores with granular shaped

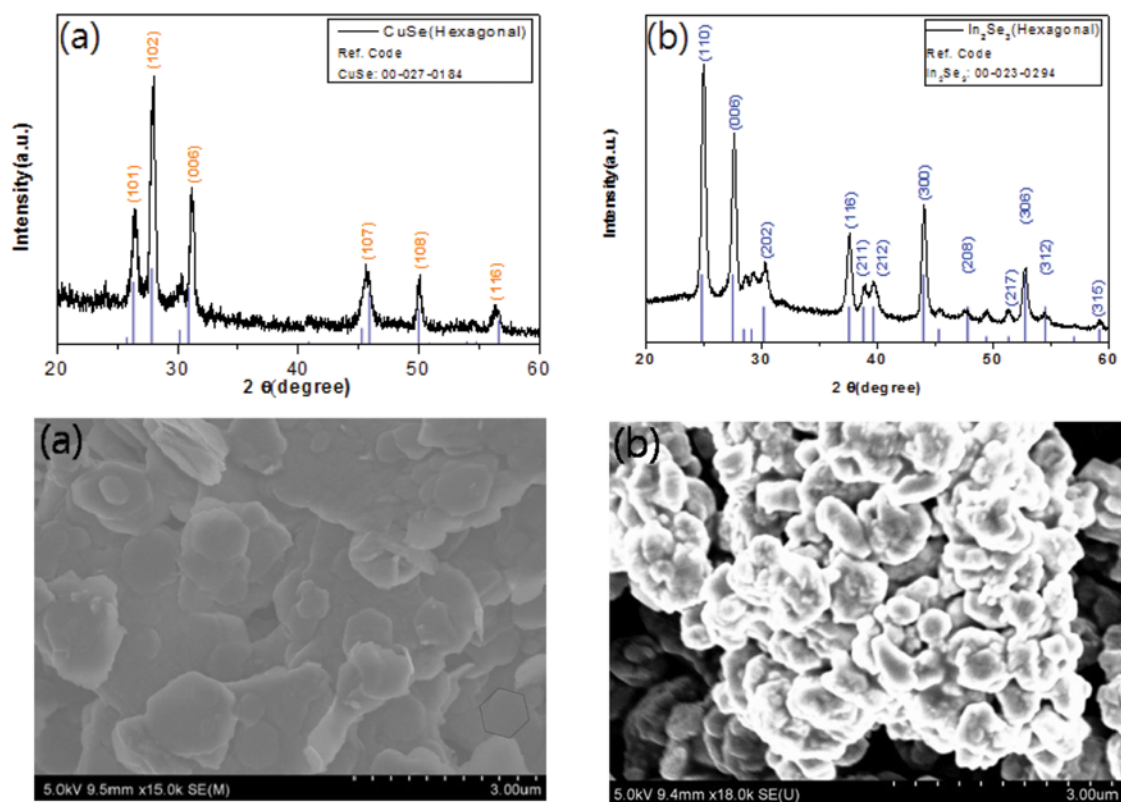


Fig. 2. XRD spectrum and SEM image of (a) CuSe and (b) In₂Se₃ nanoparticles.

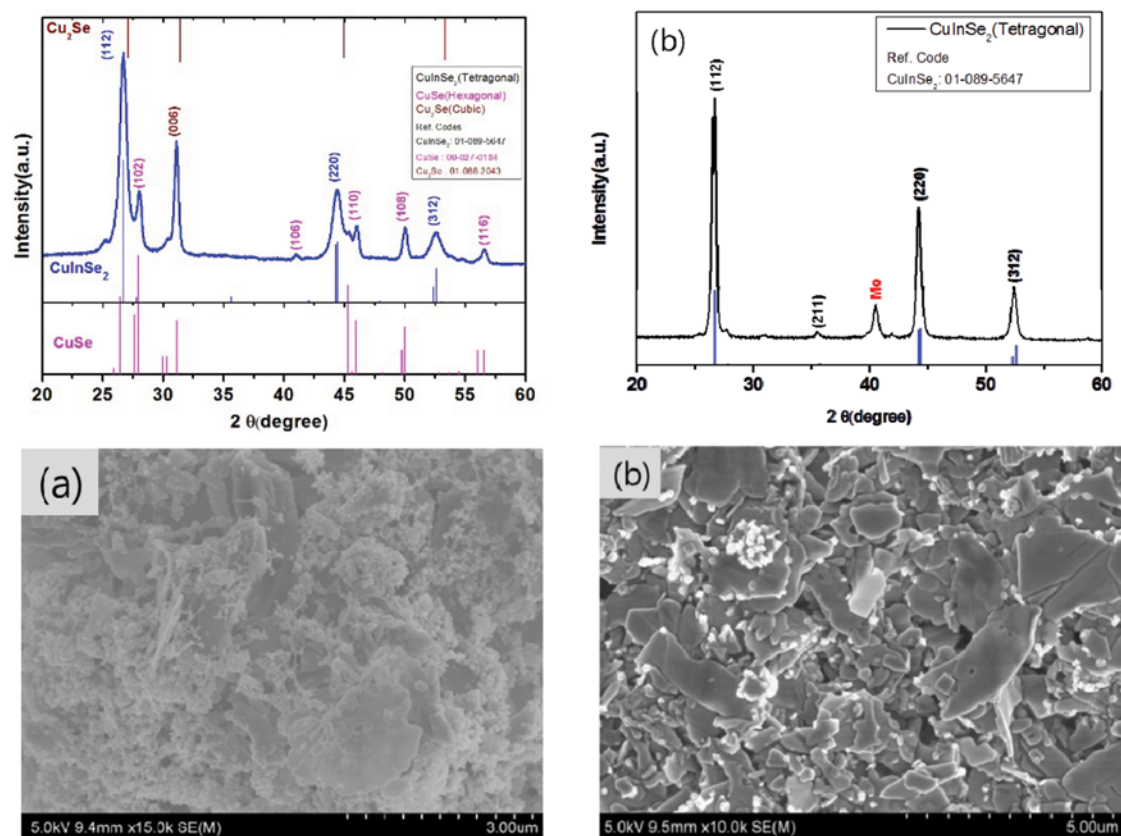


Fig. 3. XRD and SEM image of (a) vacuum-annealed and (b) selenized CIS films.

grains. This is due to the evaporation of volatile substances such as Cl₂ or In₂Se₃ during annealing [8]. Even a slight evaporation of these species during annealing may cause the formation of secondary phases like CuSe or Cu₂Se, and cease the formation of CISE phase in the film. This is quite clear from the XRD of vacuum-annealed film. In contrast, the surface of selenized film was covered by denser flake-shaped grains of different size without any voids. This is due to the sufficient supply of Se vapor during selenization as presumed and promoted the formation of CISE phase [8].

To further confirm the phase purity, Raman spectral measurements were carried out on CISE films and are shown in Fig. 4. The spectrum of vacuum-annealed film showed two major peaks at 175 cm⁻¹ and 258 cm⁻¹ related to CISE (A1 mode) and Cu₂Se phases, respectively. However, for films annealed under Se vapor showed only one major peak at 175 cm⁻¹, which indicates the formation of single phase CISE with improved crystallinity. These results well agreed with XRD and SEM analysis. Normally, the presence of A1 mode is a characteristic observation in I-II-VI₂ chalcopyrite. In our case, the appearance of this mode at 175 cm⁻¹ confirms the formation of pure CISE phase by the present method [14-15].

The elemental composition of the CISE films was estimated from the EDAX analysis and is represented in Table 1. The EDAX analy-

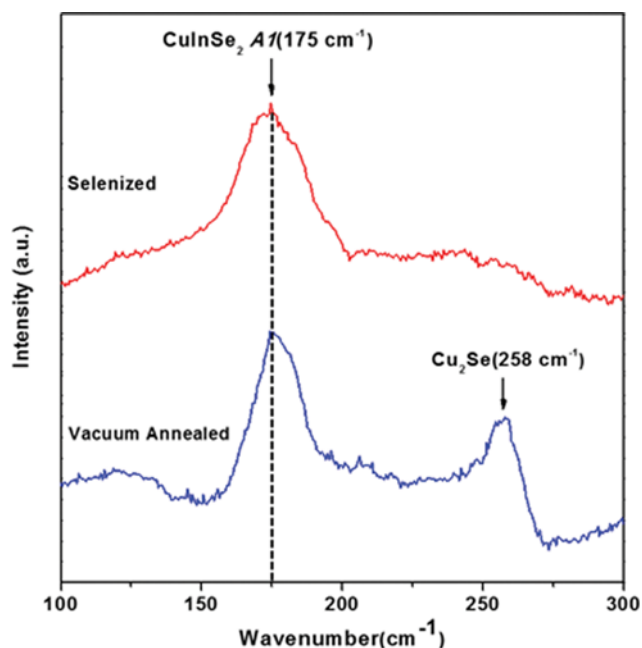


Fig. 4. Raman spectra of vacuum-annealed and selenized CISE films.

Table 1. Elemental composition of CuInSe₂ thin films from EDAX

| CIS films | Elemental composition (at.%) | | | Cu/In ratio | Atomic ratio [Cu] : [In] : [Se] |
|-----------------|------------------------------|-------|-------|-------------|---------------------------------|
| | Cu | In | Se | | |
| Vacuum annealed | 31.05 | 23.65 | 45.30 | 1.31 | 1.24 : 0.95 : 1.81 |
| Selenized | 26.61 | 24.45 | 48.94 | 1.09 | 1.07 : 0.98 : 1.96 |

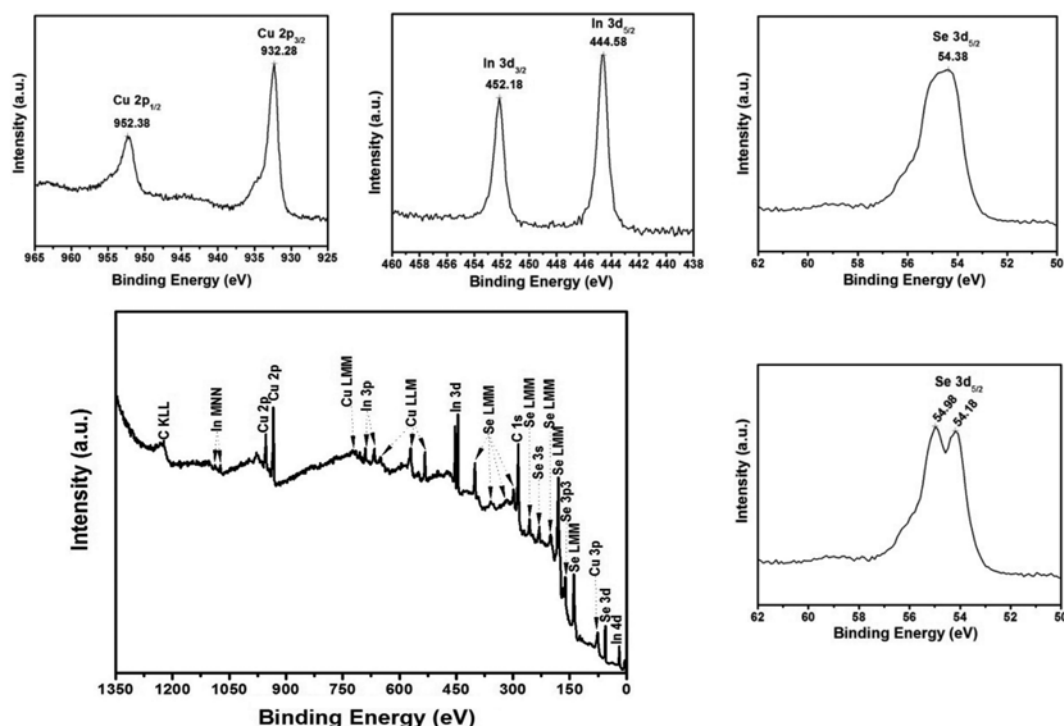


Fig. 5. (Top): XPS narrow scan of Cu-2p, In-3d and Se-3d core level spectra of selenized film. (Bottom): Wide scan survey of selenized film (left), and narrow scan of Se-3d region of vacuum annealed film (right).

sis of vacuum-annealed film exhibited a ratio of Cu/In=1.31, while that of selenized film showed a ratio of 1.09. This infers that both films are in Cu-rich stoichiometry. However, the film annealed under selenium vapor exhibited less Cu-rich environment as compared to vacuum-annealed film, which indicates the better stoichiometry of selenized film.

Fig. 5 depicts the wide and narrow XPS scans of selenized film. To compare the effect of annealing atmosphere the narrow scan of Se-3d region of vacuum-annealed film is also included in the Fig. 5. The binding energy (BE) values of $\text{Cu}2p_{3/2}$, $\text{In}3d_{5/2}$ and $\text{Se}3d_{5/2}$ are consistent with the reported BE values of CuInSe_2 films [16]. The predominant photoelectron signals noticed at 932.28 eV, 444.58 eV and 54.38 eV indicate the Cu^+ , In^{3+} and Se^{2-} valence states [17] in the selenized CISE film. This confirms the formation of pure CISE phase in case of selenized film. Note that in case of vacuum-annealed film the peak of $\text{Se}3d_{5/2}$ level was split into doublet with BE values 54.18 and 54.98 eV. The one located at 54.98 eV exhibited slightly higher intensity than the other and is attributed to copper and indium selenides [18,19]. This promotes the co-existence of secondary phases like CuSe , Cu_2Se and In_6Se_7 along with CISE phase [16,18], as we noted in the case of vacuum-annealed film from the analysis of XRD and Raman.

Further, the composition was estimated from the XPS measurements for both vacuum-annealed and selenized films, and it is in accordance with EDAX analysis. The survey scan of selenized film showed negligible amount of carbon contamination as presumed in our new route due the usage of highly volatile alcohol based solvents.

Usually, different kind of defects were identified in CISE films which depend upon its stoichiometric deviation. To probe this, low temperature (10 K) photoluminescence (PL) measurements were carried out for both films and depicted in Fig. 6. The PL spectra of these films showed a broad curve centered at ~ 0.97 eV, which is related to free-to-bound transitions of Cu-rich films [20]. This band is due to the involvement of acceptor type impurity transitions between conduction band to intrinsic defect levels (such as Cu_{In} , Se_{In} or V_{In}). A similar type of transition was also noticed in the copper-rich CISE films by Yakushev et al. [21]. The PL curve of both films

was deconvoluted into two main peaks for further investigation. The deconvoluted peaks centered at 0.96 eV and 0.97 eV were attributed to the transition of charge carriers between conduction band to acceptor level (like Se_{In} , Se_i or V_{In} defect states). The peaks centered at 0.94 eV and 0.95 eV were due to donor-acceptor transitions, i.e., V_{Se} donors states and Cu_{In} and V_{In} acceptors states [21]. However, the demonstration of a high intense PL band at 0.97 eV (which is near to the band edge of CISE phase) confirms the good structural quality of the selenized film. Further, the synthesis method developed herein shows more symmetrical and well-defined luminescence in comparison to our previously reported hot-injection prepared of CISE film [22], which is a sign of good quality in the grown CISE films. The present route is also beneficial to lowering the production cost of the CIS/CIGS solar cells due to the reduction of processing steps in the preparation of CISE absorber. It also capable of producing nearly carbon free CISE films due to the usage of short chain and low boiling point solvents such as alcohols or amines.

CONCLUSIONS

CuInSe_2 thin films were deposited successfully by air-spray coating method using synthesized binary CuSe and In_2Se_3 nanoparticle ink, in that surfactants and binders were not involved in the nanoparticle synthesis and ink preparation, respectively. A mixed phase growth of Cu_2Se and CuInSe_2 was observed in case of vacuum-annealed film due to Cu-rich composition. However, a dramatic suppression of Cu_2Se phase resulted in the formation of pure CISE phase in case of selenized film. The high intense PL peak centered near to band-to-band transitions indicates good structural quality of the selenized films. The present study emphasizes the need of excess selenium supply in order to obtain good stoichiometric films. Further, the method adopted herein shows the possibility for the fine-tuning of final composition of CISE film by pre-adjusting the composition of each element in the binary.

ACKNOWLEDGEMENTS

This work was supported by the New & Renewable Energy Core Technology Program (No. 20143030011950) and the Human Resources Program in Energy Technology (No. 20154030200760) of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) granted financial resource from the Ministry of Trade, Industry & Energy, Republic of Korea.

REFERENCES

1. V.B. Chu, S. J. Park, G. S. Park, H. S. Jeon, Y. J. Hwang and B. K. Min, *Korean J. Chem. Eng.*, **33**(3), 880 (2016).
2. B. Khodashenas and H. R. Ghorbani, *Korean J. Chem. Eng.*, **31**(7), 1105 (2014).
3. D. Lee and K. Yong, *Korean J. Chem. Eng.*, **30**(7), 1347 (2013).
4. J. W. Cho, S. J. Park, W. Kim and B. K. Min, *Nanotechnology*, **23**, 265401 (2012).
5. M. Nanu, J. Schoonman and A. Goossens, *Nano Lett.*, **5**, 1716 (2005).

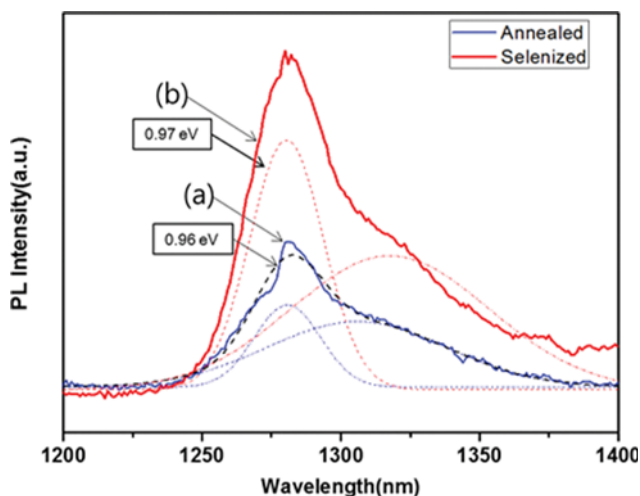


Fig. 6. PL spectra of CuInSe_2 thin films annealed in (a) vacuum and (b) selenium atmosphere.

6. T.K. Todorov, O. Gunawan, T. Gokmen and D.B. Mitzi, *Prog. Photovolt: Res. Appl.*, **21**, 82 (2013).
7. M. Buffiere, A. E. Zaghi, N. Lenaers, M. Batuk, S. Khelifi, J. Drijkoningen, J. Hamon, A. Stesmans, J. Kepa, V. V. Afanasev, J. Hadermann, J. DHaen, J. Manca, J. Vleugels, M. Meuris and J. Poortmans, *J. Phys. Chem. C*, **118**(47), 27201 (2014).
8. A. Cho, S. Ahn, J. H. Yun, J. Gwak, S. K. Ahn, K. Shin, H. Song and K. H. Yoon, *Sol. Energy Mater. Sol.*, **109**, 17 (2013).
9. H. Yoon, J. H. Woo, Y. M. Ra, S. S. Yoon, H. Y. Kim, S. J. Ahn, J. H. Yun, J. Gwak, K. H. Yoon and S. C. James, *Aerosol Sci. Technol.*, **45**, 1448 (2011).
10. A. R. Uhl, C. Fella, A. Chirila, M. R. Kaelin, L. Karvonen, A. Weidenkaff, C. N. Borca, D. Grolimund, Y. E. Romanyuk and A. N. Tiwari, *Prog. Photovolt: Res. Appl.*, **20**, 526 (2012).
11. M. D. Kannan, R. Balasundaraprabhu, S. Jayakumar and P. Ramana-thaswamy, *Sol. Energy Mater. Sol.*, **81**, 379 (2004).
12. M. A. Green, K. Emery, Y. Hishikawa, W. Warta and E. D. Dunlop, *Prog. Photovolt: Res. Appl.*, **23**, 1 (2015).
13. F. Kang, J. P. Ao, G. Z. Sun, Q. He and Y. Sun, *Mater. Chem. Phys.*, **115**, 516 (2009).
14. C. H. Chung, S. H. Li, B. Lei, W. Yang, W. W. Hou, B. Bob and Y. Yang, *Chem. Mater.*, **23**, 964 (2011).
15. J. C. W. Ho, T. Zhang, K. K. Lee, S. K. Batabyal, A. I. Y. Tok and L. H. Wong, *ACS Appl. Mater. Interfaces*, **6**, 6638 (2014).
16. J. Yang, Z. Jin, T. Liu, C. Li and Y. Shi, *Sol. Energy Mater. Sol.*, **92**, 621 (2008).
17. P. H. Chuang, C. C. Lin and R. S. Liu, *ACS Appl. Mater. Interfaces*, **6**, 15379 (2014).
18. C. Calderon, P. B. Perez, O. Rodriguez and G. Gordillo, *Microelec-tron. J.*, **39**, 1324 (2008).
19. L. S. Hamideche, A. Amara, M. Mekhnache, O. Kamli, A. Benald-jia, A. Drici, J. C. Bernede, M. Guerioune, N. Benslim and L. Bechiri, *Mater. Sci. Semicond. Process.*, **15**, 145 (2012).
20. J. Krustok, A. Jagomagi, J. Raudoja and M. Altosaar, *Sol. Energy Mater. Sol.*, **79**, 401 (2003).
21. M. V. Yakushev, A. V. Mudryi, V. F. Gremenok, V. B. Zalesski, P. I. Romanov, Y. V. Feofanov, R. W. Martin and R. D. Tomlinson, *J. Phys. Chem. Solids*, **64**, 2005 (2003).
22. U. Farva, M. A. Khan and C. Park, *Korean J. Chem. Eng.*, **29**, 1453 (2012).