Materials Letters 170 (2016) 151–155

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Solid solution synthesis of $(In_{1-x}Ga_x)_2Se_3$ Nanocrystals $(0 \le x \le 1)$ by a triethylene glycol based solution process

Yaxi Hu [a], Jian Wang [a], Junyun Lai [a], Xuerong Zheng [a], Huanli Ji [a], Hui Liu [b], Zhengguo Jin [a,*]

[a] School of Materials Science and Engineering, Key Laboratory for Advanced Ceramics and Machining Technology of Ministry of Education, Tianjin University, Tianjin 300072, PR China

[b] School of Materials Science and Engineering, Hebei University of Technology, Tianjin 300401, PR China

ARTICLE INFO

Article history:
Received 4 October 2015
Received in revised form
16 January 2016
Accepted 4 February 2016
Available online 6 February 2016

Keywords:
$(In_{1-x}Ga_x)_2Se_3$
Nanoparticles
Solution process
Solid solution
Solar energy materials

ABSTRACT

$(In_{1-x}Ga_x)_2Se_3$ nanocrystals $(0 \le x \le 1)$ were synthesized by a facile, air pressure ethylenediamine/N-dodecyl mercaptan co-assisted triethylene glycol solution process using $InCl_3 \cdot 4H_2O$, $GaCl_3$ and Se powder as precursors. The synthesized products were deposited on clean glass substrates by nanocrystals ink dip-coating method, and then were annealed at 500 °C for 1 h. Morphologies, solid solution stoichiometries, phase compositions, band gap energies and Hall parameters of the synthesized $(In_{1-x}Ga_x)_2Se_3$ nanocrystals with solid solution range of $0 \le x \le 1$ were investigated. Results showed that the solid solution stoichiometry could be well tuned by changing precursor atom ratios in the reaction solution. $(In_{1-x}Ga_x)_2Se_3$ products showed a phase transformation from wurtzite to zinc-blende in the range from x=0.4–0.5, accompanying change of band gap energies and Hall parameters.

1. Introduction

In_2Se_3, Ga_2Se_3 and $(In,Ga)_2Se_3$(IGSe) have attracted great attention these years due to their unique electrical and optical properties as well as their applications in various fields [1,2]. In_2Se_3 can be applied in phase change random access memories (PRAM), visible light sensors and as a buffer layer for thin film solar cells [2,3]. Ga_2Se_3 is a good candidate for passivation of heterogeneous interface structure [4]. Both In_2Se_3 and Ga_2Se_3 are regarded as promising negative electrode materials for lithium batteries [2,5]. Moreover, In_2Se_3, Ga_2Se_3 and IGSe films have been commonly employed as precursor layers for preparation of chalcopyrite $CuInSe_2$, $CuGaSe_2$ and $Cu(In_{1-x}Ga_x)Se_2$(CIGSe) which has been known as excellent light-absorbing materials for high-efficiency (beyond 20%) thin film solar cells [6,7]. For fabricating high-quality CIGSe, it has been defined that the [Ga]/[In+Ga] ratio in IGSe precursor layers plays an important role. Philip Jackson et al. [8] reported that an efficiency 19.0–19.5% CIGS solar cells was achievable in the range: $0.21 < Ga/(Ga+In) < 0.38$ by the well-known three-stage co-evaporation process, in which IGSe precursor was used as evaporation source in the first and third stages. In addition, intentionally adding a gallium gradient in IGSe precursor layers at the first stage has shown to yield an effective improvement of device efficiency [9].

In recent years, the ink-coating technique, as a non-vacuum solution route, has been suggested to produce the chalcopyrite absorbing layers. It used chemically synthesized nanocrystals to create printable ink [10,11]. The light-absorbing thin films could be prepared by coating the ink on substrates. Evidently, such a technique may lead to cheaper fabrication cost, less environmental pollution and material loss [12]. Here, we present a ethylenediamine/N-dodecyl mercaptan co-assisted triethylene glycol (TEG) solution process to synthesize $(In_{1-x},Ga_x)_2Se_3$ nanocrystals $(0 \le x \le 1)$ for nanocrystal colloidal inks technique. The synthesized products were deposited on clean glass substrates by nanocrystals ink dip-coating method, and then were annealed at 500 °C for 1 h. Morphologies, solid solution stoichiometries, phase composition, band gap energies and Hall parameters of the synthesized $(In_{1-x}Ga_x)_2Se_3$ nanocrystals with solid solution range of $0 \le x \le 1$ were investigated by FESEM, EDS, XRD, UV–vis–NIR and Hall measurements.

2. Experimentals

In a typical process, 0.21 mmol $InCl_3 \cdot 4H_2O$ and 0.09 mmol $GaCl_3$, corresponding to a In/Ga atomic ratio of 7/3, were dissolved into 10 ml TEG in a beaker as cationic precursor solution by ultrasonic treatment for 20 min. 0.45 mmol Se powders, 1 ml ethylenediamine (EN) and 0.075 ml N-dodecyl mercaptan (NDM) were poured into 40 ml TEG solvent in a 100 ml three-necked flask which was connected to a heating mantle and a reflux condenser.

* Corresponding author.
E-mail address: zhgjin@tju.edu.cn (Z. Jin).

http://dx.doi.org/10.1016/j.matlet.2016.02.018
0167-577X/

The flask was heated with a rise rate of 15 °C/min and magnetic stirring under nitrogen stream to solution temperature of 230 °C where the cationic precursor solution was quickly injected into the Se precursor solution. The reaction solution was refluxed at 210 °C for 30 min, and then cooled to room temperature by water-bath quenching. The synthesized products were washed ultrasonically with excessive amounts of absolute ethanol, followed by high speed centrifugation for five times. The purified products were dried at 100 °C in an oven or dispersed in absolute ethanol to form a colloidal ink with solid content of about 10 mg/ml for characterization. The nanocrystal products were deposited on glass substrates by colloidal ink dip-coating method and then were annealed in a closed graphite crucible within a small amount of solid Se powders under Ar protective atmosphere in a tube furnace at 500 °C for 1 h. In order to investigate the In/Ga solid solution, Ga/(In+Ga) values in the precursor solutions were set as 0, 0.1, 0.2, 0.3, 0.4, 0.45, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0, and the other processing procedure mentioned above was followed.

Characterization: XRD was detected by D8 advanced X-ray powder diffractometer with CuKα radiation (Germany). Morphologies were observed by Hitachi S-4800 FESEM (Japan). EDS spectra were recorded on EDAX Genesis MX2 spectrometer attached to the Hitachi S-4800 FESEM. UV–vis–NIR spectra were measured by Shimadzu UV-2700 spectrophotometer (Japan). Hall parameters were measured by Ecopia HMS-3000 (Korea).

3. Results and discussion

Fig. 1 A–D shows SEM images of the $(In_{1-x}Ga_x)_2Se_3$ nanocrystals synthesized with x=0.2, 0.4, 0.6 and 0.8, respectively. It is observed that the as-synthesized $(In_{1-x}Ga_x)_2Se_3$ nanocrystals have near-granular shape. The average particle diameters of the four samples calculated by a size measurement software are 48.97 nm, 54.60 nm, 61.36 nm and 84.00 nm, respectively, indicating that particle size is increased with the increase of x values

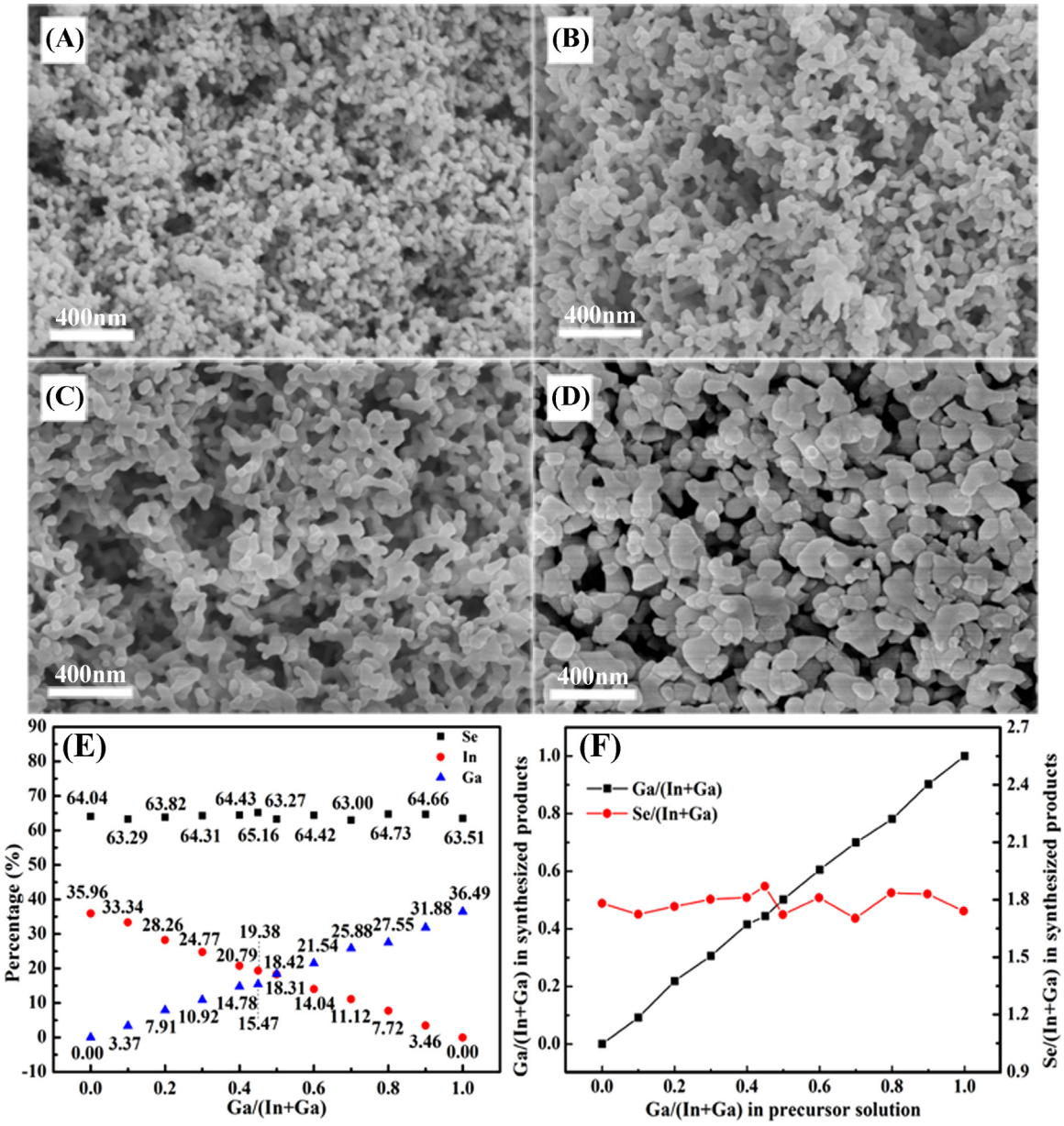

Fig. 1. SEM images of the $(In_{1-x}Ga_x)_2Se_3$ nanocrystals synthesized with (A) x=0.2, (B) x=0.4, (C) x=0.6 and (D) x=0.8 in reaction solution, (E) EDS results of as-synthesized $(In_{1-x}Ga_x)_2Se_3$ ($0 \le x \le 1$), (F) Ga/(In+Ga) ratios in synthesized products vs. in precursor solutions and Se/(In+Ga) ratios in synthesized products vs. Ga/(In+Ga) ratios in precursor solutions, based on EDS analysis.