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A Study on Copper Selenide Thin Films for Photovoltaics by a Continuous Flow Microreactor

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Highly uniform polycrystalline copper selenide (CuSe) thin films were deposited onto glass substrates using a solution-based continuous flow microreactor (CFM) method at low processing temperature conditions. The as-deposited CuSe thin films were annealed at 400°C for 1 hour under a nitrogen atmosphere. SEM, AFM, XRD, TEM, XPS, and UV-visible spectrophotometry were employed to study the properties of the CuSe thin films. The average grain size of the CuSe thin film was around 30 nm and the surface roughness was 5 nm. The estimated optical band gap was approximately 1.5 eV for the CuSe thin film after annealing at 400°C. Based on the X-ray Diffraction (XRD) and Selected Area Electron Diffraction (SAED) analyses, the CuSe thin films that were annealed at 400°C had a hexagonal structure. The chemical binding information of the CuSe thin film was studied using X-ray photoelectron spectroscopy (XPS).

Keywords Chalcogenide; continuous flow microreactor; copper selenide; photovoltaic cell; thin film

Introduction

Metal chalcogenide semiconductors are very important materials for a variety of electronic devices including photovoltaic cells and transistors. Polycrystalline thin films made of either binary I-VI, II-VI, and III-VI chalcogenide-based compounds or ternary I-III-VI chalcogenide-based compounds have optical energy band gaps that are close to the theoretical optimum conversion efficiency of solar cells in the terrestrial solar spectrum range. Chalcogenide-based thin film solar cells are better than crystalline silicon-based solar cells because they have a lower processing cost, lighter weight, and more flexibility. Copper selenide (CuSe) thin films are one of the most attractive candidates in the family of I-VI type binary chalcogenide materials for photovoltaic applications because they are good light absorbing

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polycrystalline semiconductor materials with unique physical, optical, and electronic properties. The direct band gap of CuSe is about 2.0∼2.3 eV, and the indirect band gap is about 1.1∼1.5 eV, which is close to the ideal band gap for solar cell applications [1]. The absorption coefficient of CuSe is within the range of the solar spectrum and is sufficiently high for the fabrication of thin film photovoltaic devices [2]. Copper selenide has been extensively studied over the past few decades. Chen *et al.* used copper selenide as an absorber layer and fabricated a hetero-junction structure for a $Cu_{2-x}Se/CdS$ thin film solar cell device with an efficiency of 5.38% [3]. Okimura *et al.* used CuSe as a window layer that was deposited on n-type silicon and obtained a solar energy conversion efficiency of 8.8% [4]. CuSe is also attractive because the ternary material $CuInSe_2$ can feasibly be produced by incorporating indium into this binary compound [5,6]. Additionally, $Cu_{2-x}Se$ is an important secondary phase in Cu-rich $CuInSe_2$[7]. Up to now, several methods, such as vacuum evaporation [8], electro deposition [9], and chemical bath deposition (CBD) [10], have been used to form polycrystalline CuSe thin films.

Recently, a novel solution-based deposition method was developed to synthesize the ternary chalcopyrite thin films. This approach used a continuous flow microreactor (CFM), which was capable of decoupling the homogeneous particle formation from the heterogeneous thin film growth, in order to overcome the drawbacks associated with the conventional CBD process [11–15]. The CFM process continuously introduces a fresh, pertinent amount of reactant solutions to the system. The CFM is a low cost and low temperature process, which does not require the sophisticated and expensive vacuum systems. Additionally, various substrates, including flexible ones, can be used in the CFM process in order to fabricate large area thin films. In this study, CuSe thin films were deposited onto glass substrates using the CFM process and subjected to post annealing treatment in nitrogen. This study is believed to be the first on the deposition of CuSe thin films using the CFM method.

Experimental

Preparation of Substrates

Commercial microscope glasses (Fisher Scientific) were used as the substrates. These glasses were ultrasonically cleaned with a 1 M sodium hydroxide (NaOH, Aldrich Inc) aqueous solution for 15 minutes and then rinsed with D.I. water. Finally, the substrates were dried under a stream of nitrogen gas before being used in the thin film fabrication.

Preparation of Precursor Solutions

A precursor solution of copper was prepared by dissolving 0.1 M of copper chloride ($CuCl_2 \cdot 2H_2O$, SIGMA-ALDRICH Inc.) in 200 ml D.I. water. A selenium precursor in the form of sodium selenosulfite was used for the film preparation. Sodium selenosulfite was prepared by mixing 0.05 M sodium sulphite (Na_2SO_3, SIGMA-ALDRICH Inc.) with selenium powder (Se, SIGMA-ALDRICH Inc.) in 200 ml D.I. water. The solution was stirred for 2 hour until clear sodium selenosulfite was formed. Ammonium hydroxide (NH_4OH, SIGMA-ALDRICH Inc.) was added to the sodium selenosulfite precursor solution to control the pH.

Deposition of CuSe Thin Films

The copper selenide thin films were deposited onto the substrates using the CFM process. Stream A was a 0.1 M copper chloride aqueous solution, and stream B was a 0.05 M sodium selenosulfite solution. The reactant streams A and B were mixed in a T-mixer and then impinged on the substrates, which were heated at 140°C. The flow rate of the mixed solution was about 1 ml/sec, and the impingement time was 5 min. The as-deposited CuSe thin films were annealed at a temperature in the range of 250∼400°C under a nitrogen atmosphere in order to improve the crystallization of the films and avoid their oxidations. The details for the CFM deposition procedure were described in a previous work [16].

Characterization of CuSe Thin Films

The optical properties of the thin films were measured using a UV-visible spectro-photometer (Ocean Optics In. USB-4000 optic spectrometer). A scanning electron microscope (SEM, HITACHI S-4800) and an atomic force microscope (AFM, Pucotech, PUCOSTATION STD-SPIP) were used to examine the surface morphology and roughness of the prepared polycrystalline CuSe thin films. An X-ray diffraction spectrometer (XRD, Panalytical MPD for thin film) was used to conduct the structural analysis of the CuSe films. The crystalline structures were also investigated using SAED with a transmission electron microscope (TEM, Hitachi H-7600). The chemical binding information for the CuSe thin films was studied using X-ray photoelectron spectroscopy (XPS, ESCALAB, 250 XPS spectrometer).

Results and Discussion

Optical Characterization

The as-deposited films on the substrates were thermally treated at various temperatures from 250°C to 400°C in order to study the effect of the annealing temperature on the optical band gap and surface morphology of the CuSe films. The optical band gaps of the CuSe thin films that were annealed at various temperature conditions were measured in the visible range of 300–800 nm using a UV-visible spectrophotometer. The absorption spectra showed that the relationship between the absorption coefficient and the photon energy for the direct allowed transition was $ah\nu = A(h\nu - E_g)^{1/2}$. Therefore, the optical band gap of the CuSe films was obtained by extrapolating the slope of the curves to the x-axis in a plot of the square root of $\alpha h\nu^2$ versus $h\nu$ using the absorbance from the UV-visible measurements. Figure 1 shows the UV-visible absorption spectrum of the CuSe film that was deposited on the microscope glass substrate at 400°C. This film exhibited an appropriate band gap along with a good surface morphology and low roughness. In Figure 1, the estimated optical band gap was ∼1.5 eV, and the additional optical band gaps are summarized in Table 1. In this study, the annealing temperature had an effect on the optical band gap of the CuSe thin film, where band gap decreased as the annealing temperature increased. It was reported that the indirect band gap of a pure polycrystalline CuSe thin film was 1.1∼1.5 eV in a literature [17].
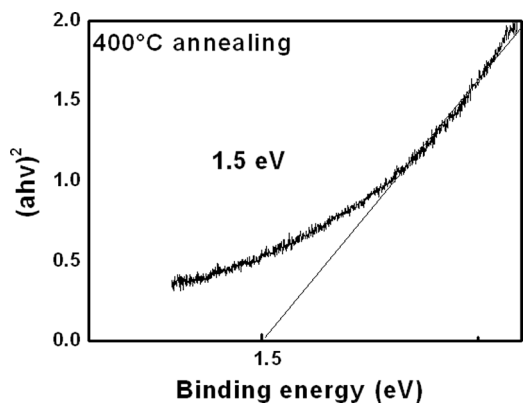
Figure 1. UV-Vis absorption spectra of the deposited CuSe film at the optimized conditions (reaction and annealing temperatures of 80 and 400°C, respectively) and its estimated optical band gap.

Surface Morphology and Roughness

A scanning electron microscope (SEM) was used to examine the surface morphology of the films. Figure 2 shows the SEM images of the CuSe thin films that were deposited using the CFM process at different annealing temperatures. The surface morphologies of the as-deposited films that were annealed at 250°C and 400°C were compared in Figure 2. The SEM images in Figures 2(a), (b), and (c) corresponded to the as-deposited CuSe thin film, the film that was annealed at 250°C, and the film that was annealed at 400°C, respectively. The formation of grains on the surfaces of the films was observed in the SEM images, and the grain sizes increased as the annealing temperature increased. The SEM image of the CuSe thin film that was annealed at 400°C had the biggest grain size and the most dense and uniform surface morphology. The CuSe thin film is not a suitable absorber layer for photovoltaic applications when the grain size is too small [18]. The CuSe thin film was also deposited using the batch chemical bath deposition(CBD) method at 80°C, and the as-deposited film was annealed at 400°C under a nitrogen atmosphere. The surface morphology of this film is shown in Figure 2(d) for comparison purposes. The CuSe thin film that was deposited using batch CBD contained a lot of pinholes and exhibited rougher, less dense surface morphology than the films that were deposited using the CFM process. The poor cell efficiency of solar cells is caused by non-uniformity and the presence of pinholes in the films. In general, chemical bath deposition (CBD) involves both homogeneous and heterogeneous reactions. The homogeneous reaction usually contributes to time variations in the deposition flux

Table 1. Estimated band gaps of the CuSe thin films that were prepared using the CFM process with different annealing conditions

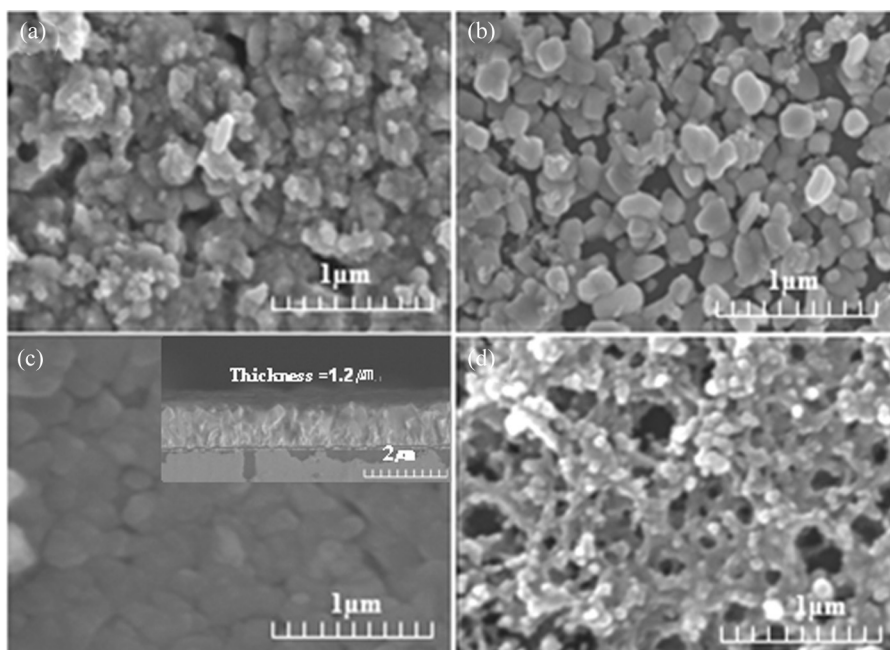| Annealing temperature	Band gap
as – deposited	1.80 eV
annealed at 250°C with N_2	1.75 eV
annealed at 400°C with N_2	1.50 eV

Figure 2. SEM images of the CuSe thin films that were deposited on the glass substrates at varying annealing temperatures: (a) as-deposited, (b) after annealing at 250°C, (c) after annealing at 400°C for 1 h in nitrogen gas, (d) SEM data of the CuSe thin film that was prepared using the CBD process.

and uncontrolled particle formation and agglomeration [15]. The homogeneous reaction that occurs in the chemical bath solution can be controlled using a CFM. The conventional batch CBD process produced films with large aggregates that exhibited coarse morphologies because the homogeneous reactions dominated the process. In this study, CuSe thin films with good surface morphologies were successfully synthesized for photovoltaic applications using the CFM process. The inset image in Figure 2(c) shows a cross sectional image of the CuSe thin film that was prepared using the CFM method. The film thickness was around 1.2 µm, which was close to the required thickness for the absorber layer of photovoltaic devices [19], and the film was quite dense according to the SEM cross sectional image.

AFM was used to examine the surface roughness of the prepared CuSe films. Figure 3 shows the two dimensional AFM image (5 µm × 5 µm) of the CuSe thin films that were annealed at 400°C. From this image, the film was uniformly smooth, and the substrate surface was well covered with fine spherical and elliptical grains. The average grain size was around 30 nm, and the surface roughness was around 5 nm. The AFM image in Figure 3 suggested that the film had a crystalline phase with similar sized grains uniformly distributed over the surface.

Structural Characterization

The structure and crystalline orientation of the polycrystalline CuSe thin films that were deposited onto the glass substrates were determined using XRD analysis.
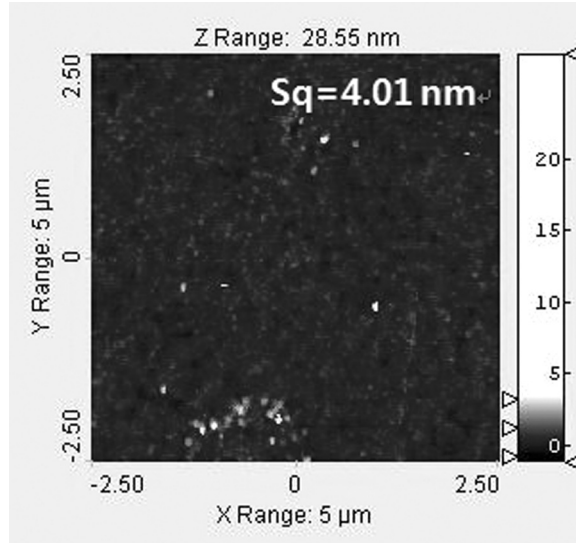
Figure 3. AFM image of the CuSe thin film deposited at the optimized conditions (reaction annealing temperatures of 80 and 400°C, respectively).

Figure 4 shows the X-ray diffraction pattern of the CuSe thin film that was deposited using the CFM process. No major diffraction peaks were observed in the XRD spectra for the as-deposited films in Figure 4(a). It was indicated that either the crystallites of the films were very small or the as-deposited film was amorphous. The as-deposited films were annealed at 400°C in a nitrogen atmosphere in order to improve the crystallinity of the films and to avoid oxidation. The XRD patterns of the CuSe films that were thermally treated after the CFM deposition are presented in Figure 4(b). Peaks at $2\theta = 27.83°$, $45.55°$, $53.17°$, and $66.10°$ corresponded to the (102), (110), (201), and (207) crystal planes of the CuSe structure, respectively, in the
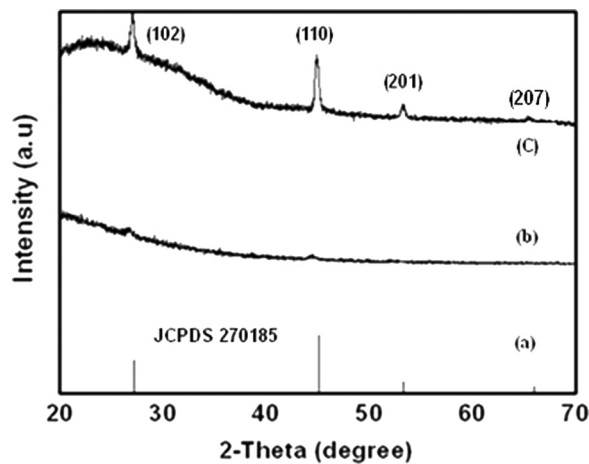

Figure 4. XRD pattern of the CuSe thin film deposited on the glass. (a) reference data of JCPDS 270185, (b) as–deposited, (c) after annealing at 400°C for 1 h in nitrogen gas.
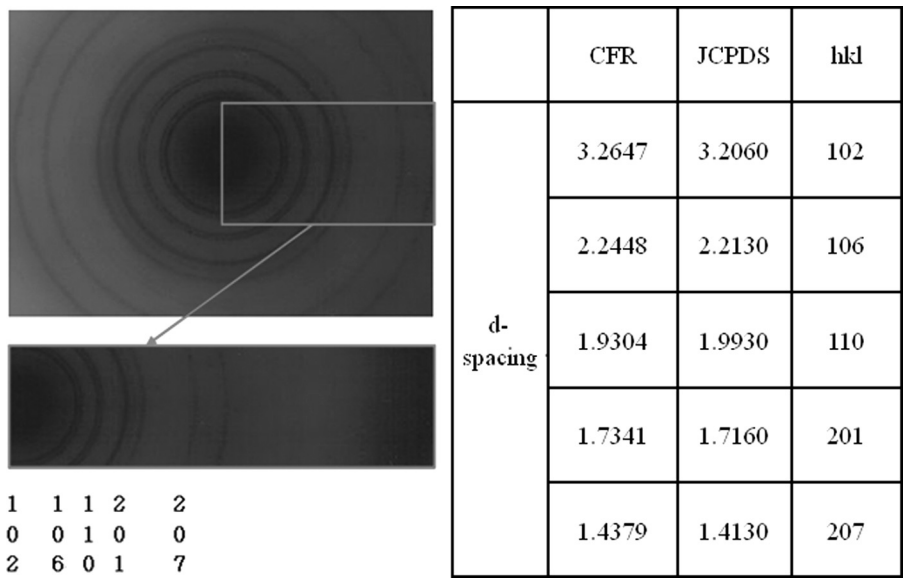
	CFR	JCPDS	hkl
	3.2647	3.2060	102
	2.2448	2.2130	106
d-spacing	1.9304	1.9930	110
	1.7341	1.7160	201
	1.4379	1.4130	207

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1  1  1  2    2
0  0  1  0    0
2  6  0  1    7
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Figure 5. TEM-electron diffraction pattern of CuSe that was prepared using the CFM process (Index: JCPDS 270185, Structure: Hexagonal) and the d-spacing data along with the structural orientation.

X-ray diffraction spectra of the annealed film. These diffraction peaks matches well to the values of the standard (JCPDS 270185), and the film was indexed as CuSe with a hexagonal structure.

SAED analysis was carried out using a TEM in order to further determine the crystalline structure of the prepared CuSe thin films. In the high resolution TEM, definite crystalline diffraction was observed, and the electron diffraction patterns indicated the formation of a polycrystalline structure that matched the hexagonal CuSe (face-centered hexagonal lattice structure, JCPDS-270185) structure. The electron diffraction pattern along with the d-spacing data obtained from the TEM is presented in Figure 5. The XRD and SAED analysis confirmed that a CuSe thin film with a hexagonal structure was successfully obtained from the CFM process.

X-ray photoelectron spectroscopy (XPS) was performed in order to determine the chemical composition and binding information of the CuSe thin film that was annealed at 400°C. The CuSe thin film was first etched using Ar gas stream at a flow rate of 0.02 nm/s for 30 seconds in order to remove any impurities on the surface of the thin film. Figure 6 shows the high-resolution XPS spectra in the range of 0–1200 eV. The observed binding energy peaks located at 928.9 and 949.1 eV corresponded to the electronic states of Cu $2p_{3/2}$ and Cu $2p_{1/2}$, respectively. The peaks at 54.5 and 51.5 eV were attributed to the electronic state of Se $3d_{5/2}$ and Se $3d_{3/2}$, respectively. For the XPS peaks, the binding energy position of Se was shifted by 1 eV compared to the reference values because Se has at least six very different chemical structures, and each structure produces a specific XPS signal with a different binding energy. The chemically deposited film might have been contaminated by oxygen when the film was exposed to the environment during the preparation. These shifts are very sensitive to the chemical preparation of the films [20,21].
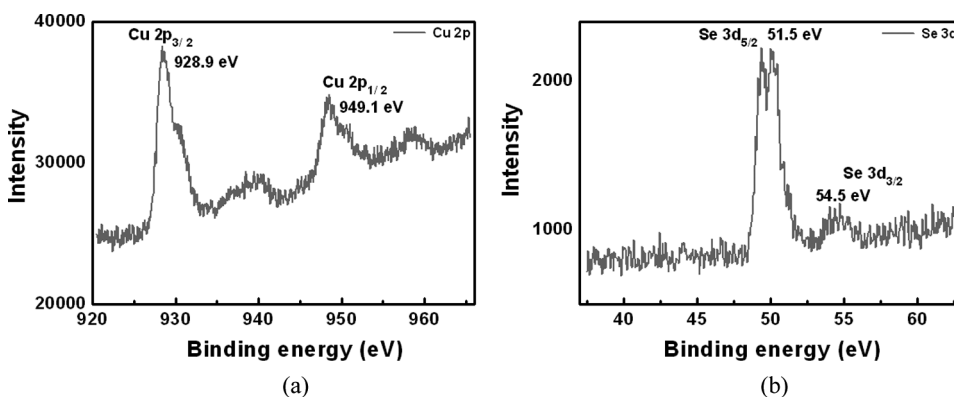
(a)   (b)

Figure 6. XPS spectra of the CuSe thin film deposited using the CFM process at the optimized conditions (reaction annealing temperatures of 80 and 400°C, respectively).

Conclusions

Polycrystalline CuSe thin films were successfully deposited on glass substrates using the CFM method at low processing temperature conditions for use in photovoltaic cell devices. A series of experiments were carried out in this study in order to characterize the physical, optical, and structural properties of the CuSe thin film. The SEM and AFM measurements indicated that the film with an average grain size around 30 nm and a surface roughness of 5 nm was uniformly deposited using the CFM process. Based on the UV-vis absorption, the estimated optical band gap was ~1.5 eV for the prepared film. From the XRD and SAED analyses, the CuSe thin film that was annealed at 400°C had a hexagonal structure. The chemical binding information was obtained from the XPS analysis and confirmed that the CuSe thin film was successfully deposited using the CFM process.

Acknowledgements

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