Optical Materials 37 (2014) 338–342

Contents lists available at ScienceDirect

Optical Materials

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

Synthesis and characterization of thermally evaporated Cu_2SnSe_3 ternary semiconductor

K. Hamdani [a], M. Chaouche [a], M. Benabdeslem [a], L. Bechiri [a,*], N. Benslim [a], A. Amara [f], X. Portier [b], M. Bououdina [c,d], A. Otmani [e], P. Marie [b]

[a] LESIMS, Département de Physique, Faculté des Sciences, Université Badji Mokhtar – Annaba, BP. 12, 23200 Sidi Amar, Algeria
[b] CIMAP, Centre de recherche sur les ions, les matériaux et la photonique, CEA, UMR 6252 CNRS, ENSICAEN, UCBN, 6 Boulevard du Maréchal Juin, 14050 Caen cedex, France
[c] Nanotechnology Centre, University of Bahrain, PO Box 32038, Bahrain
[d] Department of Physics, College of Science, University of Bahrain, PO Box 32038, Bahrain
[e] LRPCSI, Faculté des Sciences, Université de Skikda, BP26 route El-Hadaek, 21000 Skikda, Algeria
[f] LEREC, Département de Physique, Faculté des Sciences, Université Badji Mokhtar – Annaba, BP. 12, 23200 Sidi Amar, Algeria

ARTICLE INFO

Article history:
Received 20 April 2014
Received in revised form 5 June 2014
Accepted 17 June 2014
Available online 11 July 2014

Keywords:
Cu_2SnSe_3
Mechanical alloying
X-ray diffraction
TEM

ABSTRACT

Copper Tin Selenide (CuSnSe) powder was mechanically alloyed by high energy planetary ball milling, starting from elemental powders. Synthesis time and velocity have been optimized to produce Cu_2SnSe_3 materials. Thin films were prepared by thermal evaporation on Corning glass substrate at T_s = 300 °C. The structural, compositional, morphological and optical properties of the synthesized semiconductor have been analyzed by X-ray diffraction (XRD), energy dispersive X-ray analysis (EDAX), scanning electron microscopy (SEM) and transmission electron microscopy. The analyzed powder exhibited a cubic crystal structure, with the presence of Cu_2Se as a secondary phase. On the other hand, the deposited films showed a cubic Cu_2SnSe_3 ternary phase and extra peaks belonging to some binary compounds. Furthermore, optical measurements showed that the deposited layers have a relatively high absorption coefficient of 10^5 cm^{-1} and present a band gap of 0.94 eV.

1. Introduction

Cu(In, Ga)Se_2 (CIGS) is widely studied owing to its promise as a low cost material for high-efficiency thin film solar cells. Recently, a CIGS thin film solar cell with a record efficiency of 20% has been reported [1]. Both the cost and scarcity of In and Ga are the first reason to replace thin film materials containing only abundant earth elements. Cu_2SnSe_3 (CTSe) is a semiconductor compound that belongs to the I_2–IV–VI_3 ternary family which consists of abundant and extremely low toxicity materials in the earth's crust. These ternary compounds have been extensively studied mainly because they have potential applications such as photovoltaic and acousto-optic near infrared devices [2]. The precursor Cu_2SnSe_3 (CTSe) and $Cu_2ZnSnSe_4$ (CZTSe) are emerging absorbers for thin-film solar cells that contains earth abundant elements, with a near optimum direct band gap energy in the range 0.74–1.5 eV and a large absorption coefficient >10^4 cm^{-1} [3–6]. Cu_2SnSe_3 has been synthesized by various techniques [7–11]. Here, we report on the physical properties of latter materials obtained by direct synthesis of CTSe using a mechanically alloyed nanopowder.

2. Experimental details

Copper (granular, 99.99%), tin (granular, 99.99%), and non-metal selenium (pellets, 99.99%) were used as starting materials. Such materials were weighed to give a molar ratio of Cu:Sn:Se/2:1:3. Ball-to-powder weight ratio was maintained at 2:1. Milling was conducted in a planetary ball mill (Fritsch premium line P-7) [12]. The milling time was 2 h and the rotational speed was fixed at 300 rpmin. In order to prevent from nanoparticles oxidation in air, the nanoparticles were taken out in a glove box.

X-ray diffraction (XRD) was used to characterize the structural properties of the powders and thin layers. The powders were prepared by milling and the layer onto the glass substrates by thermal evaporation technique as described elsewhere [13] at a substrate temperature of 300 °C. The measurements operated on a Philips Xpert NPD Pro diffractometer with Cu $K\alpha_1$ radiation (λ = 1.5406 Å) using a step size of 0.02° and step time of 2 s. Surface morphology observation and chemical analysis were performed using a Jeol JSM 6400 scanning electron microscopy (SEM). Energy

* Corresponding author. Tel.: +213 38871968.
E-mail address: bechiril94@yahoo.fr (L. Bechiri).

http://dx.doi.org/10.1016/j.optmat.2014.06.022
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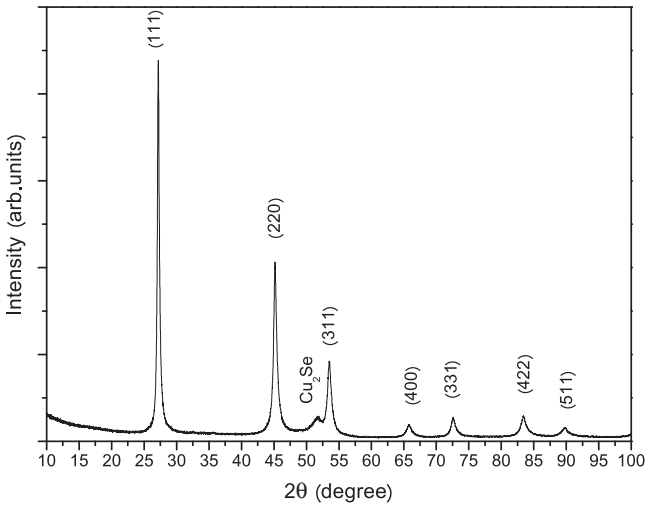

Fig. 1. XRD patterns of the as-synthesized Cu_2SnSe_3 powder prepared by mechanical alloying.

dispersive X-ray (EDAX) spectroscopy measurements were also carried out to determine the chemical composition of the samples during the SEM observations. Scanning electron microscopy (SEM) was used to analyze the morphology of the powder's nanoparticles. Transmission electron microscopy (TEM) samples were prepared by dropping diluted nanoparticles solution onto carbon film copper grids and a 2010 FEG JEOL microscope operated at 200 kV was used to observe the powders. Optical properties of the as-prepared thin layers were characterized by UV–Vis absorption spectroscopy recorded with a Perkin Elmer Lambda 950 UV–Vis spectrometer.

3. Results and discussion

3.1. Powder sample

Fig. 1 shows a typical XRD pattern from the powder. CTSe with cubic structure has been identified with the standard pattern of Cu_2SnSe_3 (JCPDS No. 03-65-4145). The diffraction peaks at $2\theta = 27.18°$, 45.30°, 53.46°, 65.82°, 72.45°, 83.62° and 89.63° can be attributed to the (111), (220), (311), (400), (331), (422), and (511) plans of Cu_2SnSe_3 respectively. The film showed that a dominant orientation is following the (111) planes. From the XRD pattern of the Cu_2SnSe_3 powder, the deduced cubic lattice parameter is $a = 0.569$ nm. This latter value is in good agreement with the Cu_2SnSe_3 powder data from (JCPDS Card No. 03-065-4145). An extra plane namely (311) belonging to Cu_2Se (Bellidoite) (JCPDS Card No. 00-075-0889) was identified at 51.95°. The average crystal size of the Cu_2SnSe_3 nanoparticles was estimated to be 24.12 nm using Debye–Scherrer equation [14]:

$$Xc = \frac{K\lambda}{\Delta(2\theta)_{hkl}\cos\theta_{hkl}}$$

where Xc is the average crystalline size, K is the shape factor, λ is the X-ray wavelength, $\Delta(2\theta)_{hkl}$ (0.375°) is the line broadening at half the maximum intensity (FWHM), and θ is the Bragg angle corresponding to the main diffraction line.

Fig. 2(a) shows a typical low-magnification SEM image of the Cu_2SnSe_3 powder, with an average pelota diameter of 100 μm. Various grain sizes are also shown in the SEM image. A magnified SEM view (Fig. 2b) of pelota exhibits an asparagus appearance

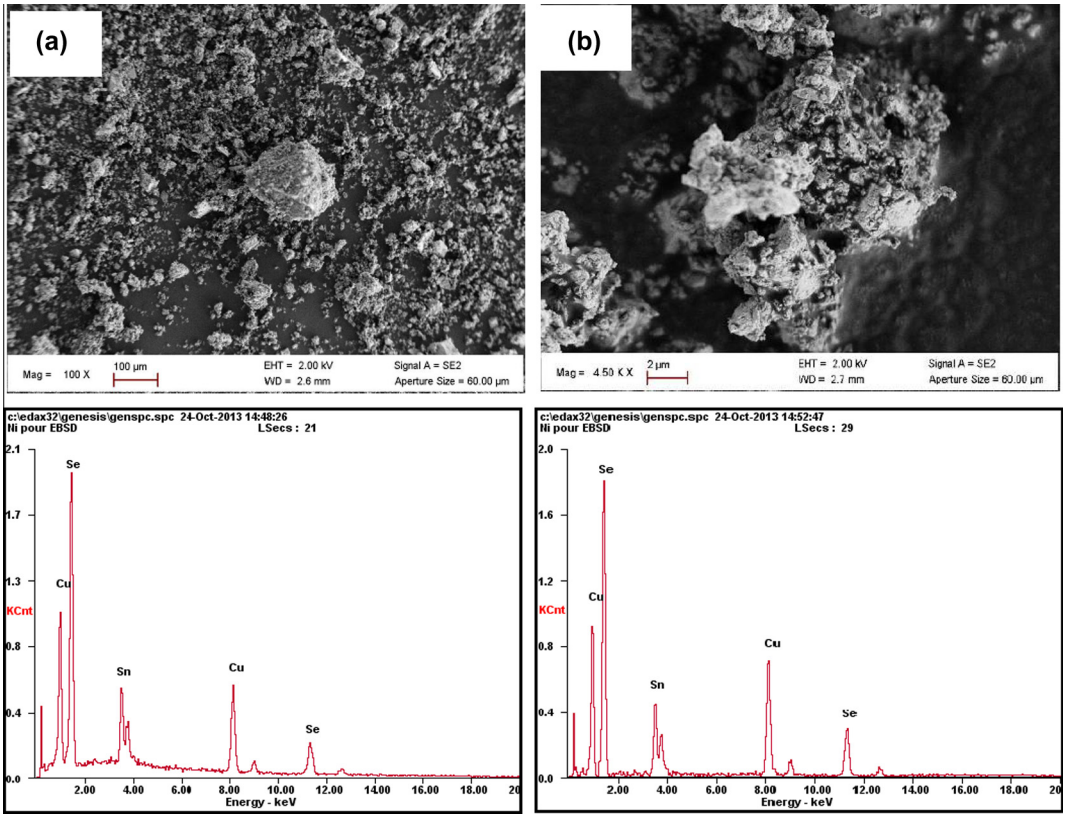

Fig. 2. (a) Low magnification SEM image of the Cu_2SnSe_3 powder and (b) a magnified SEM image of the individual Cu_2SnSe_3 pelota. The EDAX spectrum for each image is presented.