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Deposition and Characterization of CIGS Thin Films Deposited by Chemical Spray Process

YUJIE ZHANG,[1] HOYOUNG JUN,[1] JAE YOUNG PARK,[1] SEON YOUNG PARK,[1] SANG OUK RYU,[2] AND SI OK RYU[1,*]

[1]School of Chemical Engineering, Yeungnam University, Gyeongsan, S. Korea
[2]Department of Electronics Engineering, Dankook University, Cheonan, S. Korea

$CuIn_{0.7}Ga_{0.3}Se_2$ (CIGS) thin films were successfully deposited by chemical spray method under air environment and then the as-deposited films were annealed in a furnace. In order to study the influence of annealing temperature and condition on the properties of the CIGS films, annealing temperature was varied from 200°C to 500°C under nitrogen as well as in selenization conditions. The annealing temperatures and conditions exerted an effect on the properties of the prepared thin films. Based on the XRD measurements, the optimum annealing condition to synthesize the CIGS thin films was 500°C under both conditions. The crystalline structure of the film annealed at 500°C was in good agreement with the tetragonal structure in the reference. The surface morphology of the thin film under selenization condition was smooth, dense with lager grain size. XRD, SEM, UV-vis, XPS and ICP-AES were employed to study the influence of annealing temperature on the physical properties of the films.

Keywords CIGS; thin film solar cell; absorber; spray process; selenization

Introduction

CIGS is an I-III-VI_2 compound semiconductor material composed of copper, indium, gallium and selenium. The material is a solid solution of copper indium selenide (CIS) and copper gallium selenide(CGS), with a chemical formula of $CuIn_xGa_{(1-x)}Se_2$, where the value of x can vary from 1 (pure CIS) to 0 (pure CGS). It is a tetrahedrally bonded semiconductor, with the chalcopyrite crystal structure. The band-gap varies continuously with x from about 1.0 eV (for CIS) to about 1.7 eV (for CGS). The absorption coefficient of CIGS in the terrestrial solar spectrum range is known to be sufficiently high for the fabrication of thin film photovoltaic devices. It is considered as a promising light absorbing material for the thin film photovoltaic cells due to its unique physical, optical, and electronic properties [1, 2]. CIGS solar cells with efficiencies around 20% have been claimed by both the National Renewable Energy Laboratory (NREL) and the Zentrum für Sonnenenergie und Wasserstoff Forschung (ZSW), which has the best record worldwide in efficiency to date for any thin film solar cell [3].

*Address correspondence to Prof. Si Ok Ryu, School of Chemical Engineering, Yeungnam University, 214-1 Dae-dong, Gyeongsan, Gyeongbuk 712-749, Republic of Korea (ROK). E-mail: soryu@ynu.ac.kr

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The high-efficiency CIGS thin films are usually deposited by the vacuum-based methods like sputtering [4, 5], co-evaporation [6, 7] and CVD-based deposition techniques [8]. However, these technologies cause high production costs due to their expensive vacuum system and high temperature conditions [9]. In addition, environmental toxic templates are often used for the synthesis of inorganic materials in those methods [10]. For these reasons, CIGS thin films have been tried to be prepared by different methods with the aim of fabricating low cost and high efficiency solar cells.

In our study, we deposited the CIGS thin films by chemical spray method. Spray deposition method is a simple technology in which an ionic solution is sprayed onto the heated substrate using a stream of clean and dry N_2. The CIGS thin films were deposited on the glass substrates using the chemical spray method. The as-deposited thin films were then thermally treated. In order to study the influence of annealing temperature and condition on the properties of the CIGS films, annealing temperature were varied from 200°C to 500°C for 30 minutes under nitrogen and selenization condition, and then their structural and physicochemical properties were characterized using X-ray diffraction spectrometer (XRD), scanning electron microscopy (SEM), UV-visible spectrophotometer, ICP-AES and X-ray photoelectron spectroscope (XPS).

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Experimental

Preparations of Substrates

The commercial microscope glasses (Fisher Scientific) were used as substrates for the deposition of CIGS thin films. Before the deposition, the substrates were ultrasonically cleaned with 1M aqueous solution of sodium hydroxide (NaOH), acetone, methanol and DI water (AMD procedure) for 15 minutes, respectively. They were then dried with a nitrogen gas before being used for the deposition.

Preparations of Precursor Solutions

For the CIGS thin film deposition using chemical spray method, the precursor solution was prepared by dissolving 0.1M of aqueous copper chloride ($CuCl_2.2H_2O$, Sigma-Aldrich Inc), 0.4M of selenourea (CH_4N_2Se, Sigma-Aldrich Inc), 0.03M of gallium chloride ($GaCl_3$, Sigma-Aldrich Inc), and 0.07M of indium chloride ($InCl_3$, Sigma-Aldrich Inc) in the DI water at room temperature with constant stirring. The Copper to Indium to Gallium to Selenium ratio was 1 : 0.7 : 0.3 : 4. The pH value of the solution was changed by the addition of ammonium hydroxide (NH_4OH, Sigma-Aldrich Inc).

Deposition of $CuIn_{0.7}Ga_{0.3}Se_2$ Thin Films

The precursor solution was deposited on the substrate which was taped on a temperature-controlled hot plate to maintain a surface temperature at 155°C during the spraying. The flow rate of the solution was ∼0.3 ml/min and nitrogen gas was used as a carrier gas for spray. All experiments we carried out under atmospheric conditions. In order to improve the crystallization of the films and to eliminate the residual porosity and structural free volume in the films, the as-deposited CIGS thin films were thermally treated at various temperatures under nitrogen and selenization conditions, respectively. The film thickness could be controlled by the number of repeated cycles. The observation of color changes

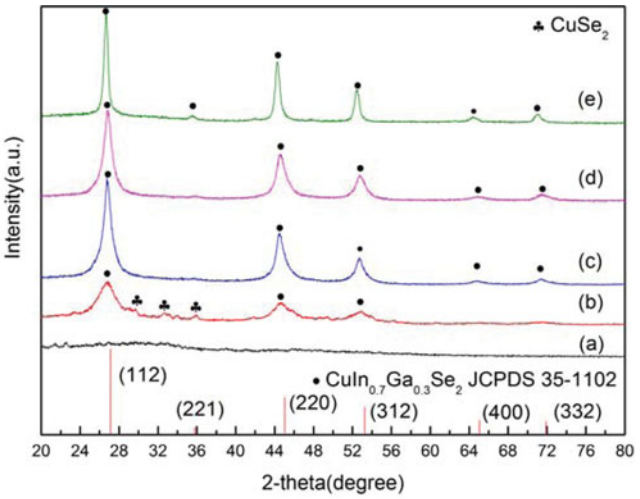

Figure 1. XRD spectra obtained from the CIGS thin films annealed under nitrogen condition for 30 minutes; (a) as-deposited, (b) 200°C, (c) 300°C, (d) 400°C, and (e) 500°C.

during the process confirmed that the reactions among $CuCl_2 \cdot 2H_2O$, $InCl_3$, $GaCl_3$ and CH_4N_2Se were in progress as the spraying process being continued.

Characterization of CIGS Thin Films

The structure of the CIGS thin films were characterized with X-ray diffraction spectrometer (XRD, Siemens D-5000). The surface morphology was analyzed by scanning electron microscopy (SEM, HIACHI S-4800 FESEM). The optical band gaps of the prepared CIGS thin films were measured using a UV-visible spectrophotometer (Ocean Optics USB-4000) at room temperature. The chemical binding information of the CIGS thin films were acquired by an X-ray photoelectron spectroscope (XPS, VG ESCALAB 200-IXL). ICP-AES is a well-established analytical technique for determining trace elements in a wide variety of samples.

Results and Discussion

The influences of annealing factor on the growth of CIGS structures using the chemical spray method were investigated by varying the annealing temperature and condition. The as-deposited CIGS thin films were annealed at 200∼500°C under nitrogen and selenization condition for half an hour, respectively. The phase and crystalline orientation of the CIGS thin film structure were determined by XRD and their XRD pattern was presented in Fig. 1 and 2. Figure 1 presents the XRD spectra obtained from the prepared CIGS thin films annealed at four different temperatures, which were 200°C, 300°C, 400°C, and 500°C under nitrogen condition for 30 minutes. In the XRD measurements, the changes in the crystallographic orientation of the CIGS thin films were observed after the thermal treatment. The extent of those changes was affected by the annealing temperatures. After the sample was annealed at 200°C, the diffraction peaks at $2\theta = 29.692^\circ$, 32.634° and 35.963° were confirmed by $CuSe_2$ with JCPDS 00-026-1115. This indicates that when the thin films were annealed at low temperature under nitrogen condition, the four elements

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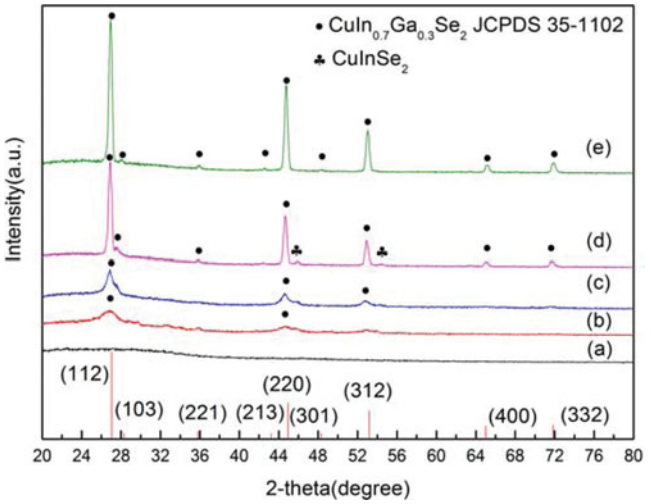

Figure 2. XRD spectra obtained from the CIGS thin films annealed under selenization condition for 30 minutes; (a) as-deposited, (b) 200°C, (c) 300°C, (d) 400°C, and (e) 500°C.

did not incompletely react. After the sample was annealed at 300°C, however, $CuSe_2$ phase was disappeared. It could be attributed to the incomplete reaction to synthesize CIGS compound due to the limited heat energy at lower annealing temperature. When the annealing temperature was increased from 300°C to 500°C, however, the extent of CIGS diffraction peaks was significantly enhanced. In the samples annealed at 300°C and 400°C, though there were no impurity phase, the diffraction peaks only matched with (112), (220), (312), (400) and (332) peaks of CIGS phase. Higher diffraction peaks of CIGS phase were founded in the sample annealed at 400°C. In the optimum annealed sample (at 500°C), the diffraction peaks at $2\theta = 26.589°$, $35.501°$, $44.251°$, $52.389°$, $64.355°$ and $71.190°$ correspond to the (112), (211), (220), (312), (400), and (332) crystallographic planes of the tetragonal CIGS structure, respectively. These X-ray diffraction peaks were in good agreement with the data base of JCPDS 35-1102 for tetragonal chalcopyrite phase.

Figure 2 shows XRD patterns of CIGS thin films annealed at 200∼500°C under selenization condition for 30 minutes. With increasing annealing temperature, the diffraction peak was more distinct, indicating the result of better crystallization and bigger grain size. The peaks other than CIGS were observed when the as-deposited thin film was annealed at 400°C under selenization condition and the peaks were $CuInSe_2$ based on JCPDS 01-070-3084. When the temperature was increased at 500°C, it could be seen that the film had the basic chalcopyrite crystal structure; diffraction peak 112 was the strongest, only single-phase tetragonal $CuIn_{0.7}Ga_{0.3}Se_2$ was detected. The diffraction peaks located at $2\theta = 26.900°$, $28.004°$, $35.932°$, $42.572°$, $44.774°$, $48.303°$, $53.155°$, $65.130°$ and $71.770°$ correspond to the (112), (103), (211), (213), (220), (301), (312), (400) and (332) crystallographic planes of the tetragonal CIGS structure, respectively. These X-ray diffraction peaks were in good agreement with the data base of JCPDS 35-1102 for tetragonal chalcorite phase. Comparing the XRD data with the nitrogen condition, it's obviously observed that selenization made the extent of CIGS peaks stronger and much different from other compounds, like $CuInSe_2$, CuSe.

SEM was employed to examine the effect of the annealing temperature conditions on the surface morphology of the films. Figure 3 and 4 show the SEM images of the CIGS thin

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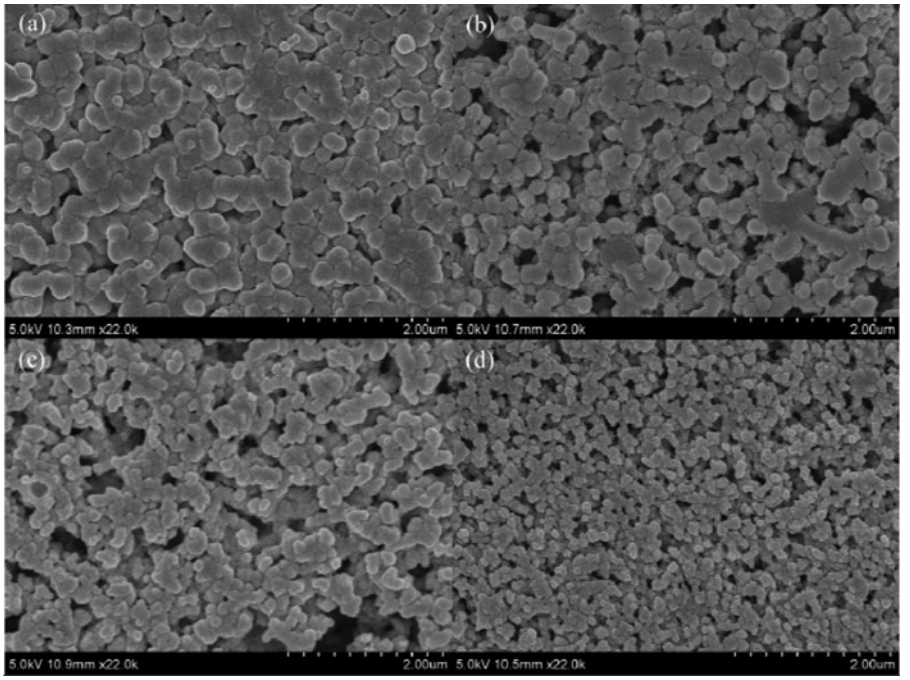

Figure 3. SEM images of CIGS thin films annealed under nitrogen condition at (a) 200°C, (b) 300°C, (c) 400°C and (d) 500°C.

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films that were deposited by the spray process in air and then annealed at 200∼500°C under nitrogen and selenization condition, respectively. Figure 3 shows the surface morphologies of the films deposited on the substrates, which was heated at 155°C, and then the as-deposited films were annealed at 200°C, 300°C, 400°C and 500°C, respectively, for half an hour without any selenization process. As can be seen from the Figure 3 (a), both of $CuSe_2$ and CIGS were combined. From the Figure 3 (b) and (c), the prepared CIGS thin films not only show lots of irregular pinholes but also exhibit rougher and less dense surface morphologies throughout the surface. At optimum annealing temperature of 500°C, however, the film was well formed with uniformity, large grain size and dense surface. It was clearly observed that the granular structure becomes more compact. Figure 3 confirmed that the change of the grain size, thickness, and surface morphology were strongly dependent on the annealing temperatures.

Figure 4 shows the SEM images of CIGS thin film annealed at 200∼500°C for 30 minutes under selenization condition. As presented in Figure 4 (a), (b) and (c), the prepared CIGS thin films not only show lots of irregular pinholes but also exhibit rougher and less dense surface morphologies throughout the surface. The gran size was increasing with the increasing the annealing temperature, which agreed with the XRD data. In Figure 4 (d), when the annealing temperature was increased to 500°C, the grain size was sufficiently enlarged – with the thickness of $\sim 1\mu$m and made the surface morphology well-defined, quite smooth and dense without pinholes. Based on the results of SEM images, the grain size was significantly large without the pinholes after selenization. It is generally accepted that CIGS films with larger grains give higher conversion efficiency for solar cell applications.

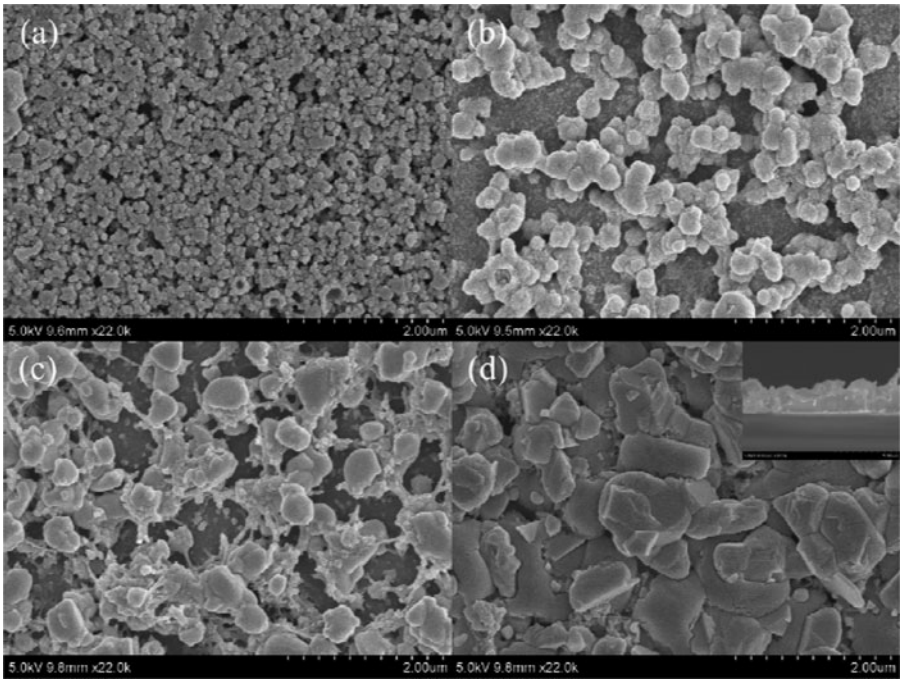

Figure 4. SEM images of CIGS thin films annealed under selenization condition at (a) 200°C, (b) 300°C, (c) 400°C and (d) 500°C.

The reliability of the analytical methods for CIGS layers was investigated by ICP-AES. ICP-AES is a well-established analytical technique for determining trace elements in a wide variety of samples. Table 1 shows the atomic concentrations and the significant atomic ratios for the optimum CIGS thin films which are Cu-rich. An important decrease of the Cu/(In+Ga) atomic ratio and increase of Se/metal can be observed after selenization treatment. The selenization data was significantly better than the nitrogen condition without selenization.

The optical band gaps of the CIGS thin films were measured in the visible range of 300–800 nm using a UV-visible spectrophotometer. The absorption spectra give the relation between the absorption coefficient and the photon energy as the Tauc formula $(\alpha h\nu)^n = B(h\nu\text{-}E_g)$, where B is constant, α is the absorption coefficient, E_g is the band gap energy, and n is equal to 2 for direct transition and 1/2 for indirect transition. In general, the optical band gap of the prepared thin films can be estimated by extrapolating the slope of the straight line portion of the plot of $(\alpha h\nu)^2$ against $h\nu$ to the x-axis. According to the XRD and SEM data, we selected the optimum annealing temperature for both nitrogen

Table 1. Composition of the CIGS thin films analysed by ICP-AES

Sample	Cu(%)	In(%)	Ga(%)	Se(%)	Cu/(In+Ga)	Ga/(In+Ga)	Se/metal
Nitrogen condition	39.71	19.47	9.55	31.27	1.369	0.329	0.455
Selenization condition	25.27	19.46	8.87	46.41	0.892	0.313	0.866

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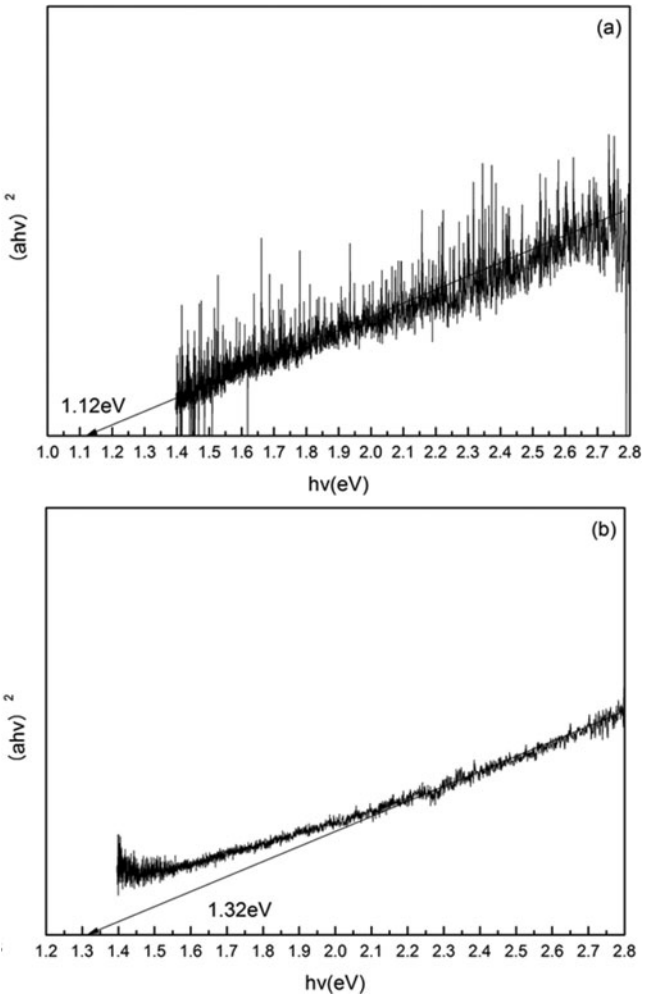

Figure 5. UV-vis absorption spectrum of CIGS thin films annealed at 500°C under (a) nitrogen condition and (b) selenization condition.

condition and selenization conditions to be 500°C. As shown in Figure 5 (a) and (b), the optical band gap value of CIGS thin films annealed at 500°C under nitrogen condition and selenization condition were estimated to be ∼1.12eV and ∼1.32eV, respectively. And the estimated optical band gap for selenization condition matched well with the band gap of $CuIn_{0.7}Ga_{0.3}Se_2$ [11].

XPS was performed to obtain the chemical composition and binding information of the thermally treated CIGS thin films. In the range of 0-1200 eV, the high-resolution XPS spectra of CIGS thin film deposited on the hot plate 155°C by the chemical spray method and then annealed at 500°C under selenization condition for 30 minutes are presented in Figure 6. Figure 6 displays the XPS survey spectra of the Cu 2p, In 3d, Ga 2p and Se 3d of CIGS thin film deposited. Figure 6 (a) represents the Cu 2p core level spectrum. The observed peak located at 932.48eV coincides with the binding energy for Cu $2p_{3/2}$ and the peak at 952.18eV corresponds to the binding energy for Cu $2p_{1/2}$ electrons which

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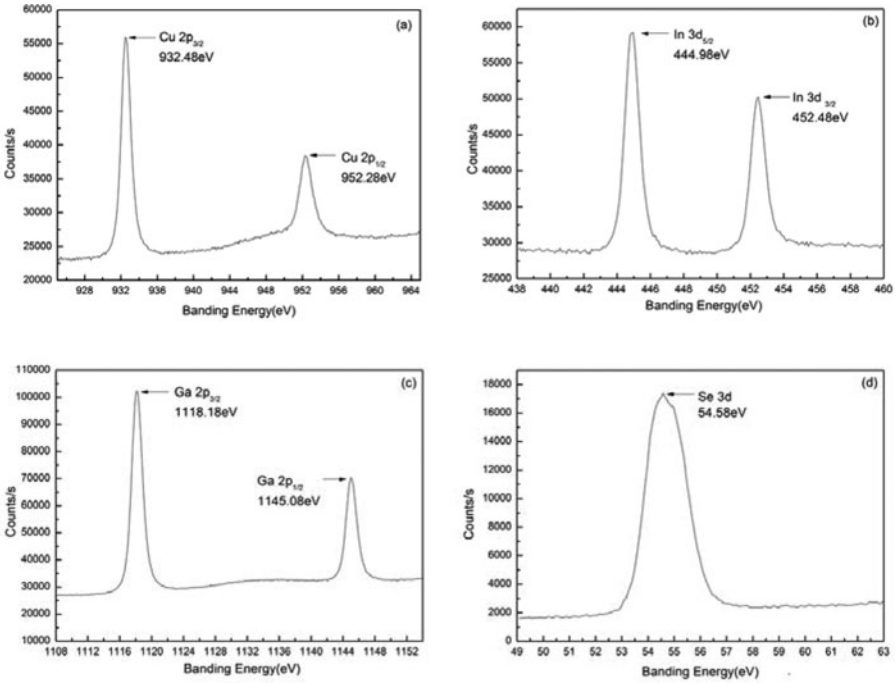

Figure 6. XPS spectra of the CIGS thin film annealed at 500°C under selenization condition for 30 minutes.

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have a peak splitting of 19.7eV, indicating Cu^{+} [12]. Figure 6 (b) shows the In 3d core level spectrum. The observed binding energy peaks located at 444.88 eV and 452.48 eV are attributed to the electronic state of In $3d_{5/2}$ and In $3d_{3/2}$. The indium 3d peaks with a peak splitting of 7.6 eV, matching well with In^{3+} [13]. The two peaks of Ga $2p_{3/2}$ and Ga $2p_{1/2}$ were located at 1118.08 eV and 1144.88 eV, respectively, showing a peak separation of 26.80eV, which were also consistent with the literature value for Ga^{3+} [14]. Carbon is ubiquitous and is present on all surfaces for XPS analysis. In XPS analyses of samples prepared outside the high vacuum chamber, relatively thick carbon layers are formed on the surfaces, and the corrected XPS peak positions are independent of the apparent or experimentally obtained binding energy [15]. It is a common practice to use the carbon C 1s peak at 284.6 eV as a reference for charge correction; in this study, 285.68eV was observed. Based on the corrected binding energy of C 1s, the corrected binding energy of Se 3d is 53.5 eV([54.58-(285.68-284.6)]eV), which is consistent with that of Se^{2-}[16]. The XPS peaks obtained in this work are consistent with the values reported in the literatures.

Conclusions

In this work, we studied the effects of the structural, physical and optical properties of CIGS thin films deposited on the glass substrates, using chemical spray method in terms of the annealing temperature of the as-deposited CIGS thin films. On the basis of XRD analysis, it was found that the tetragonal structure of $CuIn_{0.7}Ga_{0.3}Se_2$ was formed in the annealed films and that the crystal growth of the $CuIn_{0.7}Ga_{0.3}Se_2$ films was affected by the annealing temperature. An optimum condition for the post thermal treatment was 500°C

in this study for both nitrogen and selenization conditions. In the SEM images, the thin film annealed at 500°C under selenization condition indicated that the grains were large and dense throughout the surface of CIGS thin films. The band gap of the CIGS thin films annealed at 500°C under nitrogen and selenization condition were ∼ 1.12eV and ∼1.32eV, respectively. Based on the ICP-AES data, the selenization process altered the physicochemical properties of the films. According to the XPS data, the peaks of the thin films annealed under selenization condition are consistent with the values reported in the literatures. All these results demonstrate that the selenization is a very important process for synthesizing CIGS thin films.

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References

[1] Peza-Tapia, J. M., Morales-Acevedo, A., & Ortega-Lopez, M. (2009). *Sol. Energy Mater. Sol. Cells*, *93*, 544.
[2] Pathan, H. M., Desai, J. D., & Rokhande, C. D. (2002). *Appl. Surf. Sci.*, *205*, 47.
[3] Wang, G., Wang, S. Y., Cui, Y., & Pan, D. C. (2012). *Chem. Mater.*, *24*, 3992.
[4] Hsu, C. –Y., Huang, P. –C., Chen, Y. –Y., & Wen, D. -C. (2013). *Int. J. Photoenergy*, Article ID 132105, *7*.
[5] Chen, G. S., Yang, J. C., Chan, Y. C., Yang, L. C., & Huang, W. (2009). *Sol. Energy Mater. Sol. Cells*, *93*, 1531.
[6] Furue, S., Ishizuka, S., Yamada, A, Iioka, M., & Higuchi, H. (2013). *Sol. Energy Mater. Sol. Cells*, *119*, 163.
[7] Jung, S. H., Ahn, S. J., Yun, J. H., Gwak, J. Y., Kim, D. H., & Yoon, K. G. (2010). *Current Appl. Phys.*, *10*, 990.
[8] Naghavi, N., Spiering, S., Powalla, M., Cavana, B., & Lincot, D. (2003). *Prog. Photovolt: Res. Appl.*, *11*, 437.
[9] Eberspacher, C., Fredric, C., Pauls, K., & Serra, J. (2001). *Thin Solid Films*, *387*, 18.
[10] Dhashi, D., Nakada, T., & Kunioka, A. (2001). *Sol. Energy Mater. Sol. Cells*, *67*, 261.
[11] Fiat, S., Koralli, P., Bacaksiz, E., Giannakopoulos, K. P., Kompitsas, M., Manolakos, D. E., Cankaya, G., & Kompitsas, M. (2013). *Thin Solid Films*, *543*, 64.
[12] Liu, Y., Yao, D., Shen, L., Zhang, H., Zhang, X. D., & Yang, B. (2012). *J. Am. Chem. Soc.*, *134*, 7207.
[13] Li, X. M., Niu, J. Z., Shen, H. B., Xu, W. W., Wang, H. Z., & Li, L. S. (2010). *Cryst. Eng. Comm.*, *12*, 4410.
[14] Zhong, J. S., Zhao, H. J., Zhang, C. L., Ma, X., Pei, L., Liang, X. J., & Xiang, W. D. (2014). *J. Alloy. Compd.*, *610*, 392.
[15] Yamashita, T., & Hayes, P. (2008). *Appl. Surf. Sci.*, *254*, 2441.
[16] Han, Q. F., Liu, Q., Duan, C. H., Du, G. P., & Shi, W. Z. (2011). *J. Electron. Mater.*, *40*, 1452.