Materials Science in Semiconductor Processing 18 (2014) 128–134

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

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

Effect of Al content on the performance of $Cu(In,Al)Se_2$ powders prepared by mechanochemical process

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ARTICLE INFO

Available online 28 November 2013

Keywords:
$Cu(In,Al)Se_2$
Mechanochemical processing
X-ray diffraction
Optical properties

ABSTRACT

$Cu(In,Al)Se_2$ (CIAS) powders with varying Al/(In+Al) ratios x (x=0, 0.15, 0.23, 0.38, 0.57) were synthesized by mechanochemical process (MCP). Composition, morphology of CIAS powders was investigated by energy dispersive analysis and scanning electron microscopy, respectively. Influence of Al content on structural and optical properties of CIAS was detected by X-ray diffraction and UV–Vis spectroscopy, respectively. The results show molecularity and stoichiometry deviation of composition were small. Particle aggregation and inhomogeneous distribution of Cu, In, Al and Se element is observed at early milling stage. Field emission transmission electron microscopy image confirms that the particles can be milled to several hundred nanometers. Chalcopyrite characteristic peaks of $CuInSe_2$ are clearly observed. CIAS crystalline size decreases as Al_2O_3 increases in the products. CIAS (1 1 2) peaks shifts to high value and lattice constants for CIAS samples decrease with the Al additions. The band gap enlarged from 1.01 eV to 1.29 eV by adding Al. Al_2O_3 impurities impact CIAS powder grain size and the band gap seriously. All CIAS samples detected by hot probe method show the p-type conductivity.

1. Introduction

In $CuInSe_2$ (CIS) based materials, $Cu(In,Ga)Se_2$ (CIGS) is successfully used as absorber layers in highly efficient solar cell structures as its excellent properties: low cost, stable performance and high optical absorption coefficient. However, there are other options available such as $Cu(In,Al)Se_2$ (CIAS), which using aluminum partial substitute indium. Though CIAS is less study until now, it appears a good alternative to this compound as aluminum can alloy with $CuInSe_2$ and produce a larger band gap than Ga due to the smaller size of the Al atom for equivalent substitution. Moreover, the aluminum is more abundant and therefore less expensive than gallium or indium. A CIAS solar cell with 16.9% efficiency is demonstrated using a CIAS thin film deposited by four-source elemental evaporation [1]. Though the vacuum methods have been used to produce CIAS absorb layers for solar cells [2–4], the complex and expensive control system limits their large scale industrial production. Non-vacuum nanoparticle-based coating process is a promising alternative as its relatively simple procedures and low initial investment [5]. CIS based nanoparticles are essentials for this process, so the high-efficiency and low-cost method to prepare CIS based nanoparticles is expected.

Mechanochemical process (MCP) has advantages of high energy efficiency, high productivity and short processing cycle time to synthesize chalcopyrite CIS, $CuIn(S,Se)_2$ (CISS) [6,7] and CIGS [8,9] particles. CIS or CIGS powders synthesized by MCP has been used for fabricating thin films via screen printing [10,11], spin-coating [12], even thermal evaporation [13]. The composition, morphology, crystalline structure and the energy gap of the MCP particles influence the conversion efficiency of CIS-based solar cells.

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http://dx.doi.org/10.1016/j.mssp.2013.11.015

In this work, CIAS powders with various Al contents (x=0, 0.15, 0.23, 0.38, 0.57) were prepared by low-cost MCP and the obtained CIAS powders were characterized. Composition, morphology and X-ray elemental maps of CIAS powders milled for different periods have been observed. Then the effect of different Al contents on microstructure of these powders has been studied. Band gaps of CIAS compounds have also been estimated from the absorption spectra. Moreover their conductivity type has been detected.

2. Experimental procedures

CIAS powders with different Al contents were synthesized by milling copper (<20 μm, 99.99%), indium (<60 μm, 99.999%), aluminum (<90 μm, 99.0%) and selenium (<5 μm, 99.5%) mixtures with a given molar ratio Cu:(In+Al):Se=1:1:2.1. Excessive amount of Se was used as Se volatilized during MCP [14]. Al content was varied to obtain different CIAS powders. The composition ratio of Al/(In+Al) x was from 0 to 0.57. The experiments were carried out in an agate vial loaded on a planetary ball mill (KXM-Y-ISP-L) milled for 120 min. The ball-to-powder weight ratio and rotational speed were10:1 and 600 rpm, respectively.

Morphology, composition and corresponding X-ray elemental map of CIAS powders milled for different periods were observed using scanning electron microscope (SEM, JSM-6360LV by JOEL) attached with energy dispersive spectroscope (EDS, INCA by Oxford, 20 kV). Final product was also observed by field emission transmission electron microscope (FETEM, TECNAI F20 by Philips, 200 kV). Structures of milled CIAS powders and the influence of Al content on the structural properties has been studied by X-ray diffraction (XRD, PW1710 by Philips) with copper Cu $K\alpha$ radiation of wavelength 1.5406 Å.

All the samples were characterized by UV–Vis spectrophotometer with the integrating sphere diffuse reflectance accessory (Lamda 900 by Perkin-Elmer), and the absorption spectra of CIAS samples were recorded. The samples were prepared for measurement by piling a small amount on a layer of barium sulfate powder, after which the sample powder was spread into a thin uniform layer using a glass rod. Barium sulfate was used as a standard to study the influence of Al content on optical properties and the corresponding band gaps has been estimated.

Moreover, obtained CIAS powders were consolidated to tablets to detect their conductivity type by hot probe method. In this method a voltmeter is attached to the sample, and a soldering iron was used to be heat source. The heat source will cause charge carriers to move away from the lead. When the soldering iron is placed on the positive lead of a voltmeter attached to an n-type semiconductor, a positive voltage reading will result as the area around the heat source/positive lead becomes positively charged [15].

3. Results and discussion

3.1. Compositional analyses

The composition of $CuInSe_2$ is a topic of main importance since many cell properties are influenced by deviations from stoichiometry. Compositional characteristics of milled powders with different Al contents were detected by EDS. Al content x in the final products was varied from 0 to 0.57. Atomic percentage concentrations of CIAS powders are demonstrated in Table 1. Two parameters, Δm and Δs, were calculated to describe the deviations from the stoichiometric composition, which determine the deviations from the molecularity and stoichiometry [16], respectively. For CIAS powders, the expression of Δm and Δs can be calculated by Eqs. (1) and (2).

$$\Delta m = \frac{[\mathrm{Cu}]}{[\mathrm{In}+\mathrm{Al}]} - 1 \tag{1}$$

$$\Delta s = \frac{2 \times [\mathrm{Se}]}{1 \times [\mathrm{Cu}] + 3 \times [\mathrm{In}+\mathrm{Al}]} - 1 \tag{2}$$

Both molecularity and stoichiometry deviation values of composition here are small, less than 0.23. CIAS4 has larger deviations exceed 0.2 may due to the existence of impurities. The results demonstrate that the obtained CIAS were the near stoichiometric powders with slightly selenium deficiency ($\Delta s < 0$) as Se volatilized during MCP.

3.2. Morphology analysis

Mixed Cu, In, Al and Se powders were repeated cold welded and fractured throughout MCP. Its morphology and elemental distribution was changed from time to time. Morphology and corresponding X-ray elemental map of CIAS powders milled for different periods are shown in Fig. 1. Particles aggregation was observed when the mixture was milled for 10 min, and most of the agglomerated particles are larger than 50 μm (Fig. 1(a)). X-ray elemental maps in Fig. 1(a) show an inhomogeneous distribution of Cu, In, Al and Se element. Al and In aggregates significantly

Table 1
Composition analysis of CIAS powders milled for 120 min by EDS.

Samples	Composition (at%)				Al content x	Molecularity deviation, Δm	Stoichiometry deviation, Δs
	Cu	In	Al	Se			
CIAS0	26.2	25.5	–	48.3	0	0.03	−0.06
CIAS1	26.6	21.6	3.7	48.1	0.15	0.05	−0.06
CIAS2	28.6	18.9	5.6	46.9	0.23	0.17	−0.08
CIAS3	27.4	15.8	9.5	47.3	0.38	0.08	−0.08
CIAS4	24.6	13.1	17.6	44.7	0.57	−0.20	−0.23