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Synthesis of copper indium diselenide nanostructure by solvothermal method

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Abstract:

This paper studies the synthesis of $CuInSe_{۲}$ nanostructure from a solvothermal method with diethyamine as a solvent. Various morphologies $CuInSe_{۲}$ were obtained by changing solvothermal conditions. From the reaction of cupric chloride, indium chloride and selenium powder in an autoclave with diethylamine as solvent different nanostructure morphologies were obtained. The effect of the experimental parameters including time, temperature and concentration of the reactions were studied. The crystalline structures and morphologies of products were characterized by means of X-Ray diffraction (XRD) and Field-Emission scanning electron microscopy (FE-SEM) images. The results show that through selective processing conditions, the phase, morphology and dimensions of the obtained CIS nanostructures can be controlled.

Keywords: $CuInSe_{۲}$, nanostructure, solvothermal synthesis, solar cell.

Introduction

In recent years, ternary chalcopyrite semiconductor nanostructures are being intensively investigated for low cost photovoltaic applications. With a direct band gap of ١.٠٢ eV and a high absorption coefficient of more than $١٠^{٤}$ $cm^{-١}$, $CuInSe_{۲}$ has been regarded as a favorable absorber material for use in thin film solar cells [١-٣]. The ternary compound $CuInSe_{۲}$, which belongs to the I-III-$VI_{۲}$ family, has emerged as a leading material for high efficiency and radiation-hard solar cell applications. In fact, devices based on $CuInSe_{۲}$ have achieved conversion efficiency up to around ١٧٪ in solar cells [٤].

Using particle size and morphology as control parameters to tailor band gap provides a novel approach to the development of materials for device applications. Nanocrystalline materials have a wide range of optical and electronic properties that are accessible in the nanoscale [٥].

Nanocrystals have been prepared with various synthetic methods. Many approaches involve aqueous solution and the classical techniques of colloidal chemistry [٦]. Many techniques have been established to prepare $CuInSe_{۲}$ including evaporation [٧], spraying [٨], electrodeposition [٩], sputtering [١٠] and selenization [١١]. However, these techniques usually require either a high temperature or special devises, and some of them use toxic agents or organmetallic compounds [١٢]. In addition, it is difficult with almost all of these methods to maintain satisfactory stochiometry [١٣]. 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 [١٤] We have been interested in the use of a solvothermal route, which is carried out at low temperature and does not require organometallic or toxic precursors; to produce various kinds of nanocrystalline materials [١٥]. Here we report a solvothermal route to chalcopyrite $CuInSe_{۲}$ nanocrystals using alkylamines as a solvent. In diethylamine $CuInSe_{۲}$ nanostructure was obtained as nanorod, nanoplate and nanoparticles.

Experimental

The nanostructures were synthesized using a solvothermal processing. A stoichiometric mixture of selenium powders, $CuCl_{۲}\cdot ۲H_{۲}O$ and $InCl_{۳}.٤H_{۲}O$ was first dissolved in an anhydrous solvent. The anhydrous solvents used include ethylenediamine and diethylamine.

The solution was then loaded into an ٨٠-mL Teflon-lined stainless steel autoclave up to ٤٥٪ of the total volume. For the solvothermal synthesis, the sealed autoclave was heated to a reaction temperature of ١٨٠ °C, ٢١٠ °C, and ٢٤٠ °C for ١٥ h. and then cooled down to room temperature.

After the synthesis, the precipitates were centrifuged and washed with distilled water and absolute ethanol several times to remove the solvent and by-products. The samples were placed in a ٦٠ °C oven for ٦-h to obtained dried powders. The dried powders were analyzed using scanning electron microscopy (SEM) operated at ٢٠ Kv. and X-ray diffraction technique.

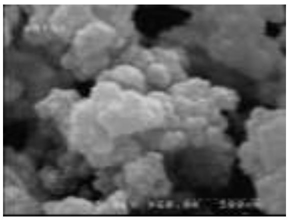
Results and Discussion

CuInSe٢ nanopowders having various morphologies, shapes, and dimensions were obtained. The effect of temperature is first presented, followed by effect of; finally, the crystalline nanostructures are presented and discussed.

Effect of temperature

Here, we examine the effects of temperature using diethylamine as solvent. particles (Fig. ١A), plates (Fig. ١B), and rods (Fig. ١C) were obtained at ١٨٠ °C, ٢١٠ °C, and ٢٤٠ °C, respectively.

XRD patterns of the samples ١٨٠, ٢١٠, and ٢٤٠ ºC are shown in Fig. ١. As it can be shown in Fig. ١, only the chalcopyrite phase can be detected in the patterns. The diffraction peaks of sample ٢١٠ ºC can be indexed to the pure phase of CuInSe٢ with the chalcopyrite structure and no peaks of other impurities were detected. This pattern is in good agreement with the literature [١٦].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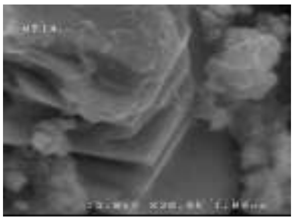
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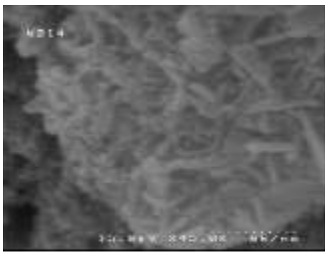
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Fig.٢. FE- SEM images of CIS samples ١٨٠°C (a), ٢١٠°C (b), ٢٤٠°C (c) synthesized at ١٢ h. and a selenium concentration of ٤* ١٠-٢ M.

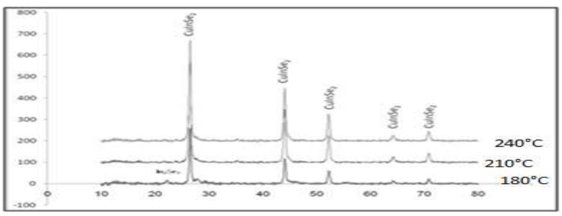
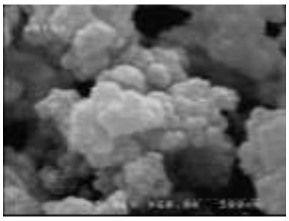


Fig٢. XRD diffractogram of CuInSe٢ synthesized at ١٨٠ °C , ٢١٠ °C and ٢٤٠ °C for ١٢ h.

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. ٣ shows FE-SEM images of samples obtained at ١٢ h (Fig. ٣A), ٢٤ h (Fig. ٣B) and ٣٦ h (Fig. ٣C) respectively. As can be seen in Fig. ٣, the average diameter of the spherical particle and nano rods ranges from ٣٠ - ٥٠ nm (see Fig. ٣A) and ٧٠ - ١٢٠ nm (see Fig. ٣B), respectively. Also, the average width of the nano plates is ٦٧٠ nm and their thickness is ٨٠ nm (Fig. ٣C).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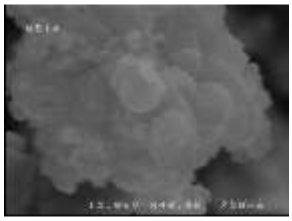
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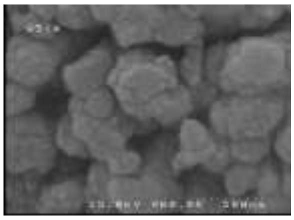
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Fig.٣. FE- SEM images of CIS samples ١٢ (a), ٢٤ (b), and ٣٦ h (c) synthesized at ٢١٠ ºC and selenium concentration of ٤* ١٠-٢ M.

Effect of concentration

Varying the selenium concentration results in different morphologies. Fig. ٤ shows the FE-SEM images of samples ٢.٥, ٥, and ٧.٥×١٠-٢ M synthesized by the solvothermal reaction. As can be seen in Fig. ٤, the morphology of precipitates obtained at selenium concentrations of ٢.٥×١٠-٢ M, ٥×١٠-٢ M, ٧.٥×١٠-٢ M are nanoparticles, nanoplates and a minor amount of nanorods, and a major amount of nanoparticles and a minor amount of nanorods, respectively.

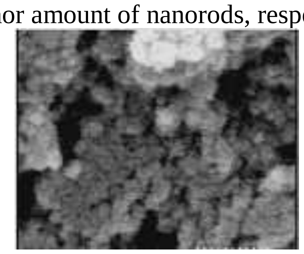
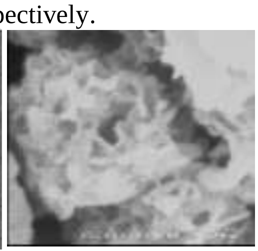
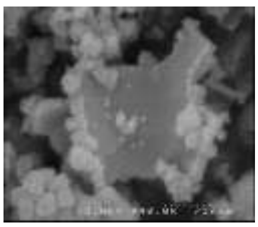

Fig.٤. FE- SEM images of CIS samples ٢.٥ (a), ٥ (b), and ٧.٥ ×١٠$^{-٢}$ M synthesized at ٢١٠ ºC and a time of ١٢ h.

Conclusions

In summary, we have successfully synthesized CuInSe$_{٢}$ particles, plate and rods. It was found that the time, concentration and reaction temperature influences the morphology, phase, and dimensions of the nanostructures. Stoichiometric CuInSe$_{٢}$ 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.

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