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Properties of $CISe_2$ Thin Films Deposited by a Solution-Based Method for Photovoltaic Applications

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The influences of the post thermal treatment conditions on the physical, structural, surface morphological and optical properties of $CISe_2$ thin films deposited by a non-vacuum spray process were investigated for solar cell applications. In order to study the effects of thermal annealing on the films, the annealing temperature of the as-deposited $CISe_2$ thin films were varied from 300°C to 500°C. The estimated optical band gaps of the as-deposited $CuInSe_2$ film and the film annealed at 500°C were ∼1.48 eV and ∼1.06 eV, respectively. A tetragonal chalcopyrite structure of $CuInSe_2$ was identified in XRD measurement. From the XRD analysis, it was confirmed that the crystal growth of the $CuInSe_2$ are affected by the annealing temperature. The film annealed at 500°C shows the best crystallinity. SEM image shows that the thickness and the grain size of the film annealed at 500°C are around 2.66 μm and 40.22 nm, respectively. The identified chemical binding states of the $CuInSe_2$ film annealed at the optimum annealing temperature were confirmed through XPS analysis. The average particle size of the film was determined using TEM and its value was around 10.6 nm.

Keywords Annealing temperature; $CISe_2$; solution-based method; spray; thin film solar cell

Introduction

Copper indium diselenide ($CISe_2$) is an attractive p-type semiconductor for use in solar cells with their high absorption coefficient, ca. $10^5\ cm^{-1}$, and a band gap energy value close to that of the solar radiation [1]. For these reasons, it is frequently chosen as the materials for photovoltaic applications. Thin film photovoltaic materials based on $CISe_2$ have been suggested to be long-term economically competitive with the currently dominating silicon-based devices [2]. Recent advances have been achieved in the production of chalcogenides for thin film solar cells using various deposition techniques based on reactive pulses, like atomic layer deposition (ALD) or chemical vapour deposition (CVD) and pulsed electro-deposition. With these methods, the key components are delivered onto the substrate in

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gaseous reactive cycles. However, their main disadvantages are the low deposition rate and the high production costs. These disadvantages have made them difficult to scale up the process to large production of solar cells. For these reasons, $CISe_2$ 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 [3]. 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.

The purpose of this study is to investigate the effect of the annealing temperature on the characteristics of the $CISe_2$ thin films deposited by a modified spray method in low cost. The prepared $CISe_2$ films were characterized with X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), UV-visible spectrophotometer and X-ray photoelectron spectroscope (XPS).

Experimental

Preparation of Substrates

The commercial microscope glasses (Fisher Scientific) have been used as substrates. They were ultrasonically cleaned in soap water, acetone, methanol, and DI water, respectively, for 15 minutes. They were dried under a stream of nitrogen gas before being used for deposition.

Fabrication of $CISe_2$ Thin Films

For the polycrystalline $CISe_2$ thin film deposition using the modified spray process, the precursor solution was prepared by mixing copper chloride ($CuCl_2$, Sigma-Aldrich Inc.), indium chloride ($InCl_3{\cdot}2H_2O$, Sigma-Aldrich Inc.), and selenourea (CH_4N_2Se, Sigma-Aldrich Inc.) at room temperature. The Cu-to-In-to-Se ratio was 1:0.7:4. The pH value of the solution was maintained to $\sim$11 by the addition of ammonium hydroxide (NH_4OH). The flow rate of the solution was $\sim$0.5 ml/min for the film deposition on the substrates during the spraying. The precursor solution was sprayed by an air pump. The films were deposited on the glass substrates heated at low temperature using non-vacuum spray system. 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 $CISe_2$ thin films were thermally treated at various temperatures ranged from 300°C to 500°C for 30 min in nitrogen conditions.

Measurements

Scanning electron microscopy (SEM; Hitachi Ltd., S-4800) was used to examine the surface morphology of the polycrystalline $CISe_2$ thin films. Optical properties of the films were measured using a UV-visible spectrophotometer (Ocean Optics Inc, USB 4000 optic spectro-meter). X-ray diffraction (XRD; Panalytical, MPD for thin film) was used for the structural characteristics of $CISe_2$ films. Chemical binding information of the $CISe_2$ thin film was obtained by X-ray photoelectron spectroscopy (XPS; VG ESCALAB, 200-IXL).

Results and Discussion

The $CISe_2$ thin films were deposited on the glass substrates by the modified none-vacuum chemical spray method at low temperature. Often the thermal conditions affect the final thin film properties. In order to confirm the effects of the post heating temperature on the crystalline phase of the film, the $CISe_2$ thin films was deposited at the low temperature conditions and then they were annealed at various temperatures ranged from 300°C to 500°C.

The crystal structure and crystallographic orientation of the polycrystalline $CISe_2$ films deposited by a non-vacuum spray method were determined by analysis of XRD spectra in comparison with the JCPDS data bases. Figure 1 shows the typical XRD spectra obtained from $CISe_2$ films deposited on a substrate heated at low temperature and then annealed at three different temperatures, which were 300°C, 400°C, and 500°C for 30 minutes under a nitrogen atmospheric condition. In the XRD measurements, the changes in the crystallographic orientation of the $CISe_2$ thin films were observed after the thermal treatment. The extent of those changes was affected by the annealing temperatures. In diffractogram of an as-deposited film, $Cu_{11}In_9$ and In_2Se_3 were observed, together with $CISe_2$ peaks. The diffraction peaks at 2-theta = 29.78°, 42.28°, and 51.81° were confirmed by $Cu_{11}In_9$ with JCPDS 03-065-4963 and at 2-theta = 28.93° and 31.58° were corresponded to In_2Se_3 (JCPDS 017-0356). This indicates that simply depositing Cu, In and Se precursors will not result in the chalcopyrite phase of $CuInSe_2$. After the sample was annealed at 300°C, impurity phases, such like $Cu_{11}In_9$ and In_2Se_3 phases, were disappeared. This implies that the amorphous Se in the film has reacted with the $Cu_{11}In_9$ and In_2Se_3 matrix grains [4] and the subsequent reaction between Cu_2Se and In_2Se_3 also lead to the formation of $CuInSe_2$ [5]: $Cu_2Se + In_2Se_3 \rightarrow 2CuInSe_2$. No distinct characteristic peaks related to $CuInSe_2$ chalcopyrite phase are found in the films annealed at temperature below 400°C. It could be attributed to the incomplete reaction to synthesize $CISe_2$ compound due to the limited heat energy at lower annealing temperature. In the annealed sample (at 300°C), though there were no impurity phase, the diffraction peaks only matched with (112), (220), and (312) peaks of

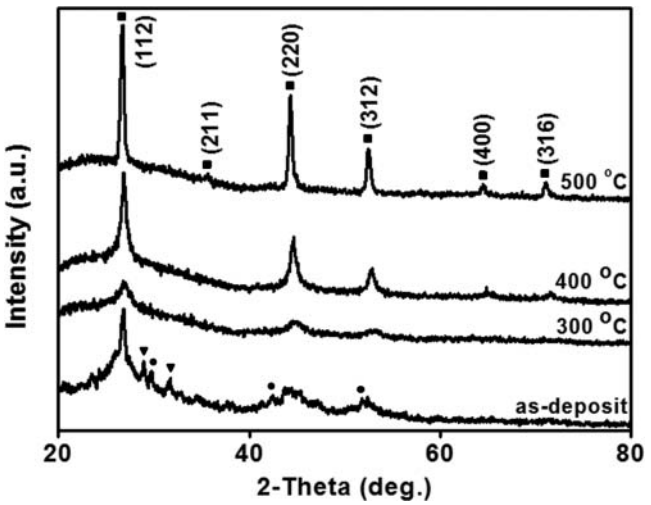

Figure 1. XRD diffraction patterns of as-deposited $CISe_2$ thin film and annealed at 300°C, 400°C, and 500°C.

$CuInSe_2$ phase. Higher diffraction peaks of $CuInSe_2$ phase were founded in the annealed sample (at 400°C). In the optimum annealed sample (at 500°C), the diffraction peaks at 2-theta = 26.56°, 35.48°, 44.23°, 52.39°, 64.34°, and 70.79° correspond to the (112), (211), (220), (312), (400), and (316) crystallographic planes of the tetragonal $CuInSe_2$ structure, respectively. These X-ray diffraction peaks were in good agreement with the data base of JCPDS 040–1487 for tetragonal chalcopyrite phase. From the XRD analysis, it was found that the crystal growth of the $CuInSe_2$ films was affected by the post-heating temperatures. According to Scherrer's equation, the crystallite size in the (112) plane direction is given by [6]:

$$\mathrm{L} = \frac{K\lambda}{\beta_{\mathrm{m}} \cos\theta}$$

The crystalline structure was determined from X-ray diffraction using Cu K_a radiation. The diffraction patterns were recorded from $2\theta = 20°$–$80°$. The operation voltage and current used are 40 kV and 40 mA, respectively. Where L is the average crystallite size, β_{m} the full width at half maximum intensity of (112) peak in radians, λ the wavelength of X-ray radiation (1.5406 Å), and K a constant related to the crystallite shape and normally is taken as 0.9. The average crystallite size is in good agreement with those between 20 nm to 60 nm in earlier works [7]. The grain size of the as-deposited film was larger than any other ones, which was 85.15 nm. The grain sizes of the samples annealed at 300°C, 400°C, and 500°C were 30.58 nm, 20.08 nm, and 40.22 nm, respectively. We confirmed that it decreased as the annealing temperature increased up to 400°C. At 500°C, however, the grain size was increased to 40.22 nm, which was favor lattice matching with p-type layer in solar cell fabrication.

Effects of the annealing temperature on the morphology of the $CuInSe_2$ films were investigated by SEM. Fig. 2 shows the surface morphologies of the films deposited on the substrates heated at low temperature and then annealed at 300°C, 400°C, and 500°C, respectively, for 30 min. As can be seen from the Fig. 2, the as-deposited film morphology shows both large $CuInSe_2$ grains and mixed small $CuInSe_2$, $Cu_{11}In_9$, and In_2Se_3 grains. From the Figs 2(b), (c), (d), after post-annealing treatment, all precursors of $CuInSe_2$, $Cu_{11}In_9$, and In_2Se_3 were combined. As presented in Figs 2(b) and (c), the prepared $CuInSe_2$ 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. It was clearly observed that the granular structure becomes more compact. The inset image in Fig. 2(d) shows a cross sectional image of the $CuInSe_2$ thin film prepared by the modified spray method. The film thickness was around 2.66 μm measured in the SEM cross sectional image. Fig. 2 confirmed that the change of the grain size, thickness, and surface morphology were strongly dependent on the annealing temperatures.

Figure 3 indicates the optical band gap measurements of the prepared $CuInSe_2$ films. Those were obtained by extrapolating the slope of curves to the x-axis in a plot of $(ahv)^2$ against hv on the basis of UV–visible absorption measurement. The effects of the annealing temperatures on the band gap of the $CuInSe_2$ thin films were presented in Fig. 3. While the extrapolated values of the optical energy band gap values for the as-deposit film, the films annealed at 300°C, and 400°C were 1.48 eV, 1.32 eV, and 1.27 eV, respectively, the estimated value from the sample annealed at 500°C was about 1.06 eV. Since there were pinholes and less dense surface morphology in the $CuInSe_2$ thin films annealed

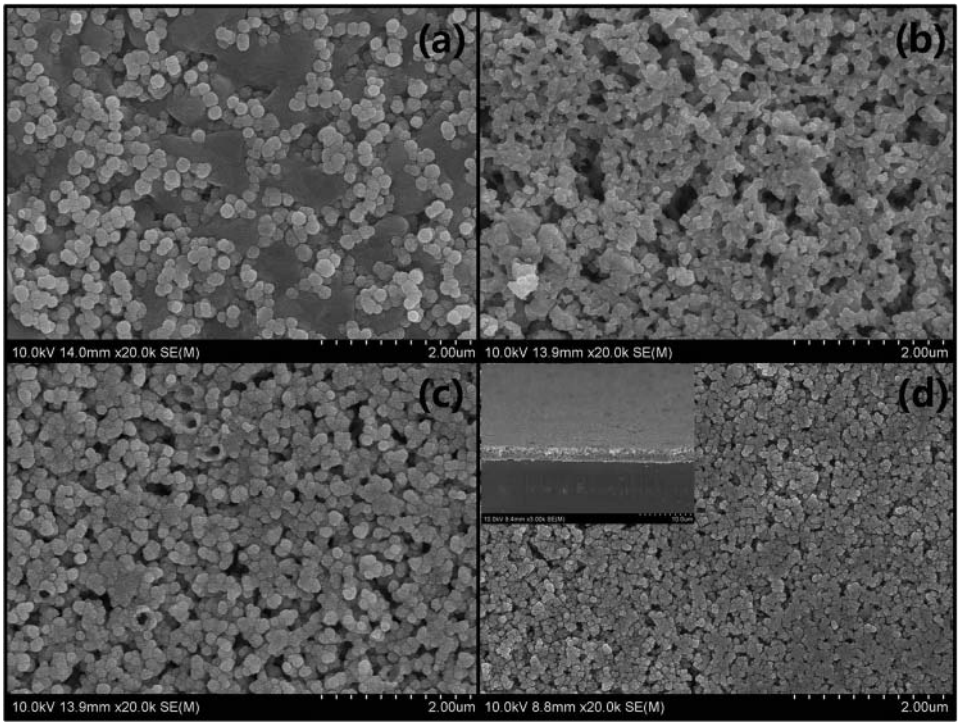

Figure 2. SEM micrographs of $CISe_2$ films grown at (a) as-deposited, annealed at (b) 300°C, (c) 400°C and (d) 500°C.

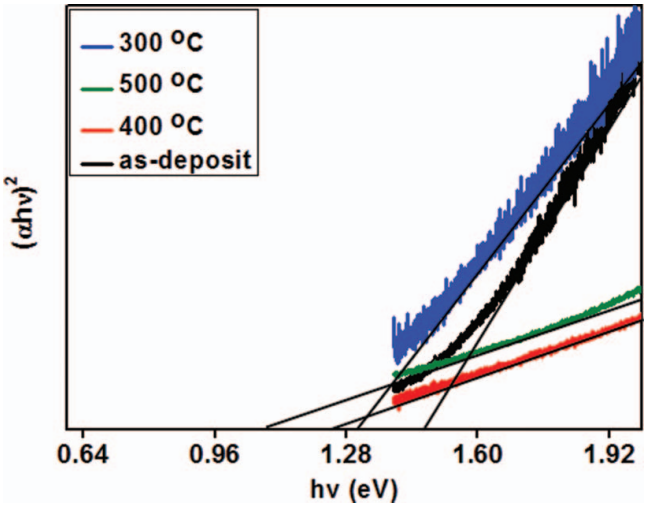

Figure 3. Optical absorption spectra of $CISe_2$ films deposited at (a) as-deposit, annealed at (b) 300°C, (c) 400°C and (d) 500°C.

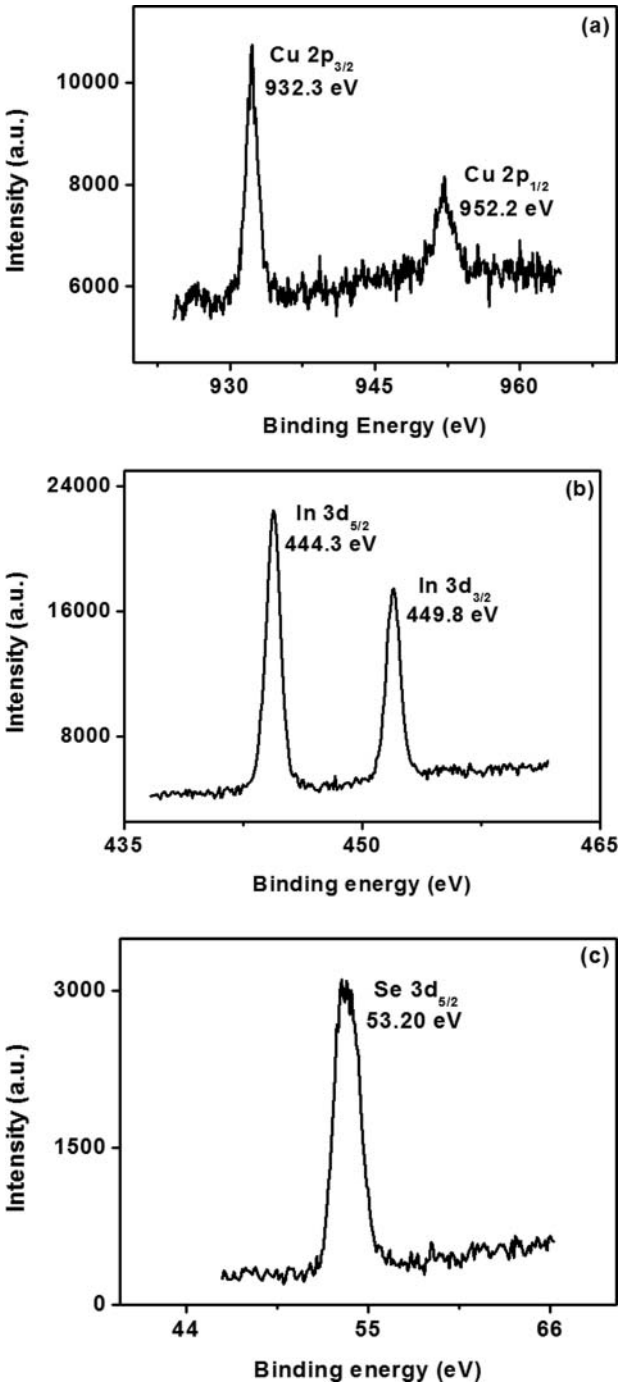

Figure 4. XPS spectra of $CISe_2$ films deposited by non-vacuum spray in the optimized condition; annealed at 500°C.

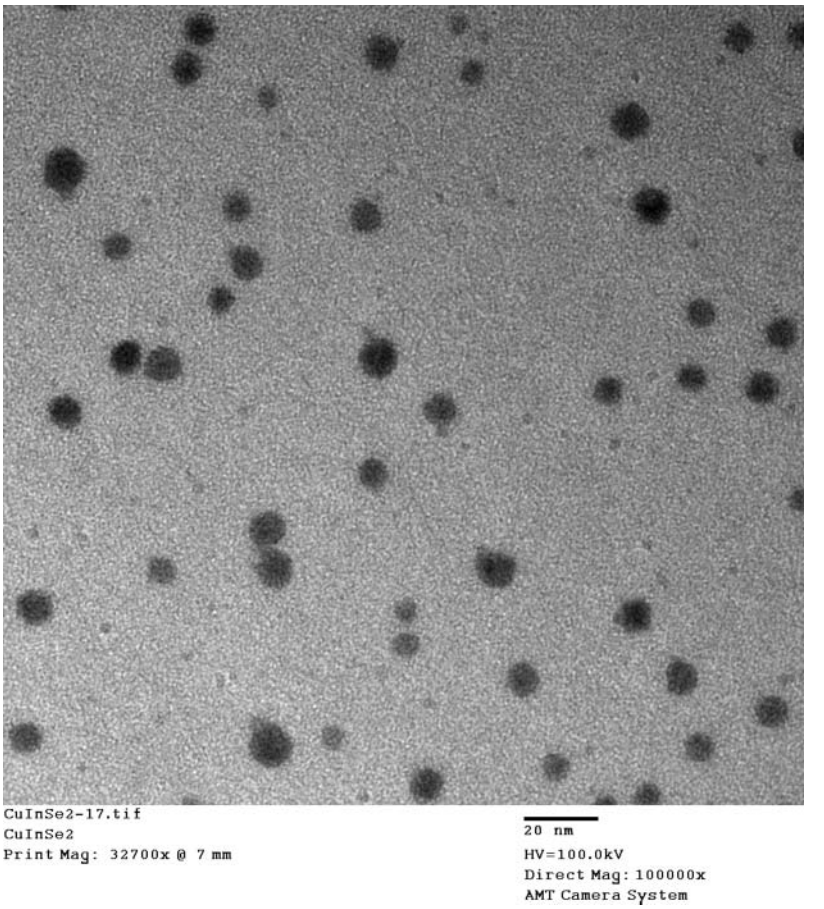

Figure 5. TEM image of $CISe_2$ film deposited for the optimized annealing temperature of 500°C.

at lower than 500°C, the $CuInSe_2$ thin film annealed at 500°C was close to the optimum band gap of about 1.04 eV.

XPS analysis was performed to identify the chemical binding states of the annealed $CuInSe_2$ film, which was prepared at 500°C. Figure 4 displays the XPS survey spectra of the Cu 2p, In 3d, and Se 3d. Fig. 4(a) shows the Cu 2p core level spectrum. The peak at 932.3 eV and 952.2 eV corresponding to the Cu $2p_{3/2}$ and $2p_{1/2}$ are in good agreement with the reported values for Cu^+ [8]. Fig. 4(b) indicates the In 3d core level spectrum. The observed peaks, centered at 444.3 eV and 449.8 eV, correspond to In $3d_{5/2}$ and In $3d_{3/2}$, respectively. The Se 3d core level is shown in Fig. 4(c). The main peak at 53.2 eV corresponds to the Se $3d_{5/2}$, as reported earlier for the $CuInSe_2$ [9].

TEM analysis was performed to determine $CISe_2$ grain size distribution. Average particle size of the $CISe_2$ film annealed at the optimum temperature, which was 500°C in this study, was about 10.6 nm as shown in Fig. 5.

Conclusions

The effects of the annealing temperatures on the structural, physical and optical properties of the $CISe_2$ thin films deposited on the glass substrates using a modified spray process

were studied in this work. From XRD diffraction patterns, it was observed that the $CISe_2$ thin films annealed at temperatures ranged from 300°C to 500°C for 30 min in a nitrogen environment had a tetragonal chalcopyrite structure with a preferred orientation along the (112) direction. In the SEM images, the film annealed at 500°C presented that the grains randomly distributed throughout the surface of $CISe_2$ films are fused inter-grain and altered the surface morphology uniformly during the thermal treatment process. Optical band gap of the films became sharper and more approachable optimum band gap (1.06 eV) when the annealing temperature was about 500°C. The XPS analysis confirmed that the $CISe_2$ thin films were successfully deposited using the modified spray process. The observed average particle size was ∼10.6 nm in TEM analysis. All these results demonstrate that 500°C is a crucial thermal treatment temperature at which structural, physical and optical properties of $CISe_2$ thin films changes.

Acknowledgment

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