Journal of Alloys and Compounds 690 (2017) 15–20

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Characterization of calcined $CuInS_2$ nanocrystals prepared by microwave-assisted synthesis

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ARTICLE INFO

Article history:
Received 23 June 2016
Received in revised form
11 August 2016
Accepted 13 August 2016
Available online 15 August 2016

Keywords:
Calcined CIS
XRD
FTIR
SEM
Raman
Transmission

ABSTRACT

In this work, $CuInS_2$ (CIS) nanocrystals are successfully synthesized by microwave-assisted technique and further calcined at several different temperatures with or without additional Ar ambient. The XRD measurements showed that a significant recrystallization might have occurred with the help of Ar ambient to introduce the increasing relative intensity of the (112) diffraction peak. Furthermore, the eliminated organic-related structures and the enlarging $CuInS_2$ nanocrystals are evidently confirmed by FTIR and SEM, respectively. Raman analysis of the CIS(CH) mode of the $CuInS_2$ nanocrystals in the calcined temperature range of 200–400 °C is presented while the lineshape is described and calculated by the spatial correlation model corresponding to the presence of a long-range order in the higher calcined temperature of $CuInS_2$ nanocrystals. Transmission can be used to figure out that the calcined $CuInS_2$ nanocrystals with Ar are related with the modification of the optical band gap energy.

1. Introduction

Ternary compound of $CuInS_2$ (copper indium disulphide, CIS) material belonging to I-III-VI semiconductor is a promising material for the high efficiency solar cell fabrication due to the high absorption coefficient (~10^5 cm^{-1}) and direct band gap of around 1.5 eV [1]. Up to now, $CuInS_2$ materials have been produced by several different methods, such as sputtering [2], spray pyrolysis [3,4], molecular beam epitaxy [5,6], sulfurization, successive ionic layer adsorption and reaction [7,8], evaporation [9,10]. Some important developing results of solar cells based on $CuInS_2$ have been made in the past several years to carry out that there are three possible structures, including the chalcopyrite (CH) phase, Cu–Au (CA) phase, and Cu–Pt (CP) phase, but CH and CA phases are usually observed at room temperature to be stable phases and coexisted in the produced $CuInS_2$ material due to the low formation energies [11–15]. As we have known that the CA phase is involved with the decreasing of grain size but the increasing of defects in grains, and further with degradation of the solar cell efficiency [16,17]. Recently, the method of microwave-assisted synthesis has been used a lot due to the advantages of being faster, simpler and more energy efficient [18]. In this way, the precursor solution is irradiated with a microwave source to let the efficient energy transfer through either resonance or relaxation and result in a somewhat rapid heating process. Moreover, the heating process can produce inhomogeneous heating of the precursor solution in a very short duration to complete a uniform distribution of particle size. Consequently, the microwave hydrothermal process might be kinetically more efficient than the conventional hydrothermal process for preparing various nano-particles [18]. However, few related works concerning the microwave-assisted synthesis of $CuInS_2$ on the physical properties have been reported, more systematic studies are quite necessary in order to develop better conversion efficiency [19–21].

In this work, we report on the use of microwave-assisted synthesis for growing $CuInS_2$ nanocrystals while the crystalline quality, defects and impurity contents are investigated by using x-ray diffraction (XRD) and Fourier transformed Infrared (FTIR) spectroscopy, respectively. In addition, the morphologies of $CuInS_2$ nanocrystals under calcined-treatment are confirmed by scanning electron microscopy (SEM). Moreover, the CIS(CH) mode in the Raman shift range of 260–340 cm^{-1} at 300 K is studied to carry out the linewidth and asymmetric of Raman lineshape in terms of the

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http://dx.doi.org/10.1016/j.jallcom.2016.08.098
0925-8388/

spatial correlation (SC) model regarding to the finite correlation length of a propagating phonon due to the calcination. In the end, transmission spectroscopy is used to verify the band gap after calcination.

2. Experimental

$CuInS_2$ nanocrystals were produced by the technique of microwave-assisted synthesis. Based on the 0.03 M ethanol, a precursor solution was prepared by stirring a mixed molar ratio of 1:1:3 for $CuCl_2$, $InCl_3$, and Na_2S to get a well-dissolved solution. Then, the obtained solution was placed into a microwave oven and heated from room temperature up to 60 °C with magnetic stirring within half an hour. Finally, the formed powder was cleansed twice with alcohol and dried at room temperature. All the $CuInS_2$ nanocrystals have to be mixed with PEG (Polyethylene glycol) and deposited on corning glass using the method of doctor blade. For comparison purpose, two samples were calcined for 2 h at the temperatures of 200 °C, and 400 °C without Argon (Ar) ambient, respectively. Three other samples were calcined for 2 h at 400 °C, 500 °C, and 550 °C with additional Ar ambient (99.999%), respectively.

For the XRD measurements, θ -2θ scans were done from 25° to 60° by the XRD spectrometer (Shimadzu XRD-6000) with a CuKα line of 1.5405 Å to study the crystal phases for the as-synthesized and calcined $CuInS_2$ nanocrystals while the FTIR spectroscopy were used to detect the defects and impurity contents. The SEM images were taken on a JEOL-JSM7001F to investigate the morphology of the as-synthesized and calcined $CuInS_2$ nanocrystals. Raman scattering were applied to study the structural quality and phase purity at 300 K by using the Renishaw system (inVia Raman microscope) while the spectra were excited by using the 514.5 nm line of an Ar^+ laser at an incident power of 10 mW with the experimental error ± 1 cm^{-1} for the linewidth and ± 0.5 cm^{-1} for the peak position, respectively. The absorption spectra were obtained from the transmission measurement setup by monochromatic light from the Oriel 1000 W halogen light source. The transmitted light passed through the sample and then to Si detector. The signal was measured by a lock-in amplifier and recorded by a computer.

3. Results and discussion

To study the structural properties, Fig. 1(a) compares the XRD θ -2θ scanning results of the as-synthesized $CuInS_2$ nanocrystals and samples calcined for 2 h at 200 °C, 400 °C, 400 °C + Ar, 500 °C + Ar, and 550 °C + Ar. It is found that the as-synthesized sample has XRD peak positions of CIS(112), CuS(103), and Cu_2S(110) corresponding to the XRD data from the standard powder diffraction file (PDF) card #27–0159, #06–0646, and #26–1116, respectively. Therefore, it is assumed that the as-synthesized $CuInS_2$ nanocrystals link to chalcopyrite (CH) structure and it is expected to focus on the peak position of (112) due to the direct connection with the crystal quality [22,23]. The diffraction peaks of (112) are still quite weak for the $CuInS_2$ nanocrystals calcined at 200 °C, probably due to the poor crystallinity and small crystallite size, however the diffraction peak of (112) is getting stronger after the calcined temperature of 400 °C. This phenomenon may be related to solid-state effects during the higher calcined temperature, as the calcined temperature was further increased to 550 °C + Ar, the (112) peak became more intense and narrower, indicating better crystallinity.

Additionally, the as-synthesized sample of (112) peak position in XRD spectra cannot be identified, perhaps more concentration of CuS during the synthesis of CIS, however a significant recrystallization might have occurred with the help of Ar ambient in the process of calcination, as a result of the interesting to note that the relative intensity of the (112) diffraction peak increases. Then, Fig. 1(b) is shown the typical selected calcined samples of the (112) diffraction peaks and the value of FWHM (full-width at half maximum) is estimated to calculate the average crystallite size (D) of the $CuInS_2$ nanocrystals by Scherrer's formula: $D = 0.9\lambda/\beta\cos\theta_B$, where λ is the X-ray wavelength, β is the value of FWHM in radians, and θ_B represents the diffraction angle at a certain crystal plane [24]. Values calculated for the crystallite size of the typical selected calcined samples are shown in Fig. 1(c), our estimated values of the as-synthesized and calcined samples at 400 °C, 400 °C + Ar, 500 °C + Ar, and 550 °C + Ar are 6.0 nm, 9.6 nm, 9.8 nm, and 10.6 nm, respectively. Thus, the XRD analysis indicated that the calcined sample at 550 °C + Ar resulted in the largest average crystallite size with the narrowest FWHM. For this work, better crystallinity means larger crystallite size, however larger crystallite is quite required for the production of the higher efficient CIS solar cell.

Further examining the contents of organics and the evolution of calcined treatments in $CuInS_2$ nanocrystals, the variations of the defect and impurity in the as-synthesized as well as the calcined $CuInS_2$ nanocrystals were investigated by the technique of FTIR. The results are displayed in Fig. 2 for the as-synthesized $CuInS_2$ nanocrystals, the peak at around 3423 cm^{-1} is appointed to be the O–H stretching variation mode of hydroxyl group but the peak at about 1622 cm^{-1} belongs to the C=O symmetry stretching vibration of [bis(2-hydoxyacetophenato)copper(II)] groups [25,26]. The spectrum also indicated the absorptions at around 1117 cm^{-1}, 1016 cm^{-1}, 657 cm^{-1}, and 530 cm^{-1} which are assigned to CIS, SO_4, CuS, and CuO, respectively [27–29]. As increasing the calcined temperature to 400 °C, not much reformed for all modes. However, the O–H stretching variation mode and the C=O symmetry stretching vibration mode start disappearing after increasing calcined temperature with additional Ar ambient (400 °C + Ar, 500 °C + Ar, and 550 °C + Ar). Then, our studies propose that the organic-related structures from the synthesis of microwave could be almost removed as the calcined temperature approaching to 550 °C + Ar along with this consequence is involved with the crystal improvement as well.

The morphology and powder size of the as-synthesized and calcined $CuInS_2$ nanocrystals were studied by SEM. As shown in Fig. 3(a), the SEM image of the as-synthesized $CuInS_2$ nanocrystals showed particulates shrouded by a large cloud of organic complexes. Therefore, this result is also identified by the FTIR spectrum for the as-synthesized $CuInS_2$ nanocrystals where contained a rich conglomeration of impurity related features and this maybe the reason for the weak signatures of our discussed XRD diffraction patterns. For the calcined temperature of 400 °C + Ar, the SEM image as depicted in Fig. 3(b) shows a distinct morphology with particulate formation of $CuInS_2$ nanocrystals. The observation becomes even apparent as the calcined temperature is raised. Thus, the trend in the increase in average size of the $CuInS_2$ nanocrystals with increase in calcined temperature is clearly illustrated by Fig. 3(b ~ f) and the current observation also indicates a rather uniform size distribution of the $CuInS_2$ nanocrystals. For the case of the calcined temperature at 400 °C + Ar in Fig. 3(d), the width of a single grain of $CuInS_2$ nanocrystals is about 100 nm with a length of about 100 nm, which is much larger than the crystal size of 9.6 nm estimated by the Scherrer's formula. This discrepancy might be understood by recording that the SEM images give the size of the $CuInS_2$ nanocrystals, which maybe as a result of agglomeration of many nano-particles. Therefore, the size of $CuInS_2$ nanocrystals as shown in the SEM image is larger than the average particle size calculated from the XRD spectra. Nevertheless, the results of SEM and XRD are consistent and show an increase in the crystal size