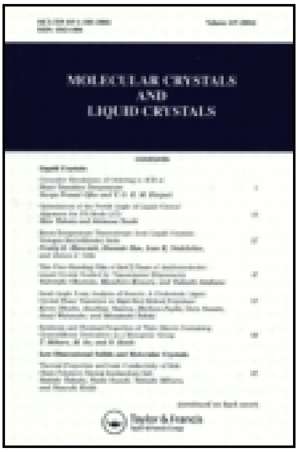

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Synthesis of $CuInS_2$ Thin Film for Solar Cells by a New Solution-based Deposition Method

Hyoung Sub Shin [a], Jin Young Lee [a], Chae Rin Kim [a], Tae Jin Lee [a], Sang Ouk Ryu [b] & Si Ok Ryu [a]

[a] School of Chemical Engineering, Yeungnam University, 214-1 Dae-dong, Gyeongsan, 712-749, S. Korea

[b] Department of Electronics Engineering, Dankook University, San-29 Anseo-dong, Cheonan, 330-714, S. Korea

Version of record first published: 18 Oct 2011

To cite this article: Hyoung Sub Shin, Jin Young Lee, Chae Rin Kim, Tae Jin Lee, Sang Ouk Ryu & Si Ok Ryu (2011): Synthesis of $CuInS_2$ Thin Film for Solar Cells by a New Solution-based Deposition Method, Molecular Crystals and Liquid Crystals, 551:1, 191-197

To link to this article: http://dx.doi.org/10.1080/15421406.2011.600645

Mol. Cryst. Liq. Cryst., Vol. 551: pp. 191–197, 2011

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.600645

Synthesis of $CuInS_2$ Thin Film for Solar Cells by a New Solution-based Deposition Method

HYOUNG SUB SHIN,[1] JIN YOUNG LEE,[1] CHAE RIN KIM,[1] TAE JIN LEE,[1] SANG OUK RYU,[2] AND SI OK RYU[1,*]

[1]School of Chemical Engineering, Yeungnam University, 214-1 Dae-dong, Gyeongsan, 712-749, S. Korea
[2]Department of Electronics Engineering, Dankook University, San-29 Anseo-dong, Cheonan, 330-714, S. Korea

Polycrystalline copper indium disulphide ($CuInS_2$) thin films were synthesized by a modified spin coating process with spraying the solutions containing precursor materials. Spin-spray deposition was performed at 25°C. The as-deposited $CuInS_2$ thin films were annealed at 400°C for 1 hour under nitrogen atmospheric condition. A scanning electron microscope (SEM) was employed to examine the surface morphology of the polycrystalline $CuInS_2$ thin films. The optical properties were measured using a UV-visible spectrophotometer. Their energy band gap was 2.0 eV. An X-ray diffraction spectrometer (XRD) was used for the structural analysis of $CuInS_2$ thin films. The chemical composition of the $CuInS_2$ thin film was studied with the aid of X-ray photoelectron spectroscope (XPS). The atomic concentrations of copper, indium, and sulfur in the film were determined from energy dispersive spectroscopy (EDS) measurements as a function of the Cu/In ratio in the aqueous precursor solutions.

Keywords Solar cell; photovoltaic cell; CIS_2; thin film; absorber layer; chalcopyrite

Introduction

Cadmium telluride (CdTe), copper indium selenide ($CuInSe_2$), copper indium gallium diselenide ($CuIn_xGa_{(1-x)}Se_2$), and amorphous silicon (a-Si) have received great attention as potential materials for second generation photovoltaic cells. Thin film solar cells have advantages including low processing cost, lighter weight, and flexibility in comparison to their crystalline silicon-based predecessors. Copper indium disulphide ($CuInS_2$) thin film is one of the most promising candidates in the family of ternary chalcopyrite materials for photovoltaic applications. It is considered as a good light absorbing polycrystalline material due to its unique physical, optical, and electronic properties. The direct band gap of $CuInS_2$ is about 1.53 eV and its value is near to the theoretical optimum conversion efficiency of solar cells [1]. The absorption coefficient of $CuInS_2$ in the terrestrial solar spectrum range is sufficiently high for its use in thin film photovoltaic devices [2]. Several methods such as spray pyrolysis, RF-sputtering, electro-deposition, ion exchange, chemical deposition, and evaporation have been reported for the formation of polycrystalline thin films of $CuInS_2$ [3]–[10].

*Corresponding author. E-mail: soryu@ynu.ac.kr

Recently, we have developed a novel solution-based deposition method, named chemical spin-spray deposition, to synthesize ternary chalcopyrite thin films. It is a modified spin coating process involving the spraying of solutions containing copper, indium and sulfur precursors on to substrates. Thin films of $CuInS_2$ were prepared on glass substrates with an ITO layer by this method. The as-deposited films by the spin-spray were thermally treated at 400°C under nitrogen (N_2) atmosphere. To the best of the authors' knowledge, such a deposition of $CuInS_2$ thin films by spin-spraying has not been previously reported.

Experimental

Preparations of Substrates and Precursor Solutions

Corning glass coupons of 25.4 mm × 76.2 mm × 1 mm dimensions were used as substrates. ITO was deposited by sputtering on top of the coupons. Thickness of ITO on the glass was 3μm and its optical transmission and electrical resistivity were 82% and 2.25×10^{-4} Ωcm, respectively. The substrates were chemically cleaned by boiling in concentrated sodium hydroxide solution for 30 minutes and then they were ultrasonically cleaned with DI water.

Precursor solutions for deposition were prepared by dissolving copper chloride ($CuCl_2 \cdot 2H_2O$), indium chloride ($InCl_3$), and sodium sulfide (Na_2S) in distilled DI water. In a typical procedure of synthesis, 0.201 g copper chloride, 0.331 g indium chloride, and 0.117 g sodium sulfide were each dissolved in 100 ml DI water with constant stirring.

Deposition of $CuInS_2$ Thin Films

For $CuInS_2$ thin film deposition, the prepared aqueous precursor solutions were sprayed onto rotating substrates loaded into a spin coater. The aqueous precursor solutions had a flow rate of 20 ml/min. Nitrogen was used as carrier gas for spray.

Spin-spray deposition, also known as zigzag spraying, was performed at 25°C as follows. First, the aqueous solution of copper chloride was sprayed followed by the aqueous sodium sulfide solution on to the substrate through a spray gun, which had a 10 ml receptacle, in pulse mode. Then the prepared $InCl_3$ solution was sprayed in pulse mode on to the as-sprayed film with $CuCl_2 \cdot 2H_2O$ and Na_2S. Subsequently, the aqueous sodium sulfide solution was sprayed on the substrate. Each spraying pulse discharged 2 ml of the aqueous solutions. This zigzag spraying sequence was carried out repeatedly until the desired film thickness was obtained. The film thickness could be controlled by the number of spraying cycles. The observation of color changes during the process confirmed that the reactions among $CuCl_2 \cdot 2H_2O$, Na_2S, and $InCl_3$ were in progress as the spraying process continued. Copper to sulfur (Cu/S) and indium to sulfur (In/S) molar ratios were controlled by varying the molar concentrations of solutions. In this study, the ratios of Cu/S and In/S in solutions were both fixed at 1:2. As-deposited $CuInS_2$ films were annealed at 400°C for one hour under nitrogen. Thickness of $CuInS_2$ thin films prepared in the present study was approximately 5 μm. A schematic diagram of the experimental setup is shown in Fig. 1.

X-ray diffraction spectrometer (XRD; PANalytical MPD for thin film) was used for the structural analysis of the $CuInS_2$ thin films. Scanning electron microscope (SEM; Hitachi,LTD S-4800 FE-SEM) was employed to examine the surface morphology of the films. The chemical composition of the $CuInS_2$ thin films was studied with the aid of X-ray photoelectron spectroscopy (XPS; VGESCALAB, 200-IXL) with Mg K radiation. Atomic concentrations of Cu, In, and S in the films were determined by energy dispersive

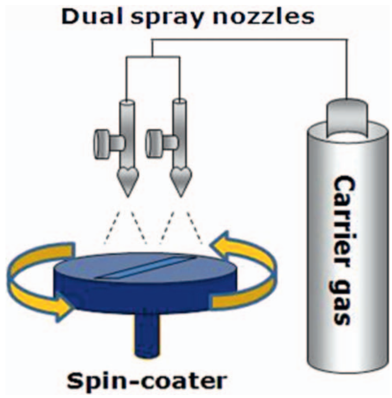

Figure 1. Schematic diagram of experimental setup.

spectroscopy (EDS; HORIBA/EX-250) as a function of the Cu/In ratio in the aqueous precursor solutions.

Results and Analysis

Structural Characterization

Phase compositions and structures of $CuInS_2$ films have been reported to depend not only on the films' growth mechanisms but also on the Cu/In ratios in the films [11]. The crystal structure and crystallographic orientation of the polycrystalline $CuInS_2$ thin films deposited by the spin-spray process was determined by XRD analysis. No major diffraction peaks corresponding to the polycrystalline $CuInS_2$ were observed in the XRD spectra for the as-deposited films. Instead, the XRD spectra were mixed with the diffraction peaks corresponding to the values of JCPDS 73-1366 for In_xS_y and the ones matching with the values of JCPDS 78-0878 for Cu_xS. It indicated that the $CuInS_2$ ternary compound was not formed yet in the as-deposited film. The as-deposited films were thermally treated at 400°C under nitrogen atmospheric condition in order to improve the crystallinity of the films and remove the residual porosity and structural free volume of the films. The X-ray spectra of the thermally treated $CuInS_2$ thin films were presented in Fig. 2. The characteristic diffraction lines located at $2\theta = 27.88°$, 32.13°/32.39°, 46.27°/46.47°, and 54.72°/55.06° correspond to the (112), (004)/(200), (204)/(220), and (116)/(312) crystallographic planes of the $CuInS_2$ structure, respectively. These diffraction peaks match very well with the values of JCPDS 85-1575 and can be indexed as $CuInS_2$ with a tetragonal structure [12]. From the XRD analysis, it was confirmed that only tetragonal structure of $CuInS_2$ were formed in the annealed films. Any peaks corresponding to either indium sulfide (In_2S_3) or copper sulfide ($Cu_{2\text{-}x}S$) was not observed in this study.

Surface Morphology and Chemical Composition

It was reported that the surface morphologies of the sprayed $CuInS_2$ films were very sensitive to the ratio of Cu/In in the solution [13]. In-rich and S-rich solutions formed nano-sized crystallites in the deposited films, generating a uniform and smooth surface. Cu-rich

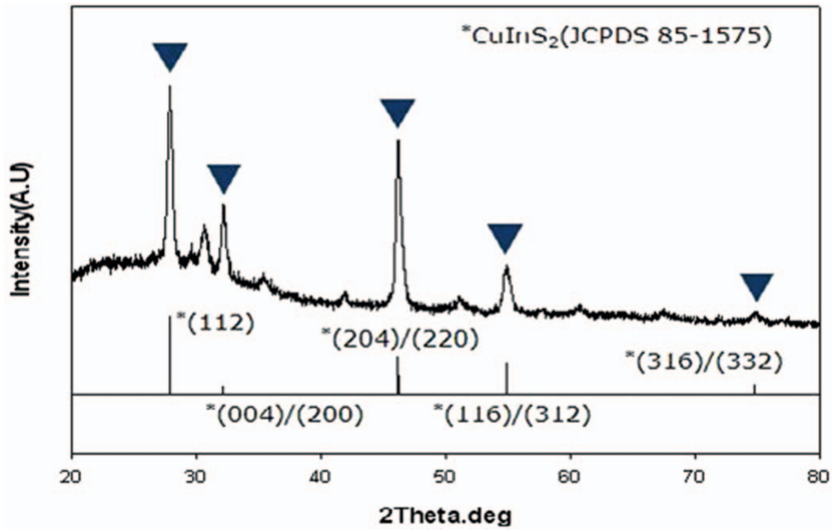

Figure 2. XRD spectrum of $CuInS_2$ thin film annealed at 400°C. The film was deposited by the spin-spray process in the molar ratio of Cu/In/S = 1:1:2.

conditions formed larger crystallites, up to micrometer size, leading to a non-uniform and rougher surface.

In this study, polycrystalline $CuInS_2$ was deposited on glass substrate with an ITO layer by a new spin-spray process instead of the conventional spray pyrolysis. The ratio of Cu/In in the solution was fixed as 1:1. The films' surface morphology observed by SEM is shown in Fig. 3. Even though large particles were observed, surface morphology was uniform. This deposition process was therefore effective in producing a uniformly distributed CIS_2 thin film. Figure 4 shows a SEM cross sectional image of the annealed glass-ITO-$CuInS_2$

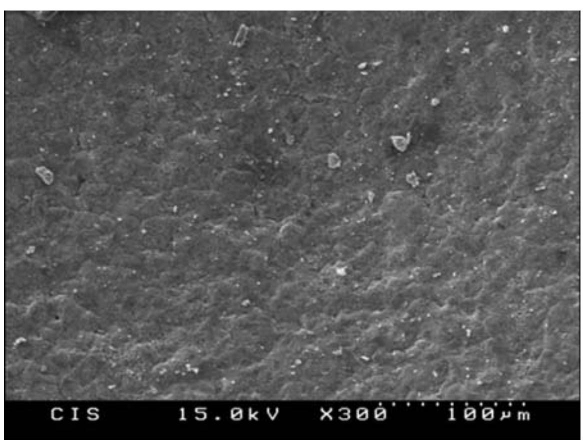

Figure 3. SEM image of $CuInS_2$ thin film deposited on ITO glass substrate by spin-spraying. Image was taken from the samples annealed at 400°C.

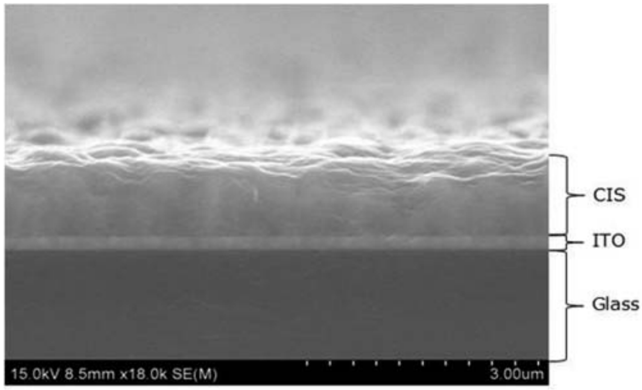

Figure 4. SEM cross sectional image of $CuInS_2$ thin film deposited on ITO glass.

thin film structure. The thickness of the $CuInS_2$ layer determined from SEM images was about 3 μm.

X-ray photoelectron spectroscopy (XPS) was performed to obtain the chemical binding information about the $CuInS_2$ thin film thermally treated at 400°C after spin-spraying. Figure 5 shows the XPS survey spectra of the Cu 2*p*, In 3*d*, and S 2*p*. Figure 5(a) presents the Cu 2*p* core level spectrum. The observed binding energy peaks located at 932.7 eV and 952.1 eV correspond to the electronic states of Cu $2p_{3/2}$ and Cu $2p_{1/2}$, respectively. Figure 5(b) shows the In 3*d* core level spectrum. The peaks at 444.6 eV and 452.6 eV are attributed to the electronic state of In $3d_{5/2}$ and In $3d_{3/2}$. The S 2*p* core level spectrum in Fig. 5(c) shows two peaks: one at 161.5 eV corresponding to S from Cu–S and the other at 162.3 eV corresponding to S from In–S [14]–[16].The peaks at 161.5 eV and 162.3 eV coincide with the electronic state of S $2p_{3/2}$ and S $2p_{1/2}$. The XPS peaks obtained in this work are consistent with the values reported in the literatures.

As shown in Fig. 6, EDS measurement was performed to determine the atomic concentrations of Cu, In, and S in the films as a function of the ratio of copper to indium in the prepared solutions. The results show a sulfur-poor composition (Cu (26.86%), In (27.76%) and S (45.39%)) of $CuInS_2$ films.

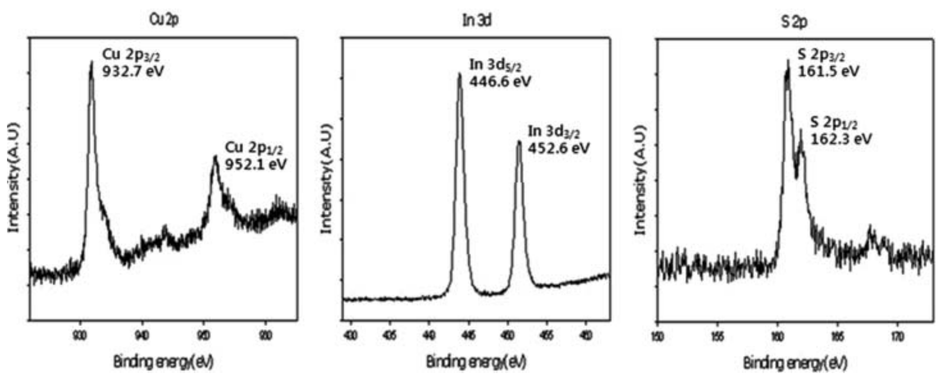

Figure 5. XPS spectra of the annealed $CuInS_2$ thin film prepared by spin-spraying: (a) Cu 2*p*, (b) In 3*d*, (c) S 2*p*.

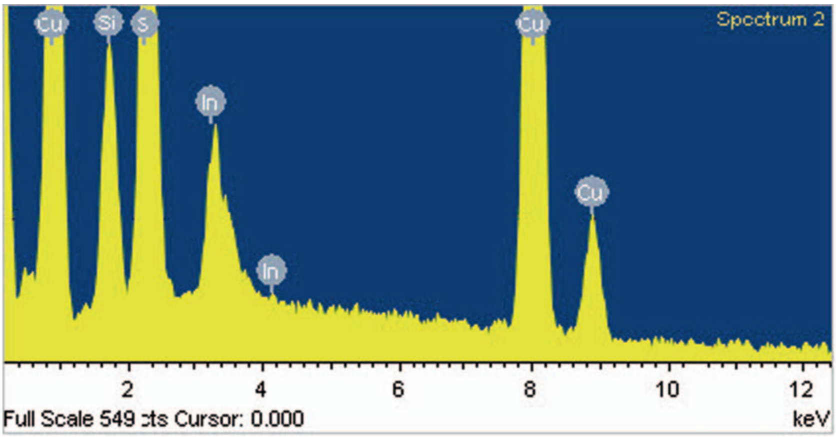

Figure 6. EDS measurements.

Conclusions

Polycrystalline $CuInS_2$ thin films for use in solar cells were successfully deposited by a spin-spray process at room temperature. The deposition method used in this study was an inexpensive solution-based process that involved no toxic or inflammable gases for the formation of $CuInS_2$ films. Molar ratios of copper to sulfur (Cu/S) and indium to sulfur (In/S) can be controlled by varying the molar concentrations of solutions. In this study, the ratios of Cu/S and In/S solutions were fixed both at 1:2. As-deposited $CuInS_2$ films were annealed at 400°C for one hour under nitrogen. Thickness of $CuInS_2$ thin films prepared in the present study was approximately 3 μm.

Acknowledgment

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2010-0013681).

References

[1] Sato, K., *Bull Ceram. Soc.*, **26**, 1629, 1991.
[2] Juan, M. P., Arturo, M.A., Mauricio, O.L., *Solar Energy Materials and Solar Cells*, **93**(5), 544–548, 2009.
[3] Pathan, H.M., Desai, J.D., Rokhande, C.D., *Appl Surf, Sci.* **205**, 47, 2002.
[4] Mauricio, O.L., Arturo, M.A., *Thin Solid Films*, **330**(2), 96–101, 1998.
[5] Tiwari, A.N., Pandya, D.K., Chopra, K.L., *Thin Solid Films*, **130**, 217–230, 1985.
[6] Krunks, M., Mikli, V., Bijakina, O., Rebane, H., Mere, A., Varema, T., Mellikov, E., *Thin Solid Films*, **361**, 61–64, 2000.
[7] Bandyopadhyaya, S., Chaudhuri, S., Pal, A. K., *Solar Energy Materials and Solar Cells*, **60**(4), 323–339, 2000.
[8] Todorov, T., Carda, J., Escribano, P., Grimm, A., Klaer, J., Klenk, R., *Solar Energy Materials and Solar Cells*, **92**(10), 1274–1278, 2008.
[9] He, Y.B., Krämer, T., Polity, A., Gregor, R., Kriegseis, W., Österreicher, I., Hasselkamp, D., Meyer, B. K., *Thin Solid Films*, **431**, 231–236, 2003.

[10] Dloczik, L., Lux-Steiner, M. C., Koenenkamp, R., *Thin Solid Films*, **431**, 131–134, 2003.
[11] Krunks, M., Mikli, V., Bijakina, O., Rebane, H., Mere, A., Varema, T., Mellikov, E., *Thin Solid Films*, **361**, 61–64, 2000.
[12] Yukawa, T., Kuwabara, K., Kuomoto, K., *Thin Solid Films*, **286**, 151, 1996.
[13] Padam, G.K., Rao, S.U.M., *Energy Mater*, **13**, 297, 1986.
[14] Atanas K., Arvo M., Vida K., Juozas M., Agu S., Leonard M., Arvo K., Malle K., *Thin Solid Films*, **516**(20), 7110–7115, 2008.
[15] R. Sharma, S. Shim, R.S. Mane, T. Ganesh, A. Ghule, G. Cai, D.H. Ham, S.K. Min, W.J. Lee, S.H. Han, *Mater. Chem. Phys.* **116** (2009) 28–33.
[16] C. D. Wagner, W.M. Riggs, L. E. Davis, J. F. Moulder, G. E. Muilenberg, *Handbook of X-Ray Photoelectron Spectroscopy*, Perkin-Elmer Corp., Eden Prairie, MN, 1978.