

Synthesis of nanostructured CuInSe₂ (CIS) powder via solvothermal processing using diethylamine as a solvent

M. Najafi^a, M. R. Vaezi^{a,*} and S. K. Sadrnezhad^b

^aDivision of Nanotechnology and Advanced Materials, Materials and Energy Research Center, Karaj, Iran

^bDepartment of Materials Science and Engineering, Sharif University of Technology, Tehran, Iran

In this paper, CuInSe₂ nanostructures have been synthesized via a solvothermal method using diethylamine as a solvent. Various morphologies of CuInSe₂ were obtained from the reaction of cupric chloride, indium chloride and selenium powder by changing the solvothermal conditions. The effect of the experimental parameters such as reaction time, temperature and concentration of the selenium powder were studied. The crystalline structures and morphologies of the products were characterized by means of X-ray diffraction (XRD) and field-emission scanning electron microscopy (FE-SEM) techniques, respectively. The results show that the morphology and dimensions of the CIS nanostructures obtained can be controlled through selective processing conditions. The optical properties and band gaps were estimated with a UV-Vis spectrophotometer. The electrical resistances of the samples were recorded by using four point probes.

Key words: CuInSe₂, Nanostructure, Solvothermal Synthesis, Optical Properties, Diethylamine.

Introduction

In recent years, the synthesis of nanostructured semiconductors has been of interest to materials scientists due to their outstanding physical or chemical properties [1]. Nanostructured semiconductor materials of ternary chalcogenide compounds such as CuInSe₂, which belong to the I-III-VI₂ family, have been extensively studied as promising materials for electronics devices, optoelectronics and solar cell applications because of their high absorption coefficient, suitable band gap, good radiation stability and easy conversion of n/p carrier type [2]. In fact, devices based on CuInSe₂ have achieved a conversion efficiency up to around 17% in solar cells [3]. Many techniques have been established to prepare CuInSe₂ including evaporation [4], spraying [5], electrodeposition [6], sputtering [7] and selenization [8]. However, these techniques usually require either a high temperature or special devices, and some of them use toxic agents or organometallic compounds [9]. In addition, it is difficult with almost all of these methods to maintain satisfactory stoichiometry [10]. Controlling parameters such as particle size and morphology, which can tailor the band gap, provide a novel approach to the development of materials for device applications [11]. Recently, solution-based methods have been used to fabricate nanostructured materials at much lower temperatures [12–14]. The solvothermal method acts as a route

for controlled synthesis of these materials.

In this paper, we used a solvothermal route to produce various types of chalcopyrite CIS nanostructures such as nanoparticles, nanorods and nanoplates using diethylamine as a solvent.

Experimental

In a typical experimental procedure, stoichiometric mixtures of selenium powder (Merck, > 99%), CuCl₂·2H₂O (Merck, > 99%) and InCl₃·4H₂O (Aldrich, > 97%) were loaded into a 80 ml Teflon-lined stainless steel autoclave filled with anhydrous diethylamine up to 80% of total volume. The autoclave was sealed and heated to the different reaction temperatures for various times. The experimental variables used in this research are listed in Table 1. Then the autoclave was cooled to room temperature naturally. The resulting precipitates were centrifuged and washed with distilled water and absolute ethanol to remove any dissoluble by-products. After being dried in vacuum at 60 °C for 4 h., the final dark product was collected.

The samples obtained were characterized using a SIMENS (PNAalytical X'Pert) X-Ray diffractometer with Cu-K α radiation at room temperature. The morphology and composition of the CIS was determined using a field-emission scanning electron microscope (FE-SEM) (Hitachi-S4160 Japan). The optical properties were recorded at normal incidence at room temperature using a (UV-VIS) spectrophotometer (PerkinElmer Spectrometer LambdaLS USA). The electrical resistances of the samples were recorded at room temperature using (FPP-5000 Automatic Resistivity Meter U.S.A) four point probes.

*Corresponding author:
Tel : +98-261-6280030
Fax: +98-261-6201888
E-mail: m_r_vaezi@merc.ac.ir

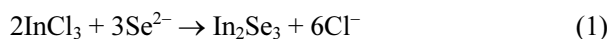
Table 1. The experimental variables used in this study

Sample	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
Reaction Temperature (°C)	150	180	210	240	210	210	210	210	210	210
Reaction Time (h.)	12	12	12	12	24	36	48	12	12	12
Selenium Concentration ($\times 10^{-2}$ M)	4	4	4	4	4	4	4	2.5	5	7.5

Results and Discussion

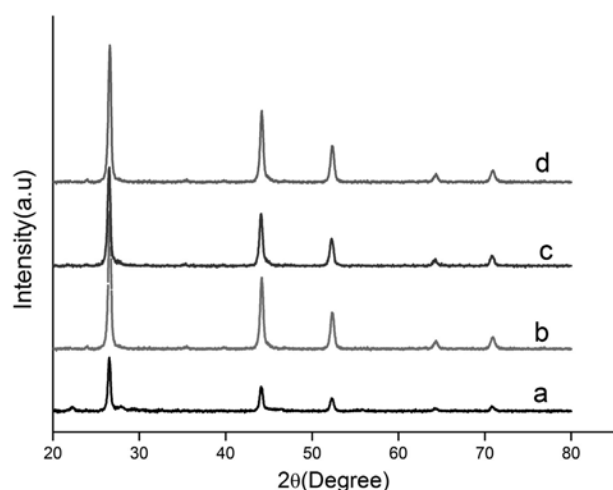
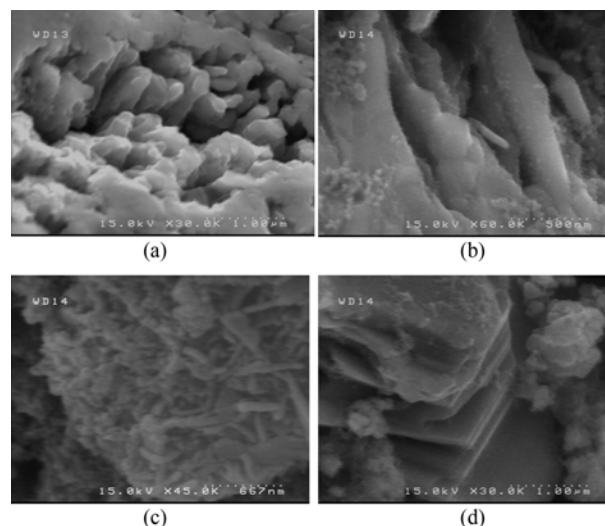
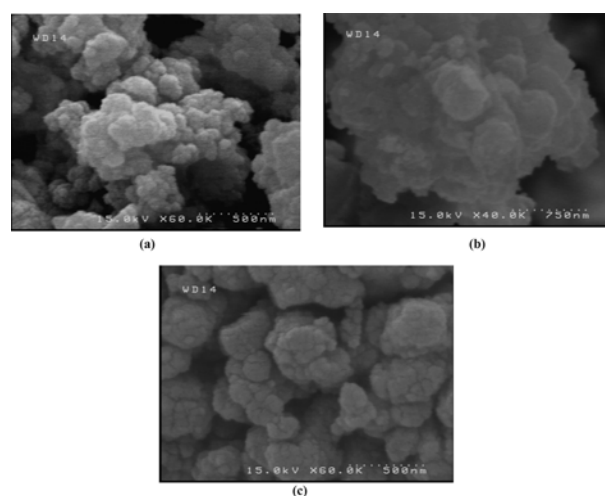
Effect of varying the temperature

XRD patterns of the samples C1, C2, C3, and C4 are shown in Fig. 1. As it can be shown in Fig. 1, only the chalcopyrite phase can be detected in the patterns. The diffraction peaks of sample C3 (Fig. 1(c)) can be indexed to the pure phase of CuInSe_2 with the chalcopyrite structure and no peaks of other impurities were detected. This pattern is in good agreement with the literature [15]. As can be seen in Figs. 1(a), and 1(b), at the lower temperatures such as 150 °C and 180 °C some impurities such as In_2Se_3 were detected in the XRD patterns at $2\theta = 22.16^\circ$. With an increase of the temperature, the intensity of this characteristic peak decreases and is diminished gradually. Therefore at 210 °C and 240 °C no peaks of impurities existed in the diffractograms. In the solvothermal process, a nucleophilic attack by amine can activate elemental selenium to form Se^{2-} . The precipitate of In_2Se_3 is due to the following equation [16]:



The morphologies of the synthesized product depend on both the temperature and the concentration of selenium and are time independent. As can be seen in Fig. 2, with an increase of the temperature from 150 °C to 240 °C, the morphology of synthesized CIS changes from nano rod to plates.

The initial nuclei play an important role as initiators

**Fig. 1.** XRD patterns of samples C1 (a), C2 (b), C3 (c), and C4 (d) synthesized at 12 h. and selenium concentration of 4×10^{-2} M.**Fig. 2.** FE- SEM images of CIS samples C1 (a), C2 (b), C3 (c), and C4 (d) synthesized at 12 h. and a selenium concentration of 4×10^{-2} M.**Fig. 3.** FE- SEM images of CIS samples C5 (a), C6 (b), and C7 (c) synthesized at 210 °C and selenium concentration of 4×10^{-2} M.

(or seeds) for the growth of one- dimensional CuInSe_2 [17], while in increase of the temperature, some of the nanorods already possessed quite large aspect ratios and had grown to hundred nanometres in length.

Effect of time

The reaction time can influence the dimensions of synthesized precipitates. The dimensions of the precipitates increase considerably with an increase of the reaction time. Fig. 3 shows FE-SEM images of samples C5, C6, and C7 synthesized by the solvothermal reaction. As can

be seen in Fig. 3, the average diameter of the spherical particle and nano rods ranges from 30-50 nm (Fig. 3(a)) and 70-120 nm (Fig. 3(b)), respectively. Also, the average width of the nano plates is 670 nm and their thickness is 80 nm (Fig. 3c).

Temperature and time play an important role in the formation of CIS nanostructures. A rise in the temperature will increase both the nucleation rate and the growth rate; hence, the crystallinity of the samples normally increases with time. Also, CIS nanostructure synthesis is governed by the occurrence of successive phase transformations (Ostwald rule of successive phase transformation). The thermodynamically least favorable phase will crystallize first and will be successively replaced in time by more stable phases [18]. The temperature, however, can also influence the type of product that has to be crystallized. The temperature can obviously affect on the rate of nucleation and crystal growth.

Effect of concentration

Varying the selenium concentration results in different morphologies. Fig. 4 shows the FE-SEM images of samples C8, C9, and C10 synthesized by the solvothermal reaction. As can be seen in Fig. 4, the morphology of precipitates obtained at selenium concentrations of 2.5×10^{-2} M, 5×10^{-2} M, 7.5×10^{-2} M are nanoparticles, nanoplates and a minor amount of nanorods, and a major amount of nanoparticles and a minor amount of nanorods, respectively. At a selenium concentration of 4×10^{-2} M (sample C3), the morphology of precipitates contains a major amount of nanorods (Fig. 2(c)). It is believed that the competition between nucleation and growth processes takes place during the time of growth. At low concentrations, such as 2.5×10^{-2} M, the nucleation rate is not noticeable and there is a low growth rate of nanoparticles. Therefore, these nanoparticles can not grow in the preferred direction and consequently the morphology of nanoparticles can exist as spherical or semi- spherical shapes (Fig. 4(a)).

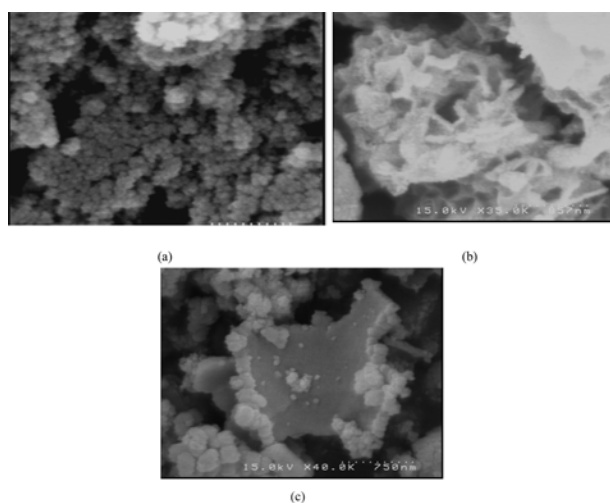
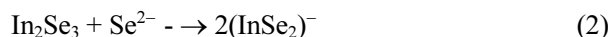


Fig. 4. FE- SEM images of CIS samples C8 (a), C9 (b), and C10 synthesized at 210 °C and a time of 12 h.

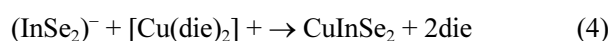
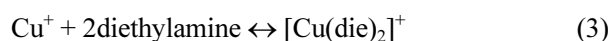
With an increase of the concentration up to a critical limit, both the nucleation rate and growth rate are increased and therefore the particles grow preferentially in one direction (for example in the longitudinal direction) and nanorods can be formed. In this research paper, according to the increase of the formation of nanorods at a concentration of 4×10^{-2} M (sample C3, Fig. 2(c)), this concentration can be considered as the critical concentration. When the concentration increases above the critical concentration, the growth rate will increase and therefore the growth occurs in other directions and the formation of plates can be observed.

At room temperature, the elemental Se is soluble in diethylamine. This dissolution is accompanied not only by a color change of the solution from opaque to brown, but also the instant disappearance of the Se powder. The reactivity of Se is enhanced by its dispersion into diethylamine. In the solvothermal reaction, the dissolved elemental Se is reduced to negatively charged Se²⁻ ions by amines in an organic nucleophilic attack. When the temperature increases, In₂Se₃ which has low solubility in diethylamine, reacts with Se²⁻ ions to form (InSe₂)⁻ (eq. 2) [17]:



The diethylamine non-aqueous solvents play an important role in controlling the nucleation and grow of the CuInSe₂ nanostructures. Diethylamine is an excellent template for the formation of one-dimensional materials [19]. Templating has an important role in the preparation of materials and compounds. Both organic and inorganic agents can be used as templating agents. Generally, this route uses channels, layers, and cavity spaces of nanoporous host structures to grow the nanoscale materials [20]. Templating contributes to the stability through new interactions such as electrostatic and London dispersion interactions and further controls the formation of a particular topology through its geometry (morphology and size) [21]. Thus, the action of a template appears to have both electronic and steric components.

In the solvothermal process, the solvent plays an important role in the formation of the chalcopyrite CuInSe₂ compound. Alkylamine can greatly enhance the solubility, diffusion, and crystallization but still provides reaction conditions mild enough to enable molecular building blocks to participate in the following formation of the solid-state phase [18]. The proposed mechanism involved in this solvothermal reaction for the growth of CuInSe₂ can be summarized as eqs. (1) to (4):



Conclusions

Stoichiometric CuInSe₂ nanorods, nanoparticles and nanoplates of a high quality have been synthesized by a

solvothermal route. This method can be easily controlled and is expected to be applicable to fabricate other nanosized ternary compounds. It was found that the solvent type, the solution concentration, the reaction temperature, and the reaction time influence the morphology, phase, and the growth dimensions of the above-mentioned nanostructures. A comparison of the X-ray powder diffraction pattern with that of known phases suggested that the material was a new phase with the Chalcopyrite structure. When diethylamine was used as the solvent, sheets with a minor amount of particles, rods, and plates were obtained at 150 °C, 180 °C, 210 °C and 240 °C with a selenium concentration of 2.5, 4, 5 and 7.5×10^{-2} M. Generally, the dimensions of the precipitates were found to increase with the reaction time but not with the temperature. Also, the variation of the solution concentration results in mixed geometries.

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