

Research Article

Fabrication and Characterization of CuInSe_2 Thin Film Applicable for a Solar Energy Light Absorption Material via a Low Temperature Solid State Reaction

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The chalcopyrite CuInSe_2 thin film synthesized via a low temperature solid state reaction from CuSe and InSe powders was investigated using X-ray diffractometry (XRD), scanning electron microscope (SEM), energy dispersive spectrometer (EDS), transmission electron microscopy (TEM), and UV-vis absorption spectroscopy. CuSe and InSe phases react and directly transform into CuInSe_2 without the occurrence of any intermediate phase. The morphology of the newly formed CuInSe_2 crystalline was close to that of the CuSe reactant particle based on the TEM results, which indicate that the solid state reaction kinetics may be dominated by the In^{3+} ions diffusion. The CuInSe_2 thin film prepared from the solid state reaction did not use the selenide process; its band gap might reach 1.06 eV, which is competent and suitable to be used for a thin film solar cell light absorption layer.

1. Introduction

For the new type-energy materials, the group IV quantum dot nanostructures for future generation solar cell applications [1] and next generation ionic conducting membranes for photochemical materials (i.e., fuels from light), batteries (i.e., electricity storage), fuel cells (i.e., electricity from fuels), and other applications [2] are highly promising. Successful results have been increasingly converted into products, and more and more organizations have developed novel advanced materials for renewable energy for the future. Many efforts have also been focused on photovoltaic cells. Among them, the ternary I-III-VI₂ semiconductor of CuInSe_2 (CIS) is one of the most important semiconductor materials used in thin film photovoltaic cells. Because of its high absorption coefficient, suitable band gap, good radiation stability, and the thickness of the absorption layers can be reduced to several micrometers [3].

High efficiency CIS solar cells are commonly prepared via the physical vapor deposition method [4–6]. This kind of

process requires a complicated facility, thereby leading to the high fabrication cost. However, the general vacuum methods have drawbacks such as the complexity in process and high production costs and are difficult to be made on a large scale, which need to be solved before the mass production of CIS solar cells. To avoid these drawbacks, nonvacuum processes have been extensively investigated in recent years, such as ink printing method [7], electrodeposition process [8, 9], spray pyrolysis method [10], chemical deposited method [11], and combustion method and nonvacuum spin-coating process [12].

A potential nonvacuum method for CIS formation is developed in this work. In the experiment, the CuSe and InSe powders are prepared by wet chemical method, which is one of the simplest and cheapest methods. The CIS thin film is thereafter obtained by spin coating from CuSe and InSe powders on the glass and then heated at 350°C for 3 h under nitrogen gas. The structure and the optical properties of the precursors and the CIS films are investigated and discussed.

TABLE 1: Experimental conditions and results.

No.	Materials	Precursors ratio	Measured by EDS (Cu : In : Se)	Time (h)	Temp (°C)	Products
1 ^a	InCl ₃ + Se	1 : 1	0 : 1 : 1.06	5	220	InSe
2 ^a	InCl ₃ + Se	2 : 3	0 : 2 : 3.01	5	280	In ₂ Se ₃
3 ^a	CuCl + Se	1 : 1	1 : 0 : 0.99	2	220	CuSe
4 ^a	CuCl + Se	2 : 1	1.74 : 0 : 1	2	220	Cu ₂ Se
5 ^b	InSe + CuSe	1 : 1	1 : 0.79 : 1.86	3	350	CuInSe ₂
6 ^b	In ₂ Se ₃ + Cu ₂ Se	1 : 1	1 : 1.32 : 1.94	3	350	CuInSe ₂ + In ₂ Se ₃

^aSamples no. 1~4 were reaction via wet chemical process using OLA as solvent.

^bThe precursors were prepared by samples no. 1~4 and reaction through low temperature solid state reaction.

2. Experimental

2.1. Materials. The copper (I) chloride (99.99%, Alfa Aesar, Ward Hill, MA, USA) and indium (III) chloride (99.99%, Acros, Geel, Belgium) used were analytical grade reagents. Selenium powder (99.99%, Sigma-Aldrich, St. Louis, Missouri, USA) was a high purity reagent. Oleylamine (70%, Kanto Chemical Co., Inc., Tokyo, Japan), hexane (99%, Acros, Geel, Belgium), and ethanol (95%, Acros, Geel, Belgium) were used as received, without further purification. The deionized water (DI water) used in this work was obtained from EMD Millipore Corporation-Direct-Q 3 system (Billerica, MA, USA).

2.2. Synthesis of InSe Particles. A typical synthesis of InSe particles was modified from Park et al.'s procedure [13]; 0.45 mmol InCl₃ and 0.50 mmol Se powder were added into 10 mL of oleylamine (OLA) at room temperature. The reaction mixture was heated to 220°C and kept at that temperature under nitrogen gas with magnet stirring for 5 h. The product was then centrifuged and washed with hexane, ethanol and DI water several times and then dried at 80°C for 3 h in a vacuum oven.

2.3. Synthesis of In₂Se₃ Particles. The In₂Se₃ particles were synthesized by annealing the reaction mixture containing 0.45 mmol InCl₃ and 0.70 mmol Se powder in 10 mL of OLA at 280°C under nitrogen gas for 5 h. The product was then centrifuged and washed with hexane, ethanol, and DI water several times and then dried at 80°C for 3 h in a vacuum oven.

2.4. Synthesis of CuSe Particles. The CuSe particles were synthesized by annealing the reaction mixture containing 0.50 mmol Se powder and 10 mL of OLA (OLA/Se) firstly mixed at room temperature, and the resulting solution was heated to 180°C. 0.46 mmol CuCl and was then quickly added into the hot OLA/Se solution; the reaction mixture was annealed at 220°C for 2 h under nitrogen gas. The product was then centrifuged and washed with hexane, ethanol, and DI water several times and then dried at 80°C for 3 h in a vacuum oven.

2.5. Synthesis of Cu₂Se Particles. The Cu₂Se particles were synthesized by annealing the reaction mixture containing 0.91 mmol CuCl and 0.50 mmol Se powder in 10 mL of OLA at

220°C for 2 h under nitrogen gas. All the products were then centrifuged and washed with hexane, ethanol, and DI water several times and then dried at 80°C for 3 h in a vacuum oven.

2.6. Synthesis of CuInSe₂ Films. The CuInSe₂ films were prepared using the as-prepared metal Se compounds as precursors in two reaction paths. In the reaction path A, the as-prepared InSe (0.25 mmol) and CuSe (0.25 mmol) were dispersed in ethanol and spin-coated on the glass with 500 rev. min⁻¹ for 20 s in air, then dried at 100°C for 1 h to remove residual solvent. The glass was transferred into closed graphite box and heated at 350°C for 3 h under nitrogen gas. In the reaction path B, the as-prepared In₂Se₃ (0.25 mmol) and Cu₂Se (0.25 mmol) were also dispersed in ethanol and spin-coated on the glass with 500 rev. min⁻¹ for 20 s in air, then dried at 100°C for 1 h to remove residual solvent. The glass was transferred into closed graphite box and heated at 350°C for 3 h under nitrogen gas. The experimental parameters were summarized in Table 1.

2.7. Material Characterization. The X-ray powder diffraction (XRD, operating at 8 kV) patterns of the as-prepared samples were recorded on Shimadzu XRD-6000 X-ray diffractometer (Kyoto, Japan) with Cu K α radiation ($\lambda = 0.15418$ nm). The morphologies and micro-/nanostructure were investigated by Hitachi 4200A (Tokyo, Japan) scanning electron microscope (SEM, operating at 10 kV) and JEOL JEM-2000EX (Tokyo, Japan) transmission electron microscope (TEM, operating at 160 kV). The measurements using energy dispersive spectrometer (EDS) were performed on Horiba EX220 (Kyoto, Japan), which was attached to TEM for compositional analyses. Thermal analysis was carried out with Perkin Elmer Pyris Diamond TG/DTA thermal analyzer (Boston, MA, USA) in nitrogen atmosphere at a heating rate of 20°C/min. UV-vis absorption spectra were recorded by Hitachi U-3010 spectrophotometer (Tokyo, Japan).

3. Results and Discussion

The phase and crystallographic structure of the as-prepared metal Se compounds were determined by XRD. Figure 1 showed XRD patterns of the as-prepared (a) InSe, (b) In₂Se₃, (c) CuSe, and (d) Cu₂Se particles, which corresponded to the cubic phase, consistent with the literature [13], the hexagonal structure (JCPDS no. 89-0658) [14], the klockmannite

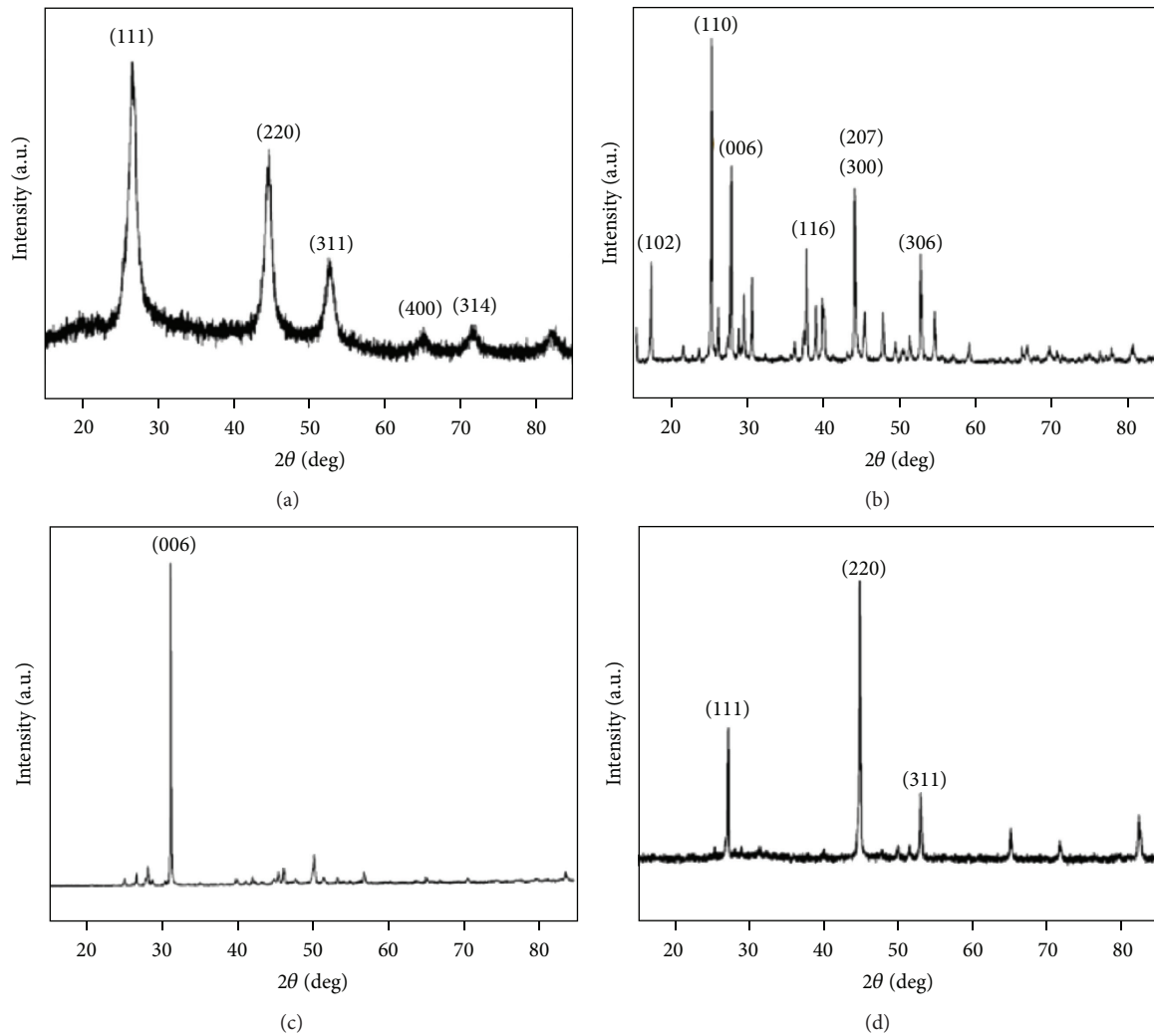


FIGURE 1: XRD patterns of as-prepared (a) InSe [13], (b) In_2Se_3 [14], (c) CuSe [14], and (d) Cu_2Se [14] particles.

structure (JCPDS no. 49-1457) [14], and the cubic structure (JCPDS no. 88-2044) [14], respectively. Figure 2 showed XRD patterns of the CIS films synthesized from (a) the as-prepared metal Se compounds: InSe and CuSe, and (b) the as-prepared metal Se compounds: In_2Se_3 and Cu_2Se , respectively. The chemical composition of the as-prepared metal Se compounds and other products was analyzed with EDS and given in Table 1.

Figure 2(a) showed XRD pattern obtained from the annealed thin film made by CuSe and InSe, which exhibited a single crystalline structure composed of CIS that corresponds to the peaks at (112), (211), (204)/(220), (116)/(312), (008)/(400), (316)/(332), and (228)/(424). The chalcopyrite phase of CIS (JCPDS no. 40-1487) was then synthesized. Figure 2(b) showed XRD pattern obtained from the annealed thin film made by Cu_2Se and In_2Se_3 , which exhibited a multicrystalline structure composed of CuInSe_2 and In_2Se_3 that corresponds to the chalcopyrite CIS and the hexagonal In_2Se_3 .

Figure 3 showed various images of the as-prepared CIS thin film from path A: (a) cross-sectioned SEM image for

the as-synthesized CIS before annealing and (b) that after annealing, (c) LR-TEM, and (d) HR-TEM and SAED (the insert) images for the as-prepared CIS. In Figure 3(a), the upper layer was identified as InSe particles with irregular shapes. The lower layer was identified as CuSe particles with a regular hexagonal shape of around $2\ \mu\text{m}$ in diameter. In Figure 3(b), the CIS thin film exhibited a regular shape of hexagonal chalcopyrite particles. The insert image was the dispersed CIS particles from its film. Figure 3(c) showed the LR-TEM image of CIS particle. Its morphology and particle size were consistent with those observed by SEM. Figure 3(d) showed the HR-TEM and inserted SAED image of CIS particle. The spacing of the crystal lattice was measured around $3.3\ \text{\AA}$, which is consistent with the crystal lattice plane of CIS under (112). The EDS analysis expected an average composition of $\text{Cu}_{1.0}\text{In}_{0.79}\text{Se}_{1.86}$, which estimated an element ratio for copper, indium, and selenium of 1.27:1.00:2.36. The CIS structure prepared through the solid state reaction showed a Cu- and Se-rich structure, but roughly correlated with the composition of CuInSe_2 .

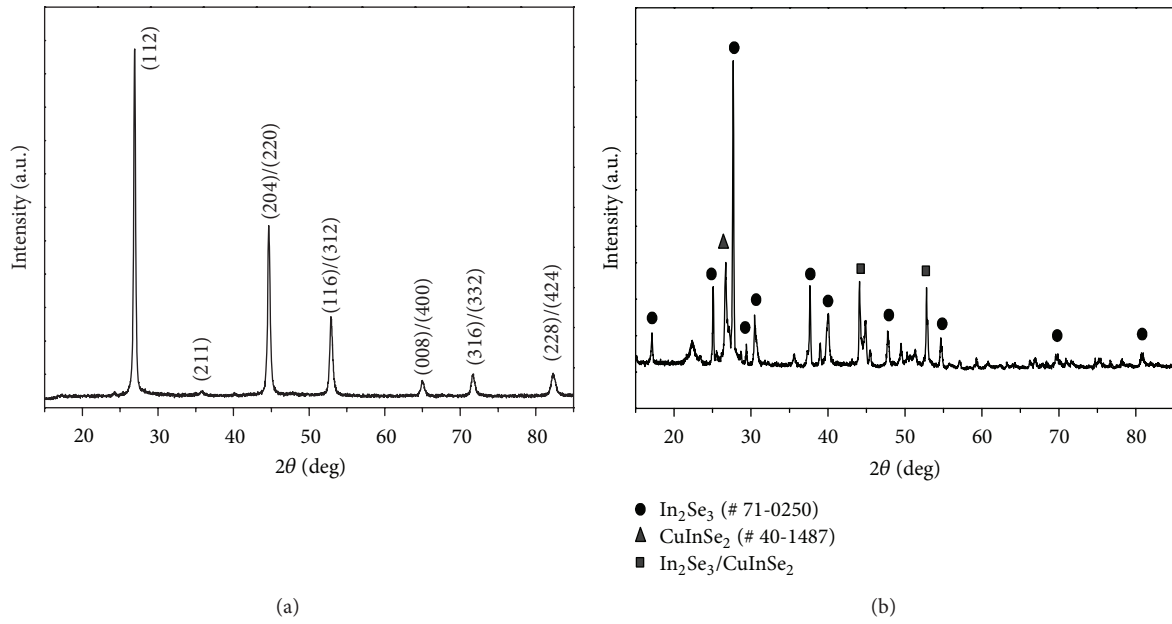


FIGURE 2: XRD patterns obtained from the annealed thin film made by (a) CuSe and InSe and (b) Cu_2Se and In_2Se_3 .

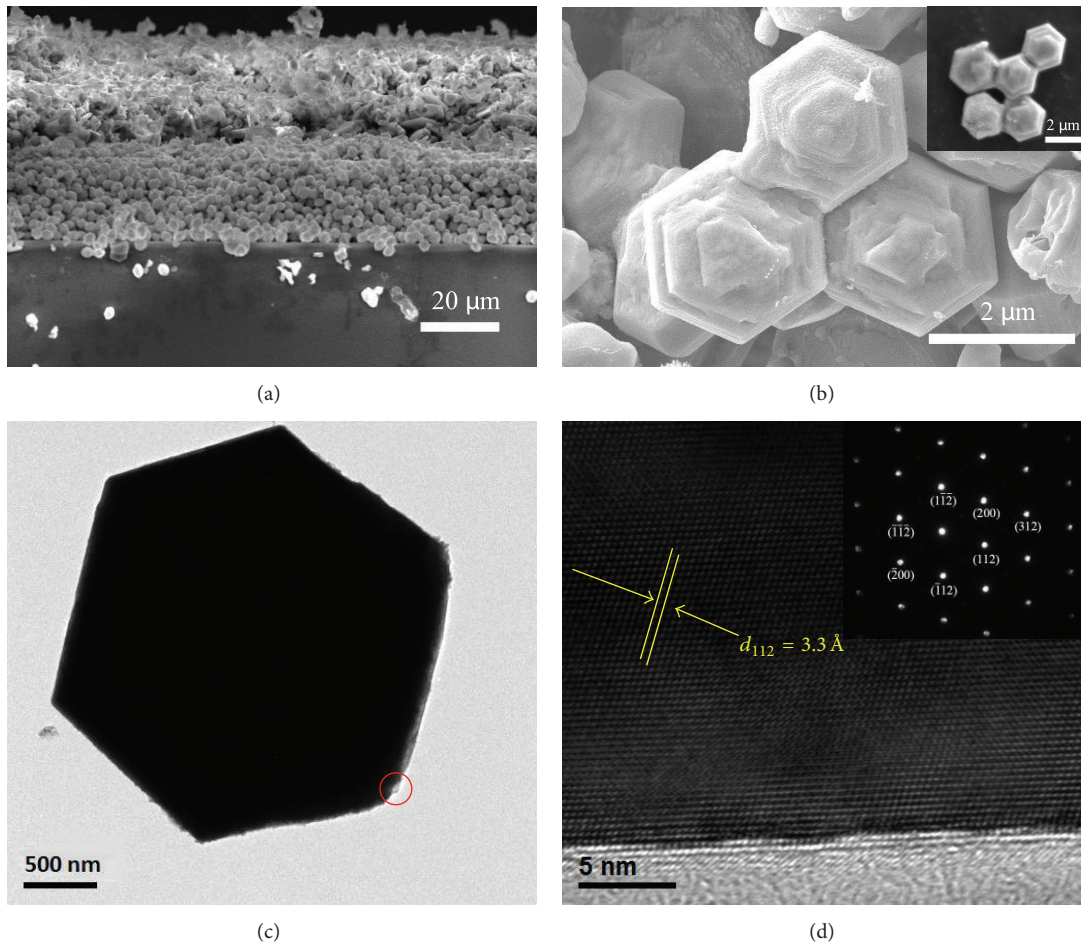


FIGURE 3: Various images of the as-prepared CIS thin film from path A: (a) cross-sectioned SEM image for the as-synthesized CIS before annealing and (b) that after annealing, (c) LR-TEM, and (d) HR-TEM and SAED (the insert) images for the as-prepared CIS.

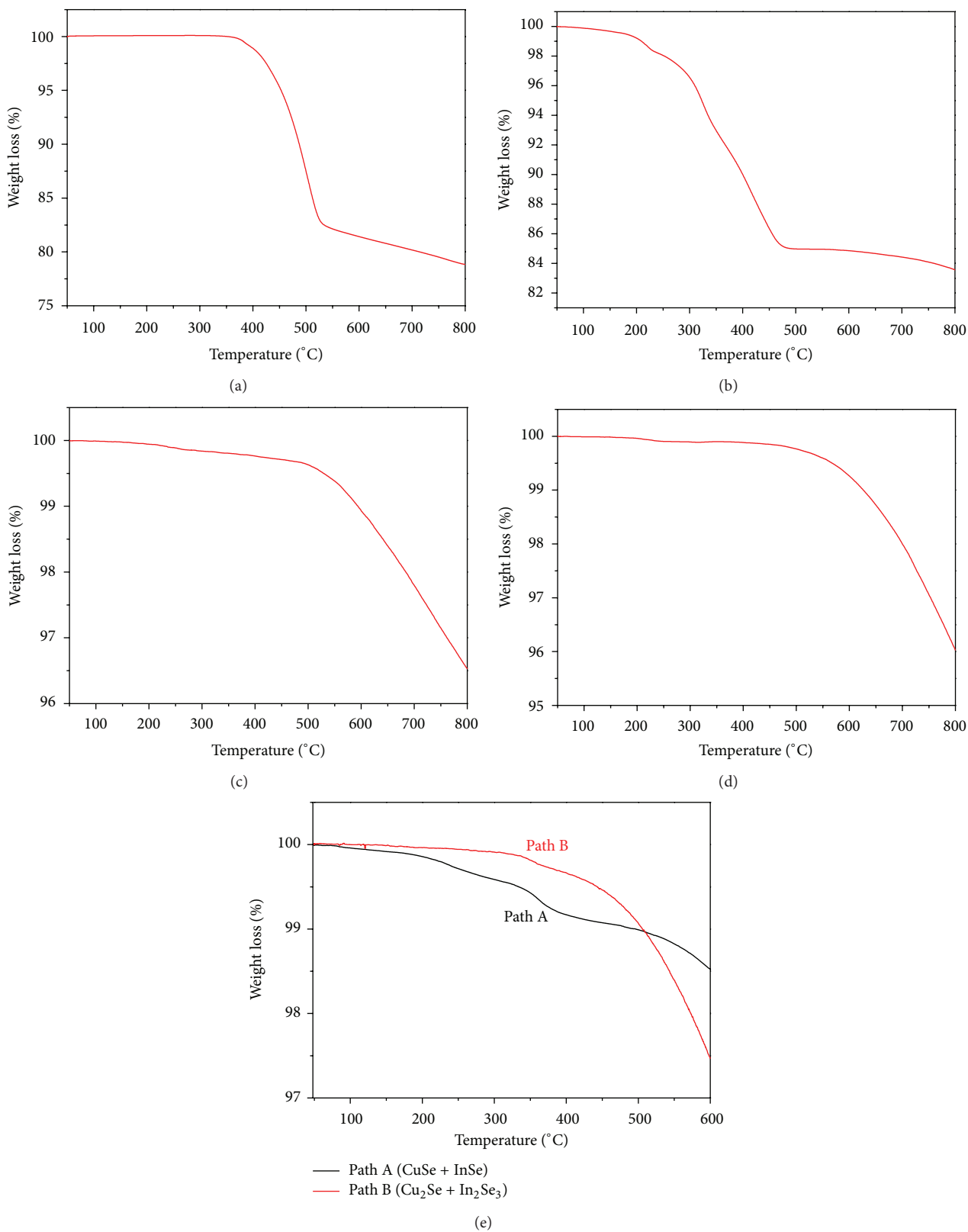


FIGURE 4: TGA curves of (a) CuSe, (b) InSe, (c) Cu₂Se, (d) In₂Se₃, and (e) CIS particles prepared by the reaction path A or B via solid state reaction.

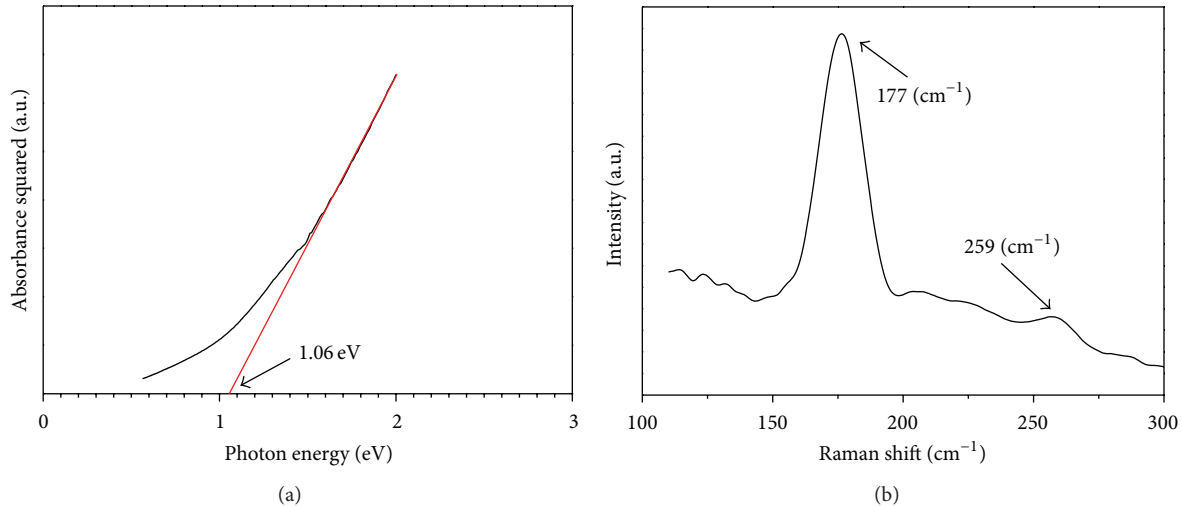


FIGURE 5: The (a) UV-vis absorption spectrum and (b) Raman spectrum of CIS thin films synthesized from the reaction path A.

Hsiang et al. [15] investigated that the CIS crystalline reaction from Cu_2Se and In_2Se_3 was close to that from the Cu_2Se reactant particle, based on the TEM result. It indicates that the solid state reaction kinetics may be dominated by the In^{3+} ions diffusion. The same situation also occurred in the experiment of path A. From TEM images, the solid state reaction kinetics of path A was most probably dominated by the In^{3+} ions diffusion. On the other hand, the reaction kinetics using solid state reaction from CuSe and InSe precursors was lower than that from Cu_2Se and In_2Se_3 precursors [16, 17]. Figure 4 showed TGA curves of (a) CuSe , (b) InSe , (c) Cu_2Se , (d) In_2Se_3 , and (e) CIS particles prepared by the reaction path A or B via solid state reaction. The figures showed the total percentage of weight loss as the increasing temperatures till 800°C . According to Figures 4(a)–4(d), only InSe had 7% weight loss, whereas almost no weight loss measured till 350°C for CuSe , Cu_2Se , and In_2Se_3 was found. Figure 4(e) showed that the weight loss of path A was about 1.5% at 600°C . The result indicated that CIS particles prepared by solid state reaction exhibited good thermal stability. In addition, the weight loss of path B was about 0.1% at 350°C and about 2.5% at 600°C , which indicated that the path B might require higher reaction temperature to form CIS phase. As a result, the path B for synthesizing CIS phase was relatively difficult at 350°C , while the solid state reaction kinetics of path A was presumably dominated by In^{3+} ions diffusion [15].

Furthermore, Figure 5(a) showed the UV-vis absorption spectrum of CIS particles prepared by reaction path A. The sample was dispersed in absolute ethanol under intense sonication for 20 min, while ethanol was used as a reference. The band gap of CIS particles was calculated using the direct band gap method from its optical absorption spectrum [7]; the value was determined as 1.06 eV, which is consistent with the reported value of 1.04 eV for the bulk CIS [18]. Figure 5(b) showed Raman spectrum of CIS thin films synthesized from the reaction path A. The main peak at around 177 cm^{-1} could be identified as the A_1 vibrational mode from chalcopyrite ordered CIS. A relatively small peak at around 240 cm^{-1}

was related to the characteristic mode from the elemental Se [19, 20]; however, scarcely Se could not be found in the form of CIS thin film. The Cu and Se binary phase were difficult to be identified in the measured spectral range: the peak at 259 cm^{-1} was the most intense one observed on Raman spectrum of CuSe [21].

4. Conclusions

In this work, CIS thin film is successfully fabricated by using CuSe and InSe binary precursors via a low temperature solid state reaction. The XRD results indicate that CIS thin film has a chalcopyrite structure with good crystallinity, which exhibits (112) prefer orientation. Particularly, CIS thin film can be preferably obtained by path A with the reaction of $\text{CuSe} + \text{InSe} \rightarrow \text{CuInSe}_2$ at relatively low temperature (350°C) and short preparation time (3 h). Besides, the weight loss indicated by TGA pattern is only 1.5% at 600°C . The value of band gap for the as-prepared CIS is calculated to be 1.06 eV, which demonstrates that this material is suitable to be used for a thin film solar cell light absorption material. Its good absorption in the visible light region also suggests that such photovoltaic material is promising for sustainable energy related applications.

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