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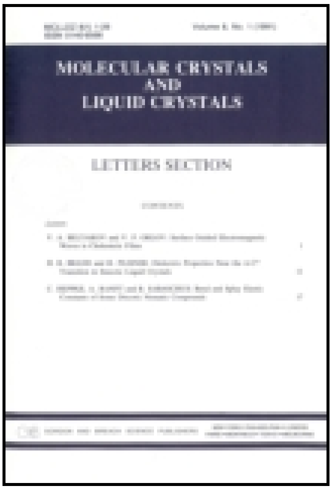

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Study on the CIGS Thin Film Formation by Modified Spray Process

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Study on the CIGS Thin Film Formation by Modified Spray Process

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The highly uniform polycrystalline $CuIn_{0.7}Ga_{0.3}Se_2$ *(CIGS) thin films for solar cell application were successfully synthesized on the glass substrates using a modified spray process and a continuous flow micro-reactor (CFM) process at low temperature. The as-deposited thin films prepared by each method were annealed under vacuum condition without additional selenization. In order to study the influence of annealing temperature on the properties of the CIGS films, annealing temperature were varied from 200°C to 400°C. The annealing temperature 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 200°C. The crystalline structure of the film annealed at 200°C was in good agreement with the tetragonal structure in the reference.* $CuIn_{0.7}Ga_{0.3}Se_2$ *thin films were also deposited by a solution-based CFM method and were then thermally treated under the same conditions as the spray. They were compared with the properties of the films deposited by the spray in order to figure out which deposition method is more effective for the synthesis of the CIGS thin films. XRD, SEM, UV-vis, and XPS 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; continuous flow microreactor

Introduction

Thin film solar cells have been received the great attention for the second generation of photovoltaic cells because they have advantages including low processing cost, lighter weight, flexibility, and possible roll-to-roll process in comparison to the crystalline silicon-based solar cells. $Cu(In,Ga)Se_2$(CIGS) thin film is one of the most promising candidates in the family of copper chalcopyrite materials for the photovoltaic application. CIGS is a direct band gap material having a wide range of band-gap energies from 1.0 eV ($CuInSe_2$) to 1.7 eV ($CuGaSe_2$), which are varied by controlling the amount of substituting Ga. The absorption coefficient of CIGS in the terrestrial solar spectrum range is known to be sufficiently high

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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]. In recent, EMPA in Swiss has achieved the 20.4% efficiency with the CIGS solar cell fabricated in a laboratory scale [3]. The high-efficiency CIGS thin films are usually deposited by the vacuum-based methods like sputtering [4] and co-evaporation [5]. However, these technologies cause high production costs due to their expensive vacuum system and high temperature conditions [6]. For these reasons, $Cu(In,Ga)Se_2$ thin films have been prepared by different methods with the aim of fabricating low cost and high efficiency solar cells. Solution-based chemical deposition processes have many advantages due to their low cost and low temperature processing natures. Those methods do not require the vacuum systems and can be used to fabricate the large area thin films on various substrates including glasses, semiconductors, metals, and plastics. Among the solution-based methods, spray [7] and a novel solution-based deposition processes were chosen for the deposition of the polycrystalline CIGS thin films. 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. We developed a solution-based method to synthesize the binary or ternary chalcopyrite materials in our previous works. This approach have used a continuous flow micro-reactor (CFM), which is capable of decoupling the homogeneous particle formation from the heterogeneous thin film growth and is able to overcome the drawbacks associated with the conventional CBD process. The CIGS thin films were deposited on the glass substrates using the spray and the CFM processes. The as-deposited thin films prepared by each method were then thermally treated under vacuum condition without additional selenization. In order to study the influence of annealing temperature on the properties of the CIGS films, annealing temperature were varied from 200°C to 400°C for 30 minutes and their structural and physicochemical properties were characterized using X-ray diffraction spectrometer (XRD), scanning electron microscopy (SEM), UV-visible spectrophotometer, and X-ray photoelectron spectroscope (XPS) in this study.

Experimental

Preparations of Substrates and Precursor Solutions

The commercial microscope glasses (Fisher Scientific) were used as substrates for the deposition of $CuIn_{0.7}Ga_{0.3}Se_2$ thin films. Before the deposition, the substrates were ultrasonically cleaned with 1M aqueous solution of sodium hydroxide (NaOH) for 15 minutes and chemically cleaned with a standard AMD (acetone, methanol, DI water) procedure. They were then dried with a nitrogen gas before being used for the deposition. The precursor solution was prepared by dissolving 0.1M of aqueous copper chloride ($CuCl_2.2H_2O$, Aldrich), 0.4M of selenourea (CH_4N_2Se, Aldrich), 0.03M of gallium chloride ($GaCl_3$, Aldrich), and 0.07M of indium chloride ($InCl_3$, Aldrich) in the DI water with constant stirring.

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

Spray Process. For CIGS thin film deposition, the prepared aqueous precursor solution was sprayed onto a substrate, which was taped on a temperature-controlled hot plate to maintain a surface temperature at 110°C. The flow rate of the aqueous precursor solution was about 2 ml/min and nitrogen was used as a carrier gas for spray. The as-deposited CIGS films were thermally treated for half an hour in a vacuum furnace in order to improve the crystallization of the prepared films and to eliminate the residual porosity and structural free volume in the films. The annealing temperature of the prepared samples was varied in the range of 200∼400°C to determine an influence of the annealing temperature on the film formation. The film thickness could be controlled by the number of repeated cycles. The observation of color changes during the process confirmed that the reactions among $CuCl_2 \cdot 2H_2O$, CH_4N_2Se, $GaCl_3$, and $InCl_3$ were in progress as the spraying process being continued.

CFM Process. In the CFM process, each of precursor solutions for the target material was initially fed into a micro-mixing element through a separate channel and their individual streams were allowed to mix together in the element. In this study, all the solutions from the mixing element were passed through the tubes, which were immersed in a water bath maintained at 90°C, before impinging on the temperature-controlled substrates. All substrates used in this study were heated at 110°C on a custom-designed heating plate. The formation of film could take place heterogeneously on the substrate surface or homogeneously in the solution resulting in particle formation. For the formation of thin films, however, the homogeneous particle formation was highly undesirable since the adsorption of the particles on the substrate surface yields powdery and non-adherent films. The homogeneous chemistry of the impinging flux could be controlled precisely by the inlet concentrations, temperature, and most importantly the residence time. The flow rate of the solutions was fixed about at 2.5 ml/min and the time for impinging was around 5 minutes. The details of the CFM deposition procedure have been described in our previous papers [8–12]. In order to improve the crystallinity of the films and investigate an effect of the annealing temperature on the properties of the films, the as-deposited CIGS thin films were thermally treated with varying the annealing temperature at increments of 100°C in the range of 200∼400°C for half an hour in a vacuum furnace.

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, HITACHI 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).

Results and Discussion

XRD analysis was carried out to determine the crystal structure of the polycrystalline CIGS thin films deposited on the glass substrates by both processes and to identify the crystallographic orientations. The X-ray diffraction patterns of the CIGS films are presented in Figs. 1 and 2. Fig. 1 represents the XRD patterns of the films synthesized by the non-vacuum spray method in comparison with the JCPDS reference data. Fig. 1(a) displays the XRD pattern of the as-deposited CIGS film. No distinct characteristic peaks related to CIGS chalcopyrite phase are found in the diffraction of the as-deposited film. This implies that the prepared film without the thermal treatment after the deposition is in amorphous phase. The as-deposited CIGS thin films were thermally treated at three different temperatures with increments of 100°C in the range of 200∼400°C for the investigation of an influence of

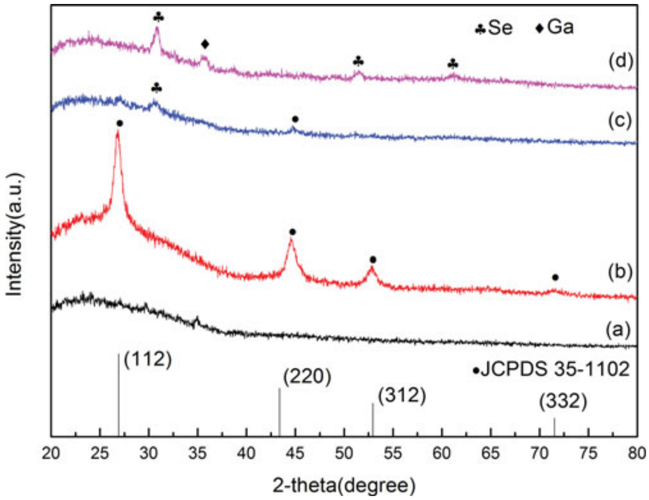

Figure 1. X-ray diffraction patterns of the $CuIn_{0.7}Ga_{0.3}Se_2$ thin films deposited by the spray process with varying the annealing temperature: (a) as-deposited, (b) 200°C, (c) 300°C, (d) 400°C.

the annealing temperature on the film properties. The X-ray spectra of the thermally treated CIGS thin films are shown in Fig. 1(b)–(d). In the XRD measurements, the changes in the crystallographic orientation of CIGS thin films are observed after the thermal treatment. The extent of those changes is affected by the annealing temperatures. In Fig. 1(b) for the film annealed at 200°C, the characteristic diffraction peaks located $2\theta = 26.744^o$, 44.631^o, 52.887^o, and 71.503° correspond to the (112), (220), (312) and (332) crystallographic planes of the $CuIn_{0.7}Ga_{0.3}Se_2$ structure, respectively. These 2θ values of the X-ray diffraction peaks are consistent with the literature values of JCPDS 35-1102, which is indexed as $CuIn_{0.7}Ga_{0.3}Se_2$ with a tetragonal chalcopyrite phase. No impurity phase is found in

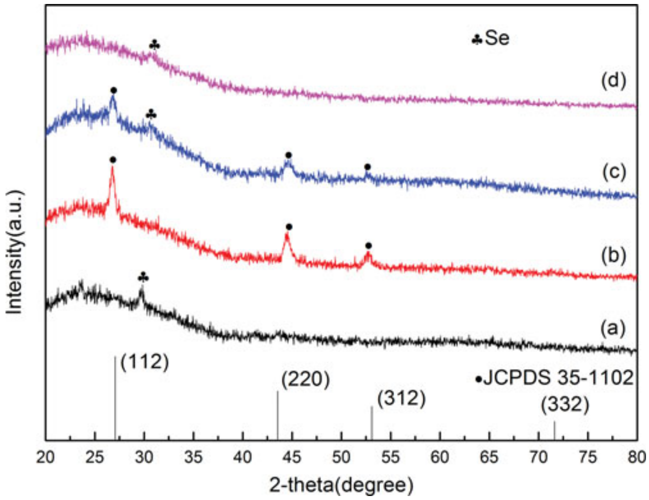

Figure 2. X-ray diffraction patterns of the $CuIn_{0.7}Ga_{0.3}Se_2$ thin films deposited by the CFM process with varying the annealing temperature: (a) as-deposited, (b) 200°C, (c) 300°C, (d) 400°C.

Fig. 1(b). Meanwhile, additional diffraction peaks other than $CuIn_{0.7}Ga_{0.3}Se_2$ were observed in the spectra of Fig. 1(c) and (d). These peaks are identified as elemental selenium and gallium. It could be attributed to the incomplete reaction to synthesize $CuIn_{0.7}Ga_{0.3}Se_2$ due to Se loss at the annealing temperature higher than 200°C. It was reported that the film annealed above 250°C had lost about 50% of Se from the prepared films [13-15]. For a complete elucidation of the formation of Se and Ga, we have to discover chemical kinetics and reaction mechanism in the CIGS film growth. More in-depth study on growth mechanism, precursor design and processing condition for the better quality of CIGS thin films are in progress. From the XRD analysis, it is found that the tetragonal structure of $CuIn_{0.7}Ga_{0.3}Se_2$ is formed in the annealed films and that the crystal growth of the $CuIn_{0.7}Ga_{0.3}Se_2$ films is affected by the post-heating temperatures. An optimum condition for the post thermal treatment is 200°C in this study. Fig. 2 shows the XRD patterns of the CIGS thin films synthesized by CFM process. The characteristic diffraction lines located at $2\theta = 26.799^\circ$, 44.484°, and 52.759° correspond to the (112), (220) and (312) crystallographic planes of $CuIn_{0.7}Ga_{0.3}Se_2$ structure, respectively. These diffraction peaks match well with the values of JCPDS 35-1102 for tetragonal chalcopyrite phase. The peaks for the impurities observed in Fig. 2 are similar to the peaks for the films synthesized by the spray method. On the basis of the XRD analyses for both solution-based deposition methods, it is found that the polycrystalline CIGS films can be successfully synthesized by both processes at a very low annealing temperature. However, the XRD peaks for the films prepared by the spray process are slightly more consistent to the values of JCPDS 35-1102 reference data than the films deposited by the CFM process.

In order to study the annealing effect on the morphology of the CIGS thin films, the films were annealed at 200°C, at which temperature we obtained the best diffraction peaks matching to the reference data, for half an hour in three different heating rates of 25°C/min, 10°C/min, and 5°C/min [16]. The surface morphology of CIGS thin films were investigated by SEM as shown in Figs. 3 and 4. Fig. 3 shows the SEM images of the annealed films deposited by the spray method. As presented in Fig. 3(a), the prepared CIGS thin films not only shows lots of irregular pinholes but also exhibit rougher and less dense surface morphologies throughout the surface when the thin films are annealed at 25°C/min. When the heating rate is set at 5°C/min, although the surface morphology is dense, the grain size is too small. At the heating rate of 10°C/min, however, the thin film is well formed with uniformity, relatively large grain size and dense. The SEM images of the annealed films deposited by the CFM method are presented in Fig. 4. As shown in Fig. 4(b), the polycrystalline CIGS thin films are well grown with uniform grain size and smooth morphology when the furnace temperature is raised in the heating rate of 10°C/min during the annealing process as compared with the others. It is in good agreement with the result of the spray. On the basis of SEM morphology, we conclude that an appropriate heating rate in the CIGS film formation was 10°C/min in this study for both deposition methods. Even though the $CuIn_{0.7}Ga_{0.3}Se_2$ films were well formed with uniform and dense morphology, the grain size of the films was not enough large for solar cell application. It might be caused by a lack of selenization in the processes.

$CuIn_{0.7}Ga_{0.3}Se_2$ thin films were deposited by the spray and the CFM methods and then they were annealed at 200°C with a heating rate of 10°C /min for the optical characterization. As shown in Fig. 5, optical band gap of $CuIn_{0.7}Ga_{0.3}Se_2$ thin films were measured in a visible range of 300–800 nm using UV-Vis spectrophotometer. The absorption spectra give the relation between the absorption coefficient and the photon energy as the Tauc formula $(\alpha h\nu)^n = B(h\nu - E_g)$, 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,

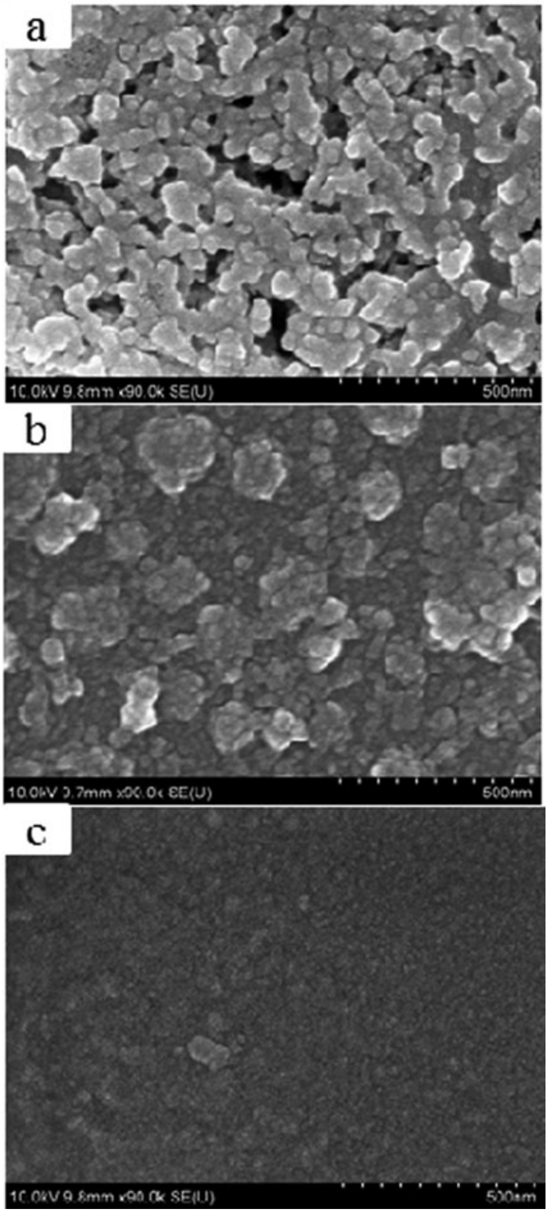

Figure 3. SEM images of $CuIn_{0.7}Ga_{0.3}Se_2$ thin films deposited by the spray process and annealed at 200°C with varying heating rates: (a) 25°C/min, (b) 10°C/min, (c) 5°C/min.

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. Fig. 5 shows the estimated optical band gaps of the $CuIn_{0.7}Ga_{0.3}Se_2$ films prepared by the spray and the CFM methods. As shown in Fig. 5, the deposition method exerted an influence on the band gaps of the $CuIn_{0.7}Ga_{0.3}Se_2$ thin films. The band gap values of the $CuIn_{0.7}Ga_{0.3}Se_2$ films are estimated to be ∼1.53 eV for the film prepared by the spray method and ∼1.96 eV

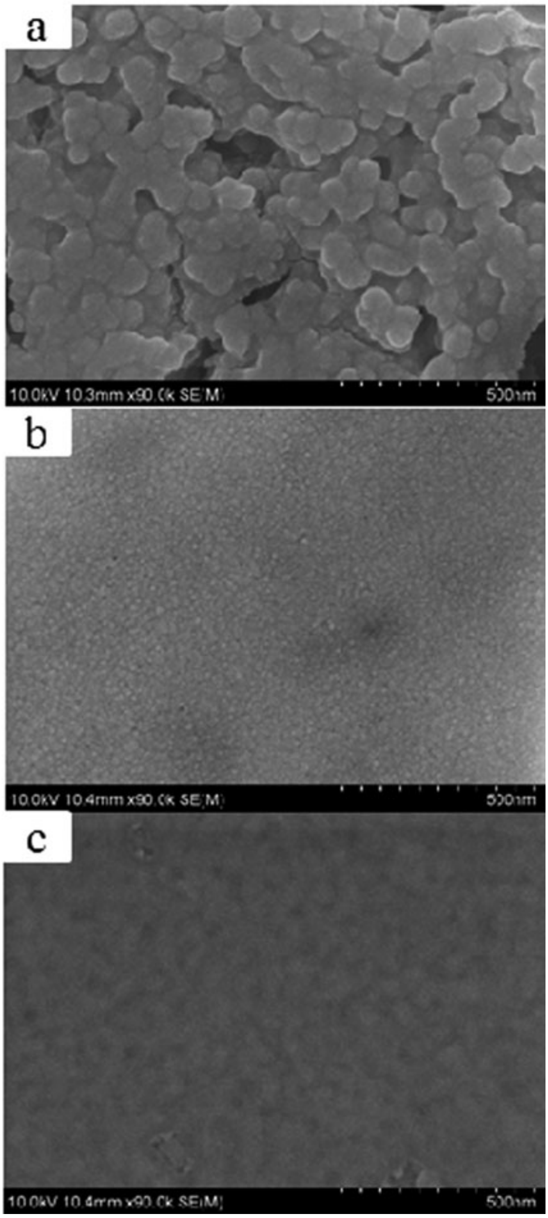

Figure 4. SEM images of $CuIn_{0.7}Ga_{0.3}Se_2$ thin films deposited by the CFM process and annealed at 200°C with varying heating rates: (a) 25°C/min, (b) 10°C/min, (c) 5°C/min.

for the film synthesized by the CFM method. The chalcopyrite CIGS films are reported to have an optical band gap in the range of 1.0 – 1.7 eV. The estimated optical band gap value of the film deposited by the spray method is more consistent with the theoretical value of the CIGS film rather than the value of the one synthesized by the CFM method. The higher optical band gap value obtained in the film formed by the CFM process might be attributed to the quantum size effect from the nanocrystalline films.

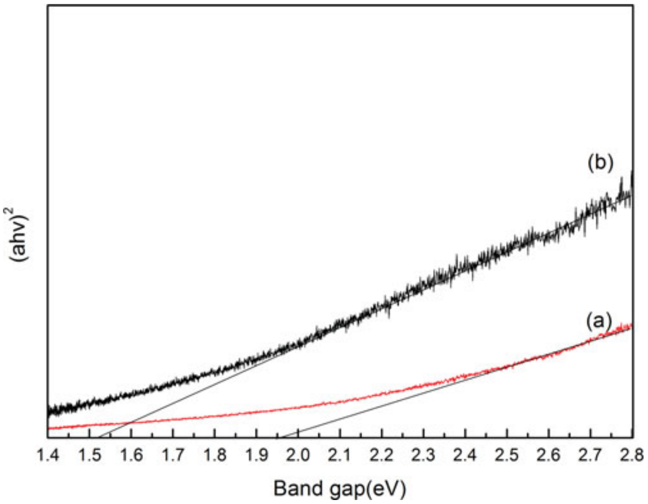

Figure 5. UV-vis absorption spectrum of $CuIn_{0.7}Ga_{0.3}Se_2$ thin films obtained by (a) CFM process, (b) spray process and then annealed at 200°C for 30 minutes with heating rate of 10°C/min.

XPS analysis was performed to identify the chemical binding states of the $CuIn_{0.7}Ga_{0.3}Se_2$ thin films, which was deposited by the spray process and then annealed at 200°C. Fig. 6 exhibits the XPS survey spectrum of CIGS and the peaks of Cu 2p, In 3d, Ga 2p and Se 3d. In Fig. 6(a), the high-resolution XPS spectrum of Cu in the 2p region

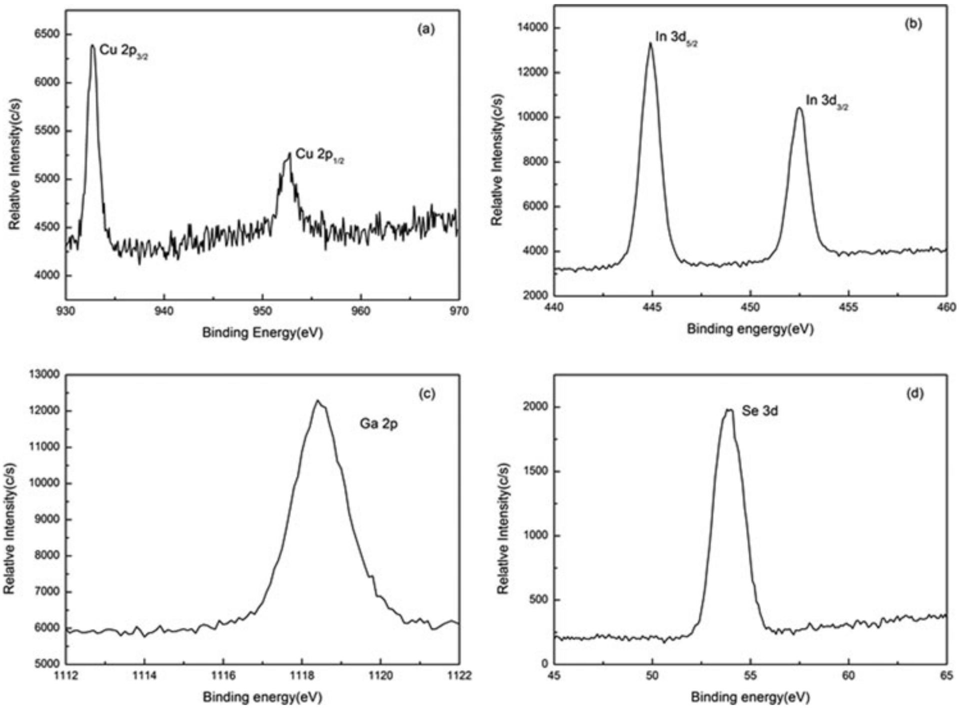

Figure 6. XPS spectra of the $CuIn_{0.7}Ga_{0.3}Se_2$ thin film deposited by the spray process and annealed at 200°C for 30 minutes.

for CIGS thin film shows the binding energies of Cu $2p_{3/2}$ and Cu $2p_{1/2}$ peaks at 932.7 eV and 952.8 eV, respectively, which are typical values for Cu^{2+}[17]. The Fig. 6(b) shows the binding energy peaks of In $3d_{5/2}$ and In $3d_{3/2}$ at 444.9 eV and 452.5 eV with a split orbit of 7.6 eV, respectively, suggesting that the oxidation state of indium from the as-obtained CIGS thin film is In^{3+} [16, 18]. As shown in Fig. 6(c), the peak located at 1118.4 eV is attributed to the electronic state of Ga 2p from Ga^{3+} [19]. The peak at 53.8 eV corresponds to the electronic state of Se 3d from Se^{-3} [20]. The XPS peaks obtained in this work are consistent with the values reported in the literatures.

Conclusions

In this study, the $CuIn_{0.7}Ga_{0.3}Se_2$ thin films are successfully deposited by the spray and the CFM methods. Both processes are carried out at low temperature processing conditions than the gas phase processing conditions. On the basis of XRD analysis, it is found that the tetragonal structure of $CuIn_{0.7}Ga_{0.3}Se_2$ is formed in the annealed films and that the crystal growth of the $CuIn_{0.7}Ga_{0.3}Se_2$ films is affected by the annealing temperature. An optimum condition for the post thermal treatment is 200°C in this study. From SEM morphology, we conclude that a proper heating rate in the CIGS film formation is 10°C /min for both deposition methods. The grain size of the films is not enough large for solar cell application even though the $CuIn_{0.7}Ga_{0.3}Se_2$ films are well formed with uniform and dense morphology. It might be caused by a lack of selenization in the processes. The estimated band gap values of the $CuIn_{0.7}Ga_{0.3}Se_2$ films are $\sim$1.53 eV for the film prepared by the spray method and $\sim$1.96 eV for the film synthesized by the CFM method. According to the comprehensive characterization of the $CuIn_{0.7}Ga_{0.3}Se_2$ films, we obtained slightly better results from the spray process than the CFM process.

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