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Hot injection synthesis of Cu(In, Ga)Se_2 nanocrystals with tunable bandgap

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ABSTRACT

$CuIn_{1-x}Ga_xSe_2$ nanocrystals (CIGSe NCs) were synthesized with different gallium (Ga) content by the hot injection process at low reaction temperature for the first time. The Ga content [x = Ga(In + Ga)] was varied such as 0, 0.25, 0.50 and 0.75 to study their influences on the structural, morphological, compositional and optical properties of CIGSe NCs. X-ray diffraction (XRD) analysis showed the peak shift towards higher 2θ angle. The lattice parameters ***a*** and ***c*** were decreased linearly as x value increases which propitiated Vegard's law. Transmission electron microscopy (TEM) analysis revealed a decrease in the particle size from 55 to 22 nm. Ultraviolet-visible-near infrared (UV-vis-NIR) absorption spectra indicated a blue shift towards the lower wavelength and bandgap was tuned from 1.04 to 1.41eV. Apart from this, CIGSe thin films were prepared by doctor blade coating method followed by annealing under Se/Ar atmosphere. The mobility of CIGSe thin film increased whereas resistivity decreased. Moreover, the photoconductivity of CIGSe annealed thin film exhibited almost 2-fold increase under an illumination of light. We realize from these results that the synthesized CIGSe NCs with x = 0.25 is expected to have the important perspective to be efficiently exploited as an absorber layer in cost-effective thin film solar cells.

1. Introduction

The I-III-IV_2 tetragonal chalcopyrite compounds, such as $CuInSe_2$ (CISe), $CuGaSe_2$ (CGSe) and $Cu(In_{1-x}Ga_x)Se_2$ (CIGSe) are established as leading light-absorbing materials for thin film solar cells because of their unique optical and electrical properties. For instance, direct bandgap, the intrinsic high optical absorption coefficient (a $\cong 5 \times 10^5\ cm^{-1}$), high quantum efficiency, long-term excitation stability and tunable bandgap energy (1.04–1.72 eV) by solid solution replacement of cognition elements, like indium with gallium [1–6]. It is noted that the conversion efficiency of CIGSe solar cells has been reported beyond 22% which is considered as the highest record for any polycrystalline thin film devices [7]. Nevertheless, the absorber layer of the high-efficiency solar cell is usually prepared by vacuum processes; which has various limitations like high production cost, complicated procedure and difficulty in the scaling up [8,9]. As a result, low-cost non-vacuum processing methods like printing, spin-coating, doctor-blade technique, spray pyrolysis and electrochemical deposition are developed in the recent times as an alternative for the preparation of the absorber layer [10–12]. These non-vacuum technologies have attracted the attention of many researchers due to the cost-effectiveness, efficient material utilization and flexibility to control the composition of the ink to result in a uniform deposition [13,14]. Consequently, the advantages mentioned above yielded a high efficiency of ~15.2% for $Cu(In_{1-x}Ga_x(S_ySe_{1-y})_2$ (CIGSSe) photovoltaics based on nanocrystal ink formulations [15]. For the nanocrystals-based printing/coating technology, the synthesis of ordered chalcopyrite and stoichiometric CIGSe nanocrystals is a crucial step to acquire a good photovoltaic conversion.

So far, various methods have been reported for the preparation of CISe and related nanocrystals, such as solvothermal [16], thermal decomposition [4,17], hot injection [18], ball milling [19] and polyol reflux [20]. Nevertheless, most of the techniques mentioned earlier are not able to constrain the size, shape, crystallinity or purity of the nanocrystals. Furthermore, it is noted the synthesized nanocrystals agglomerate seriously. Until now, the rapid hot injection method is the most successful and widely used protocol for the nanocrystals synthesis, which in turn synthesis smaller, uniform and highly dispersible nanocrystals.

Herein, we report the synthesis of CIGSe nanocrystals (NCs) which possess different Ga content by hot injection method at low reaction temperature. Furthermore, the influence of Ga content on the structural, morphological, compositional and optical properties of CIGSe NCs was investigated. Also, the ink was formulated by dispersing the synthesized CIGSe NCs (x = 0.25) in hexane followed by annealing

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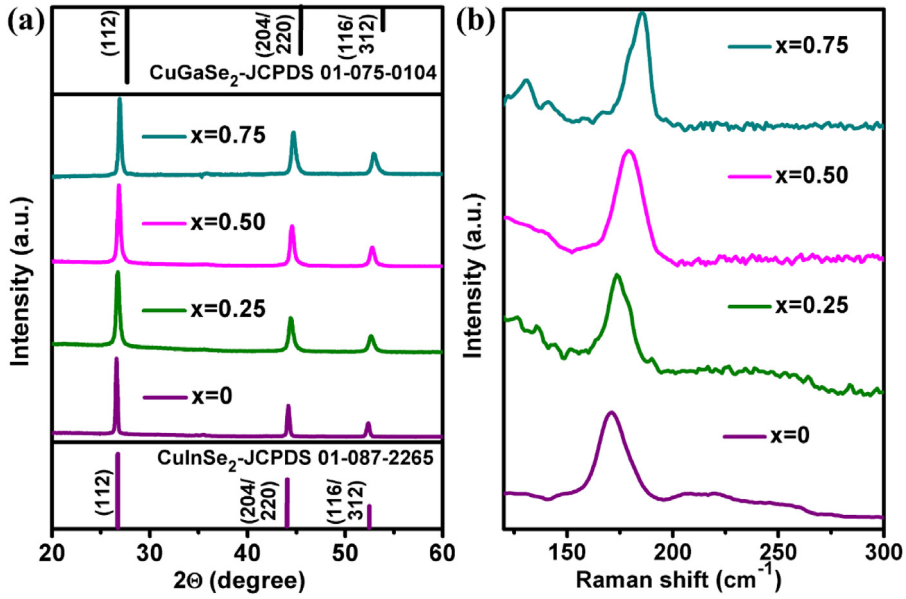

Fig. 1. (a) XRD pattern and (b) Raman spectra of CIGSe samples synthesized with different x values.

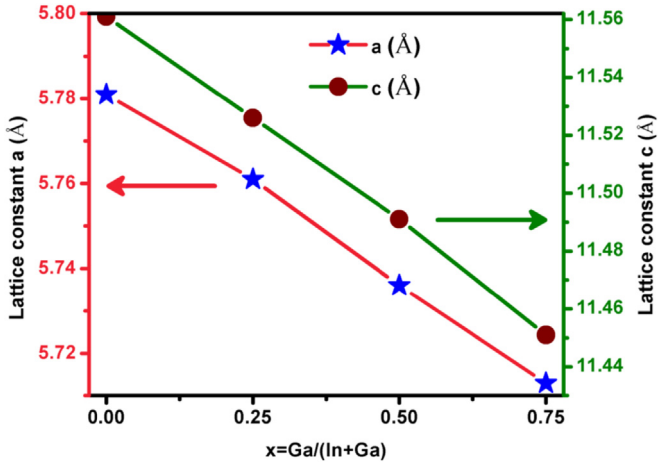

Fig. 2. The variation in the lattice constants ***a*** and ***c*** with respect to different x values.

under Se/Ar atmosphere. A detailed explanation of the various properties of as-deposited and annealed CIGSe thin films were given by using XRD, Raman, field emission scanning electron microscopy (FESEM), energy dispersive spectroscopy (EDS), Hall and Current-Voltage (I-V) measurements.

2. Experimental details

2.1. Materials

Copper (I) chloride (CuCl; 99.995%), indium (III) chloride ($InCl_3$; anhydrous 99.999%), gallium (III) chloride ($GaCl_3$; anhydrous 99.999%), elemental selenium (Se; 99.99%), oleylamine (OLA; technical grade 70%), absolute ethanol, chloroform (99.99%) and anhydrous hexane (95%) were purchased from Sigma-Aldrich. All the chemicals were used as received without further purification.

2.2. Synthesis of CIGSe NCs

A typical processing procedure for CIGSe NCs synthesis is explained: 1 mmol of CuCl, 0.25 mmol of $InCl_3$, 0.75 mmol of $GaCl_3$ and 5 ml of oleylamine were mixed at the room temperature and sonicated for 2 h at 40 °C to dissolve the precursors completely. This solution is labelled as solution A. Then, 2 mmol of elemental selenium was added into 5 ml of oleylamine at room temperature separately; this mixture is heated to 200 °C for 1 h under N_2 atmosphere. During this set period the solution gradually changes from colourless to orange and then to a brownish red. This is due to the dissolution of Se powder with oleylamine. This coloured solution is labelled as B. When the Se from solution B was dissolved entirely the temperature was decreased to 180 °C and maintained. The solution labelled as A was injected into the solution B, and the process was kept for 24 h at a constant reaction temperature of 180 °C. The details of cooling and washing procedure can be found in the previous report [17]. The above-mentioned procedure is repeated for the synthesis of $CuIn_{1-x}Ga_xSe_2$ NCs with x values of 0, 0.25 and 0.50.

2.3. Deposition of CIGSe thin films

To form a stable ink, 200 mg of CIGSe powder synthesized with x = 0.25 was dispersed in 1 ml of hexane and sonicated for 100 min. The glass substrate was cleaned by sonication in the mixture of ethanol and acetone (1:1 ratio), then in deionized water and dried using nitrogen gas. Before thin film deposition, an adhesive scotch tape is used to cover the sides of the substrate which act as a spacer/template to ensure a uniform thickness of the film. Typically, a small amount of CIGSe ink (~15 μL) is dropped at one edge of soda lime glass (SLG) substrates (1″x2″ size). A quartz glass rod with a diameter of 5 mm is used to sweep the ink onto the substrate. Typically, two alternative coatings were applied to obtain a film thickness of ~1 μm.

2.4. Annealing of CIGSe thin films

As-deposited CIGSe film was annealed under Se/Ar atmosphere using partially closed graphite box. Here 50 mg of Se powder was introduced into the graphite box along with CIGSe film and later loaded into the furnace. This process was done at a temperature of 500 °C for 20 min, and the temperature ramp was 20 °C/min.

2.5. Characterization

By using Cu-Kα radiation (λ = 1.5405 Å), the phase and crystallographic structure of samples were analyzed with the help of XRD