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Growth and characterization of $CuInS_2$ nanoparticles prepared using sonochemical synthesis

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ABSTRACT

In this study, copper indium disulfide ($CuInS_2$) nanoparticles were synthesized using the sonochemical method. The structural, optical, and electrical properties of the $CuInS_2$ nanoparticles were investigated as a function of the [Cu]/[Cu + In] molar ratio in the precursor solution. X-ray diffraction patterns show that all samples consisted of the tetragonal $CuInS_2$ phase with a preferential orientation along the (112) crystal plane. With a decrease in the [Cu]/[Cu + In] molar ratio in precursor solution, the diffraction peaks slightly shifted to lower angles. Transmission electron microscopy images confirm that the samples consisted of the tetragonal $CuInS_2$ phase with an average diameter in the range of 9.2–14.8 nm. Samples with [Cu]/[Cu + In] molar ratio greater than 0.50 were p-type semiconductors whereas those with [Cu]/[Cu + In] molar ratio of less than 0.47 were n-type semiconductors. The carrier concentrations and mobilities of the samples are in the ranges of 3.31×10^{18}–8.16×10^{15} cm^{-3} and 2.13–59.0 cm^2 V^{-1} s^{-1}, respectively. The conversion efficiency of a thin-film solar cell with the structure glass/Mo/$CuInS_2$/CdS/i-ZnO/ZnO:Al was around 1% under illumination at 100 mW/cm^2.

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1. Introduction

Chalcopyrite I-III-VI_2 semiconductors (I = Cu, Ag; III = Al, In, Ga; VI = S, Se, Te) are interesting photo-absorbers for applications related to solar energy because of their suitable band gap, high absorption coefficient, and easy to prepare n/p type conductivity [1–3]. Laboratory-scale thin-film solar cells based on p-Cu(In,Ga)Se_2 (CIGSe) and CdS heterogeneous junctions prepared using thermal evaporation with an conversion efficiency of as high as 20% have been reported [4]. However, the high cost of gallium and the toxicity of Se (from H_2Se gas) in CIGSe solar cells are the main obstacles for industrial applications. The high production cost of vacuum-based processes such as multi-stage co-evaporation also limits the widespread used of CIGSe solar cells. The chalcopyrite $CuInS_2$ is a ternary I–III–VI_2 material with a direct band gap in the range of 1.3–1.5 eV and an absorption coefficient of around 10^5 cm^{-1} [5]. The conduction type of $CuInS_2$ samples can be adjusted via a small change of the sample composition ratios. In-rich $CuInS_2$ samples [Cu/(Cu + In) molar ratio <0.5] show n-type conductivity due to S vacancy (V_s) or In interstitial (In_i) defects, whereas Cu-rich $CuInS_2$ samples [Cu/(Cu + In) molar ratio >0.5) show p or n-type conductivity, which are dominated by the defects of In vacancy (V_{In}) and Cu atoms in the In site (Cu_{In}) in samples [3]. The theoretical efficiency for homo-junction $CuInS_2$ solar cells is about 32%, and thus the $CuInS_2$ photo-absorber layer has received interest for solar energy conversion [6]. Both $CuInS_2$ and Cu(In,Ga)S_2 thin-film solar cells show long-term efficiency stability under illumination. An efficiency of 11.4% for $CuInS_2$ solar cells prepared using sputtering and subsequently sulfurized using rapid thermal processing (RTP) in sulfur vapor was reported [2]. The production capacity of industrial $CuInS_2$ solar cell modules made by SULFURCELL Co. is 35 MWp [7].

Various methods for the deposition of $CuInS_2$ chalcopyrite semiconductors onto substrates have been reported, such as evaporation [1,8,9], radio-frequency (RF) sputtering [10], and molecular beam epitaxy [11]. These methods for the deposition of $CuInS_2$ photo-absorbers onto substrates are the complex process requiring vacuum technology. In recently years, the quest for the low cost production focused on the development of non-vacuum deposition methods. Azima et al. [12] and Aldakov et al. [13] reviewed the preparation of multi-component metal sulfide/selenide samples onto substrates using non-vacuum methods. Various non-vacuum approaches for the deposition of $CuInS_2$ photo-absorber layer on substrates have also been reported, such as solution synthesis [14], spray pyrolysis [15], chemical bath

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deposition [16], and electrodeposition [17]. Recently, a simple method for the low-temperature growth and crystallization of metal sulfides has been demonstrated by means of sonochemical synthesis [18–20]. The sonochemical synthesis for the preparation of metal sulfide powders was carried out using an aqueous solution containing metal ions and thioacetamide, the latter serving as the sulfur source [21,22]. Avivi et al. [21] prepared nano-phase In_2S_3 with an average diameter of less than 40 nm at room temperature in a sonicating bath. Gorai and Chaudhuri [22] prepared cage-like indium sulfide with an average diameter in the range of submicron size using sonochemical synthesis. Chemical synthesis in an ultrasonic bath thus appears to be an improvement over tradition chemical synthesis in the solution with magnetic stirring. Although the qualities of chalcopyrite I-III-VI_2 thin films prepared using physical vapor deposition, such as RF sputtering and thermal evaporation techniques, are much better than those prepared using non-vacuum methods, sonochemical synthesis may be a simple and inexpensive technique for the synthesis of chalcopyrite I-III-VI_2 nano-inks for the preparation of $CuInS_2$ thin-film solar cells. Although there have been some attempts to prepare $CuInS_2$ nanoparticles using the sonochemical synthesis method [18–20], the performances of their solar cell are still poor. In the present work, the synthesis procedures for the preparation of $CuInS_2$ nanoparticles in an ultrasonic bath with various Cu/(Cu + In) molar ratios in the precursor solution are proposed. $CuInS_2$ thin films prepared from the obtained nano-inks were deposited on substrates using a spin-coating process. The optical and electrical properties of $CuInS_2$ thin films prepared using the sonochemical synthesis of $CuInS_2$ inks as a function Cu/(Cu + In) molar ratio in the precursor solution are studied.

2. Experimental details

2.1. Synthesis of $CuInS_2$ nanoparticles

The synthesis of $CuInS_2$ nanoparticles was carried out using the sonochemical synthesis method. Analytical-grade copper nitrate [$Cu(NO_3)_2 \cdot 2.5H_2O$], indium nitrate [$In(NO_3)_3 \cdot 5H_2O$], thioacetamide (CH_3CSNH_2, TAA), and absolute ethanol were purchased from Merck and Simga-Aldrich Co. and used as received. The copper to indium ratio [Cu]/[Cu + In] in the reaction solution bath was verified to study its effect on the preparation of $CuInS_2$ nanoparticles. 20 mL of ethanol bath, which was well stirred, contained 0.22–0.42 mmol copper nitrate, 0.32 mmol indium nitrate, and 2.86 mmol thioacetamide. The reaction solution was put into the water bath under ultrasonic irradiation (DELTA, UC-DC150H) operating at the frequency of 40 kHz, power of 200 W, and temperature of ultrasonic bath kept at 65 °C. The copper to indium ratios in the reaction bath used for the preparation of $CuInS_2$ nanoparticles are listed in Table 1. The reaction solution was sonicated for 4.5 h in order to obtain uniform $CuInS_2$ nanoparticles. The obtained $CuInS_2$ nanoparticles were rinsed with deionized water several times and dried in an oven at 90 °C. Finally, the $CuInS_2$ nanoparticles were annealed in a quartz tube at 450 °C for 1 h in order to obtain highly crystalline $CuInS_2$ powders.

2.2. Deposition of $CuInS_2$ thin films

PEG-500 (polyethylene glycol, average Mn = 500) and PEG-750 (average Mn = 750) were used to adjust the viscosity of the $CuInS_2$ ink for the preparation of $CuInS_2$ thin films on substrates. The volume ratio of PEG-500 and PEG-750 in the mixture was set at 3:2. The PEG mixture, which was mixed well, was mixed with the highly crystalline $CuInS_2$ nanoparticles. 0.2 g of $CuInS_2$ nanoparticles was added to 2 mL of the PEG mixture (PEG-500:PEG-750 = 3:2). The $CuInS_2$ inks were directly deposited onto the surface of soda-lime glass substrates or a Mo layer coated onto soda-lime glass to form the $CuInS_2$ thin films using the spin-coating process. Then, the as-deposited $CuInS_2$ films were placed in an oven and kept at 90 °C for 24 h in order to decrease the content of the PEG mixture. Then, the $CuInS_2$ thin films and a suitable amount of sulfur ($\sim$1 g) were put in a closed container made of aluminum oxide and loaded into an evacuated quartz tube with a vacuum of around 10^{-3} Torr. A three-stage temperature profile was used for the annealing of $CuInS_2$ thin films on substrates. In the first stage, the $CuInS_2$ thin films on substrates were annealed at 110 °C for 30 min in order to decrease the amount of PEG in the films. In the second stage, the $CuInS_2$ thin films on substrates and sulfur vapor provided from the sulfur powders in container were reacted at 160 °C for 30 min in order to incorporate some sulfur into the $CuInS_2$ thin films and decrease the sulfur deficits in samples. Finally, the samples were annealed at 450–550 °C for 20–90 min in order to obtain high-crystallinity $CuInS_2$ samples.

2.3. Characterization of $CuInS_2$ nanoparticles and thin films

The crystallographic study of $CuInS_2$ nanoparticles and thin films on glass substrates was conducted using an X-ray diffractometer (Siemens D5005) with CuKα (λ = 1.5405 Å) radiation. The X-ray diffraction (XRD) patterns of $CuInS_2$ samples were recorded in the 2θ range of 10° to 90°. The scan rate was set to 3° min^{-1} in order to increase the signal-to-noise ratio. The microstructures of $CuInS_2$ nanoparticles were investigated using transmission electron microscopy (TEM, JEOL JEM-1230). The surface microstructures of the $CuInS_2$ thin films on substrates were studied using field-emission scanning electron microscopy (FE-SEM, JEOL JSM 6700F). The compositions of the $CuInS_2$ thin films on glass substrates were analyzed using a scanning electron microscope (SEM, Hitachi S-3000N) equipped with an energy-dispersive analysis of X-ray (EDAX) detector. The mobility, resistivity, and carrier concentrations of the samples were measured using room-temperature Hall measurements (Ecopia Model HMS-3000) with a

Table 1
Physical properties of samples on glass substrates after three-stage annealing process.

Sample	[Cu]/[Cu + In] Molar ratio in solution bath	Molar ratios of thin film (from EDAX analysis)		Resistivity (Ω cm)	Carrier concentration (cm^{-3})	Mobility (cm^2/V s)	Direct band gap, E_g (eV)	Conduction type
		[Cu]/[Cu + In]	[S]/[Cu + In]					
(a)	0.57	0.60	1.14	5.33×10^{-1}	3.31×10^{18}	5.30	1.57	p
(b)	0.52	0.56	1.27	1.57×10^{0}	1.66×10^{18}	29.0	1.53	p
(c)	0.50	0.55	1.26	3.94×10^{1}	7.43×10^{16}	4.30	1.51	p
(d)	0.49	0.53	1.17	1.49×10^{2}	2.40×10^{16}	4.50	1.47	p
(e)	0.47	0.53	1.14	1.44×10^{1}	1.75×10^{16}	59.0	1.43	p
(f)	0.45	0.50	1.14	2.61×10^{2}	8.60×10^{15}	2.71	1.40	p
(g)	0.44	0.47	1.22	4.40×10^{2}	8.16×10^{15}	9.81	1.37	n
(h)	0.41	0.45	1.23	4.88×10^{2}	8.19×10^{15}	2.13	1.33	n

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