Quaternary Cu (In_xGa_{1-x}) Se_2 Nanoparticles Synthesis Using Heating-up Method for Photovoltaic Applications

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Received: Dec. 21, 2016, Revised: Mar. 11, 2017, Accepted: Apr. 4, 2017, Available Online: Oct. 28, 2017

ABSTRACT— In this paper, tetragonal chalcopyrite (CIGS) Cu(In_xGa_{1-x})Se_2 with x=0, 0.5, 0.8, 1 are synthesized by heating-up method. These nanoparticle structures differ in morphology and absorption properties due to the synthesis temperatures of 250, 255, 260, 265, 270 and 280 ºC, and gallium molar ratio over the total gallium and indium contents. These features are studied using scanning electron microscope, X-ray diffraction and absorption spectroscopy in visible, ultra-violet and near-infrared wavelengths. Results indicate that by increasing gallium content, absorption edge rises toward the visible light. Any modification in the absorption edge changes the band gap and as a result the energy gap and the absorption of cell increases considerably. Also in the heating-up method, increasing the reaction temperature improves nanoparticles crystallites. This leads the absorption improvement and higher cells efficiency. Produced nanoparticles are spherical shape with are varying the diameter around 30-80 nm.

KEYWORDS: CIGS nanoparticles, solar cells, non-vacuum method, heating-up method, characterization of CIGS.

I. INTRODUCTION

Today, thin films solar cells fabrication based on nanoparticles due to their fairly high efficiency and economically low production costs, becoming a routine process. CIGS based cells are one of the most famous types of second generation solar cells which provide considerable solar light absorption. Photovoltaic CIGS cells beside the capability for mass production, have higher efficiency in compare with silicon based solar cells. The band gap of these cells varies in a typical range of 1-1.7 eV when gallium and indium content change. [1-3]. Since these thin cells are produced in vacuum, their synthesis method is really costly and complicated so industrial production of these cells is not economical. Recently further attempts made toward synthesis of these materials in a non-vacuum environment to make these materials more commercially suitable. [4] CIS nanocrystals are highly effective materials for the light absorption purposes. This is true because these stoichiometric nanocrystals, not only decreases the film structures non-homogeneity at large scales, but also obviate films break down by annealing and salinization [5]. Recently several studies which have used CIS nanocrystals in solar cells have been performed [6-9].

Another disadvantage of current methods is that these methods use poisonous gasses like selenium vapor or atmospheric H_2Se_2 for producing CIGS deposited films or their oxides. Although the final product in these methods is nontoxic, still using these gasses in the early stages of production causes so many problems [10-12].

Variety of methods can be used for synthesizing the I– III–VI2 quaternary alloy systems, such as solvothermal techniques [13], hydrothermal techniques [14], single –source decomposition [15,16], and hot-injection technique [17,18]. Results from different researches indicate that crystal structure, composition, and size of the nanocrystals significantly affect their optoelectronic property and device performance

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[19]. Some of the solutions that can be employed are based on heating-up and polyol methods [20].

In this paper in order to economize the production process and optimize the product in commercial scales, non-vacuum methods are used for producing nanomaterials. The basic method which is used here to synthesize nanoparticles is called heating-up method. In this method, at first materials transfers to a glove box setup, which contains nitrogen or argon medium and materials weighted with specific stoichiometric ratios and putted in particular vessel which is attached to a banding nozzle. Whole set up has been connected to a Schlenk line and transfers to a silicon bath with a high temperature resistance [21]. The process is completed by increasing the temperature. Finally, nanoparticles appear in the vessel and by centrifugation can be separated and will be ready to use. This method is really favorable for producing solar cells due to the simplicity and low cost of the applied production method.

In this paper we report the synthesis of $Cu(In_xGa_{1-x})Se_2$ nanoparticles using heating up method and by considering different contents of x to obtain best absorbing particles in the visible region of electromagnetic spectrum. The obtained high absorption coefficient belongs to $Cu(In_{0.8}Ga_{0.2})Se_2$ which rarely mentioned before in the scientific literature. Also we have investigated the temperature effect on nanoparticles crystallite very accurately and with 5 ^{0}C intervals to manifest for the best condition to produce nearly ideal nanoparticles. This can offer a method with optimum condition and can be considered as one of the best condition for synthetizing CIGS nanoparticles.

II. EXPERIMENTAL PROCEDURES

A. *Chemicals*

Indium (III) chloride ($InCl_3$), gallium chloride ($GaCl_3$), cupper chloride ($CuCl_3$), Se powder (99.99%), and technical grade oleylamine (70%) were all purchased from Sigma-Aldrich. In order to follow up the safety procedure for chemicals, they should be unpacked and kept afterward under vacuum, nitrogen or argon atmosphere.

B. *Preparation of CIGS Nanoparticles by Heating-up Method*

In this paper, CIGS nanoparticles were produced by well- known heating-up method. In this method at first materials were transferred into a glove box and then weighted by considering materials specific stoichiometry and placed in a two-neck flask containing 12 mg of Oleylamine. One neck of the flask was connected to a stopcock valve and the other was attached to an oil bath. The stopcock valve was fastened before exiting the flask from the glove box. This configuration was then connected by a condenser to Schlenk line and then mounted in the silicon oil bath with a high temperature resistance. Stopcock valve was opened and the flask content stayed for 30 min at 60 ^{0}C under the vacuum condition. Then the vacuum pump evacuated the flask atmosphere, vacuum valve turned back and the mixture was put at nitrogen or argon atmosphere for 1 hour. at 130 ^{0}C to eliminate whole oxygen and water content. Then the mixture heated gradually up to 280 °C and kept at that temperature for 1.5 hour. Afterward the flask was disconnected, the content cooled by a water bath or an intense air stream until temperature reached 70-90 °C. At this point 10 ml ethanol and 5ml hexane was added to the flask and the mixture was centrifuged at 8000 rpm/min for 10 min until nanocrystals are isolated. The isolated nanocrystals were dispersed in hexane or toluene for further characterization purposes.

The synthesized nanoparticles have some impurities which include un-reacted materials. Therefore, in order to obtain pure particles, the product was washed several times with ethanol and distilled water, then dispersed in ethanol and centrifuged on 7000 rpm/min for several times to obtain purer nanoparticles. Finally, particles were dried at 70 °C for 12 hour. The resulting black powder was gathered and re-dispersed in ethanol or chloroform for the structural and microscopic analyses. The final products were black powders.

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III. RESULTS AND DISCUSSION

XRD Analysis

In these experiments, Indium (III) chloride ($InCl_3$), gallium chloride ($GaCl_3$), copper chloride ($CuCl_3$) and Se powder were used as the main chemical materials. As already mentioned here we produced CIGS nanoparticles where In (indium) and Ga (gallium) contents ratios were varied and by changing this ratio the optical properties of the final produced nanoparticles also changes. The In/Ga composition ratio in CIGS nanocrystals could be tuned across the entire x range from 0 to 1 by varying the In/Ga reactant ratio. The variation between the In/Ga ratio in the $Cu(In_xGa_{1-x})Se_2$ nanoparticles is clearly reflected from XRD data. At x=0, the XRD data correspond to chalcopyrite $CuGaSe_2$. As the In content increases, the diffraction peaks gradually shift toward lower 2θ angle, which is attributed to the increased lattice spacing of larger In atoms substitution for smaller Ga atoms.

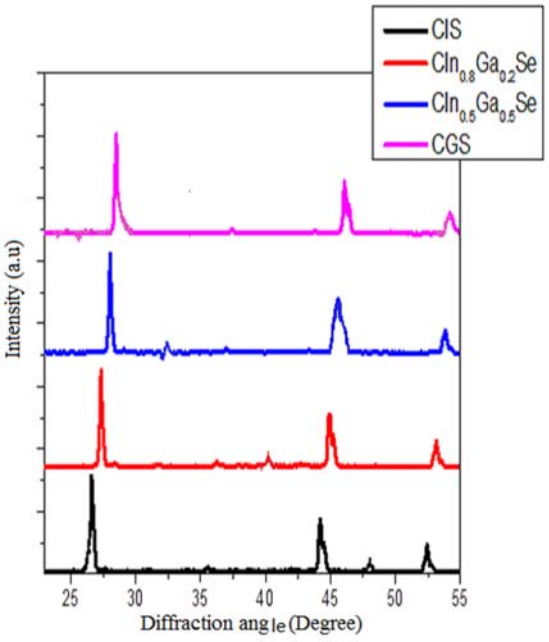


Fig. 1. Cu (In_xGa_{1-x}) Se_2 XRD patterns for different x values, by heating-up method and for 1.5 hour procedure.

As shown in XRD pattern (Fig. 1), the reaction product was delivered the peak pattern with the main peaks: CIGS [112] at about 2θ=270°, CIGS [204]/[220] at about 2θ=450°, and CIGS [116]/[312] at about 2θ=520°. This clearly showed the formation of a pure CIGS phase of the tetragonal crystal system.

It is all because of smaller lattice parameters which shift diffraction peaks toward higher angles sides [21]. Variation in the x value changes the position of peaks slightly, increasing the x value decreases Ga amount in the product and as a result X-ray diffraction occurs at lower angles. By decreasing the x value, gallium substitutes indium and since indium is smaller, the diffraction happens at higher degrees.

The recorded X-RD patterns for nanoparticles synthesized at different temperatures are depicted in Fig. 2. As the apparent diffraction angles do not change during temperature increase procedures, the only change clearly observed here is the change in the peaks heights which increases during heating-up stages. These increases are referring to the improvement which is developed in the structure of nanoparticles. As one can see for the XRD patterns for the 250-270 ºC samples, the height of the peaks increases but after that no considerable increase is observed in the heights of the peaks. Consequently, it can be concluded that the optimum temperature for the synthesis of nanoparticles by heating-up method is 270 °C.

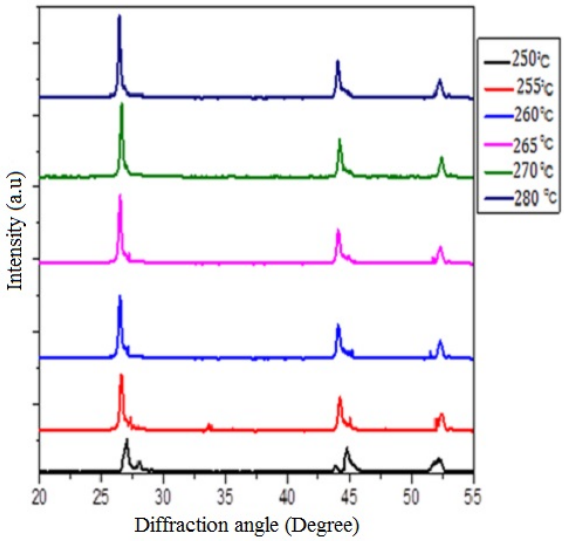


Fig. 2. Variation of $CuIn0.5Ga0.5Se_2$ diffraction peaks at different temperatures for 1.5 hour.

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SEM results

Results from SEM imaging indicates that at low temperatures only large particles of the precursor chemicals are observed (Fig. 3). When the temperature increases gradually more ions involve in the nucleation and during the synthesis procedure and the grain size of the final nanoparticles increases. Also as X-ray diffraction peaks are depicted in Fig. 2, peaks intensity improves by increasing the reaction temperature which implies that the synthesized nanoparticles become more ordered.

SEM results also indicates that the grain sizes of the synthesized nanoparticles by the heating-up method has average size of 70 nm and at the best condition (270 ºC, 1.5 hours) is about 50 nm which are affected by temperature and as mentioned before increase in temperature will increase the grain size of the synthesized nanoparticles.

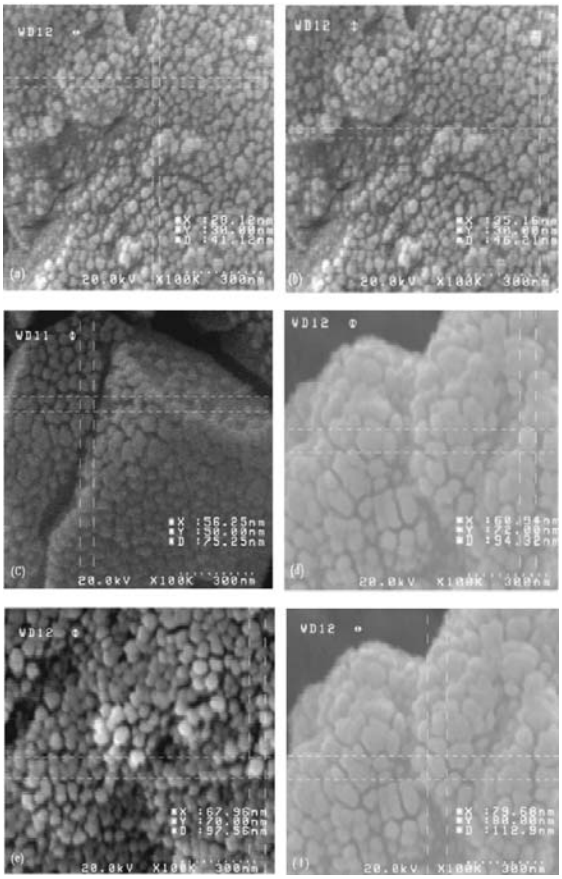


Fig. 3. $CuIn0.5Ga0.5Se_2$ nanoparticles synthesized by heating-up method at (a) 250 °C, (b) 255 °C, (c) 260 °C and (d) 265 °C, (e) 270 °C, (f) 280 °C and for 1.5 hour.

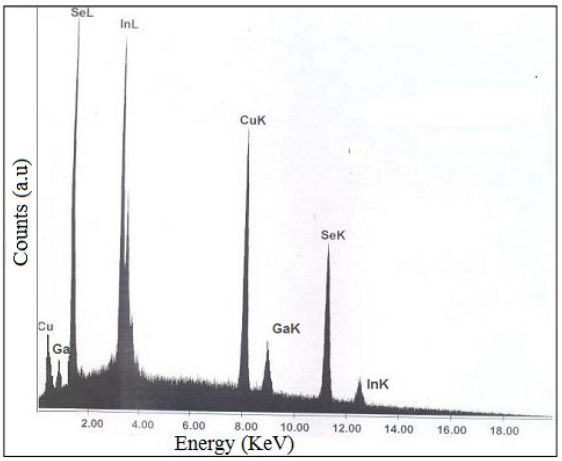


Fig. 4. EDX spectrum of CIGS nanoparticles exhibits the existence of all Cu, In, Ga and Se elements in the synthesized component.

The chemical composition of CIGS nanoparticles are ascertained using EDX analysis, as shown in Fig. 4. The existence of four elements, Cu, In, Ga and Se has been confirmed in CIGS. The results also indicate that no trace of any other element exists in the final composition. The x value has been controlled in the composition using EDX results and that the approximately stoichiometric ratio was obtained by choosing the right molar ratios of the precursor materials.

C. Absorption spectra

Metallic ionic solutions are capable to absorb visible light and the electrons inside the metallic elements can be excited easily from one electronic level to another one. Since CIGS solar cells are considered as the most important absorbing layer among the solar cells, we can search for a CIGS composition which has the highest optical absorption in the related spectral region. Fig. 5 depicts absorption spectra versus the wavelength for CIGS nanoparticles.

Figure 5 shows the light absorption for CIGS materials with different gallium contents. It is obvious that by increasing the indium to gallium ratio content increases the absorption and shifts the peak toward visible wavelengths. It is obvious that by increasing the gallium to indium ratio, an increase in the absorption peak and also shifts towards the visible wavelengths has been occurred.

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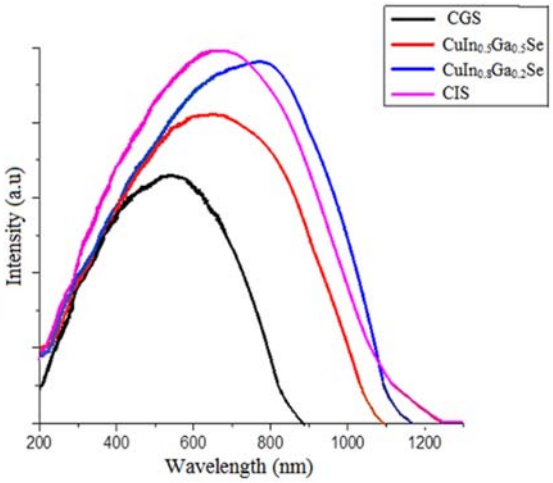
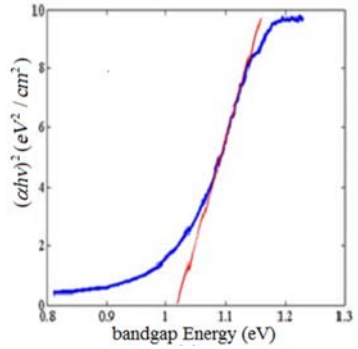
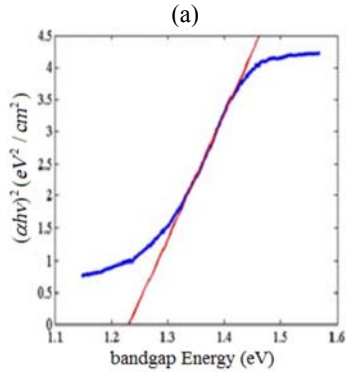


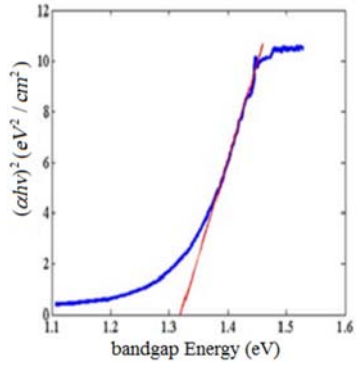
Fig. 5. CIGS absorption spectra for CGS, CuIn0.5Ga0.5Se$_2$, CuIn0.8Ga0.2Se2 and CIS nanoparticles.



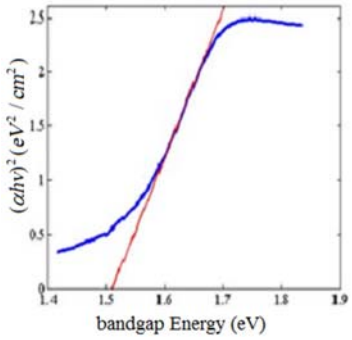
(a)



(b)



(c)



(d)

Fig .6. The band gap energy of CIGS nanoparticles, calculated by Tauc equation, (a) CIS, (b) CuIn0.8Ga0.2Se$_2$, (C) CuIn0.5Ga0.5Se$_2$, (d) CGS.

From these absorption spectra, it is possible to determine the band gap of the synthetized CIGS nanoparticles. Using the Tauc relation [8], the band gap energy can be determined by the absorption spectra:

$$\alpha hv = A(hv - E_g)^n \quad (1)$$

where A is a constant, α is the absorption coefficient, Eg is the average band gap of the synthesized material and n depends on the type of transition. For the direct band gap semiconductor, n=1/2. The average band gap was estimated from the intercept of the linear portion of $(\alpha hv)^2$ versus hv plots.

IV. CONCLUSION

In this paper CIGS nanoparticles synthesis with different Ga/In ratio using heating-up method was investigated. Results indicates that by increasing the synthesis temperature, the crystal structure of the synthesized molecules improves. The synthesized samples are characterized using XRD analysis and we find that by increasing the synthesis temperature, the resulted dispersion peaks intensity increases which indicates the improvement of crystal structure and its regularity. Also we changed gallium/ indium ratio in the CIGS samples. XRD results showed that by increasing the gallium contents the diffraction peaks appear at higher angles. By increasing the gallium contents and because the gallium atoms are smaller than indium atoms, the diffraction occurs at higher degrees and diffraction curve

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shifts to the right and toward the higher diffraction angles. The grain sizes of the synthesized nanoparticles depend on the reaction temperature and in general the grain sizes of the particles vary in the range of around 30-50 nm by using this heating-up method.

The recorded absorption spectra for the synthesized CIGS solar cells indicate that these nanoparticles have considerable absorption at the visible and near infrared region. Increasing the gallium contents causes shifts of the absorption edge towards the visible region, the variation at the absorption edge changes the band gap and as a result the energy gap changes and the absorption improves considerably.

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